

Nanochemistry Views

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After more than four and a half decades of research in the field of nanochemistry I was given the interesting opportunity to write a monthly opinion editorial for the Nano Materials Views section of the VCH-Wiley materials journals, Advanced Science, Advanced Materials, Advanced Functional Materials, Small, Particle, Advanced Engineering Materials, Advanced Optical Materials and Advanced Health Materials. This chance provided me with a superb vehicle to express opinionated and provocative views about hot button issues in nanochemistry. Dreaming up and composing these editorials has been a valuable lesson in how to write scientifically, technologically and politically correct critiques about controversial topics for a public forum, a pastime less risky for a senior scientist than a junior one. After having produced 36 of these opinion editorials on a variety of contemporary topics in nanochemistry, I thought it worthwhile to integrate them into a compendium of essays in the form of a monograph entitled Nanochemistry Views as a three score years and ten plus one, milestone in my life. I hope the reader enjoys these stories as much as I had fun writing them and at the same time learning much from knowledgeable colleagues who contributed insightful and important commentaries on my opinions, sometimes voicing heterodox views, many of which in anonymous form I included in much improved final drafts. I also received terrifically helpful editing on more-or-less every story from my talented and dynamic group of co-workers as well as excellent artistic renditions of the content of many of the stories from Wendong Wang, Chenxi Qian and ArtScientist Todd Siler.

Geoffrey A Ozin
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Geoffrey Ozin – Brief Biographical

Geoffrey Ozin is renowned for his pioneering research in nanochemistry. His work has defined, enabled and popularized a chemical approach to nanomaterials, a rapidly expanding field, a cornerstone of modern chemistry and a foundation for innovative nanotechnology in advanced materials and biomedical science. Four and a half decades of ground-breaking interdisciplinary research on nanomaterials established Geoffrey Ozin as one of the “founding fathers of nanochemistry.” This emerging and dynamic interdisciplinary field is an essential driver of the 21st century nanotechnology revolution. He was there in the 1970s at the birthing of the science that is now called nanochemistry, which synthesizes nanoscale structures and integrated nanosystems from the bottom up, literally atom-by-atom. Today nanometer-scale matter and voids are the central building blocks of nanoscience and the groundbreaking works of Geoffrey Ozin in wide-ranging fields, briefly summarized below, provided the spark that helped make it happen.

1970s: Matrix isolation laser Raman spectroscopy – Pioneering experiments on inorganic, organometallic and cluster reactive intermediates. **Naked metal clusters** – “Atom-by-atom” investigations of the controlled nucleation and growth of “ligand-free” metal clusters enabled the earliest insight into the fuzzy interface between molecular nanoclusters and quantum confined nanocrystals. **Chemistry of naked metal clusters** – “Atom-by-molecule” investigations of the reaction of small molecules with controlled-nuclearity ligand-free metal clusters provided archetype “chemisorption models” for the same molecules chemisorbed on metal surfaces. **Naked metal atom and metal cluster photochemistry** – Pioneering studies of metal atom photo-aggregation, metal cluster photo-dissociation, metal cluster photo-isomerization and metal-atom photo-insertion into the C-H bond of methane.

1980s: Nanoporous materials chemistry – Enabled the transition of the field of zeolite science from its traditional focus on catalysis and gas separation into the world of advanced nanoporous materials science with objectives centered on novel solid state devices where molecule size and shape recognition and discrimination matters. **Biomimetic nanomaterials** – Transferred some of nature’s best biomaterials ideas in the nanochemistry laboratory to originate the area of “morphosynthesis”, a self-assembly paradigm inspired by

“morphogenesis” in the natural world, exemplified by the synthesis of faux diatoms and radiolarian, hollow helicoids and rounded figurines.

1990s: Hybrid nanomaterials – Invented an entirely new class of nanocomposites, dubbed periodic mesoporous organosilicas, PMOs, with bridge-bonded organic molecules uniquely imprinted in the inorganic pore walls, creating materials properties that transcend the sum of the inorganic and organic components, finding widespread applications in microelectronics, catalysis, chromatography, dental implants and drug delivery. **Host-guest nanomaterials** – Among the first to synthesize size, shape and surface controlled insulating, semiconducting and metallic nanomaterials, nucleated, grown, stabilized and protected within the spatial confines of nanoporous hosts.

2000s: Mesoscopic materials – Pioneering research on the growth and form of self-assembled materials with structural features spanning nanoscopic to macroscopic scales, exemplified by spheres, wires, rods, tubes, helices and films, a “panoscopic” or “hierarchical” view of self-assembling materials.

Photonic crystal materials – Chemistry approach to the world’s first synthetic three-dimensional silicon photonic crystal with a complete photonic bandgap at optical telecom wavelengths. This research initiated the field of tunable photonic color materials and evolved to award winning nanotechnology platforms being commercialized by the spin-off company www.Opalux.com.

Slow photons in chemistry – Proof-of-concept research that demonstrated slow light localized at the photonic band edges of synthetic photonic crystals made of photocatalytic materials can speed up the rates of light driven chemical reactions, exemplified by organic photoisomerizations and organic photooxidations. **Nanolocomotion** – Among the first few scientists to demonstrate chemically powered ‘nanolocomotion’ based on chemical control of the motion of segmented barcode nanorod motors, whose power is obtained from the decomposition of hydrogen peroxide into water and oxygen localized at the catalytic segment of the nanorod. This work has inspired a veritable ‘nanomotor industry’. **Nanochemistry education** - The textbooks ‘Concepts in Nanochemistry’ and ‘Nanochemistry’, co-authored with former students Andre Arsenault and Ludovico Cademartiri, are the globally acclaimed academic and industry gold standard written resources for teaching and practicing a chemical approach to nanomaterials.

2010s: Ultrathin inorganic nanowires – Discovery of ultrathin bismuth sesquisulfide Bi_2S_3 nanowires with an unprecedented small diameter of 1.6 nm. This work inspired a flurry of activity around the globe to explore the composition, structure and property space of these uniquely thin one-dimensional nanomaterials. **Green nanochemistry** – Separation of poly-dispersions of non-toxic, quantum confined silicon nanocrystals into monodisperse colloidally-stable fractions with tailored organic surfaces and bright, size-tunable visible to near infrared photoluminescence, provided their size-dependent chemical, physical and biological properties, creating opportunities for the development of novel advanced materials and biomedical devices. **Solar Fuels** – Research aimed at exploiting the boundless energy of the sun to make fuels and chemicals from abundant greenhouse gas carbon dioxide rather than the current practice of continuing to deplete our legacy fossil fuels, the ultimate goal being an energy transition from an unsustainable fossil fuels based economy to a sustainable one founded on solar fuels.

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1. Life before Advanced Materials?

When I began working at the University of Toronto 40 years ago in the late sixties I decided that I would like to focus my research efforts in the field of materials chemistry. This period of time was the beginning of an exciting new era and a turning point for chemistry pioneers who decided to adapt their skills in inorganic, organometallic, organic, metal cluster and polymer chemistry towards making exciting new classes of materials by design with a purpose. This was a new approach to synthesizing materials from molecules rather than the oft used trial-and-error solid-state chemistry *modus operandi* that had been around since the beginning of the century.

At the University of Toronto I happened to be the first chemistry faculty member to make this choice. It turned out to be a risky one. I immediately met fierce resistance that threatened to destroy my career as a young faculty member before it had even begun.

I am sure the materials baby boomers will be able to relate to this little piece of scientific nostalgia.

The first of my problems was with a powerful materials science lobby who believed that anything to do with materials research and teaching belonged in the materials science and engineering departments and certainly not chemistry.

The second heartache was that my colleagues, who were used to traditional chemistry classifications – organic, inorganic, physical, theoretical, analytical - really did not know where to put me because I fell between the cracks of the traditional disciplines of organic, inorganic and physical chemistry. This was not a good place to be for a vulnerable assistant professor on his quest for tenure. In fact my chairman at the time told me it was highly unlikely I would get tenure!

The third cause of tension for me was trying to raise funds from government agencies. As well as not fitting into any particular area within our chemistry department, I also did not fit into any of the listed grant review committees and subject classifications. In this inherently interdisciplinary field, I was describing my ideas using terms from all branches of chemistry, with a little bit of physics thrown in for good measure, which must have led to a great deal of confusion for the grant reviewers who, at that stage, were not used to this sort of variegated approach to chemistry.

And the fourth giant challenge which is really the centerpiece of this story relates to perhaps the most serious problem I was confronted with. Assuming I could work around the first three problems, where on earth was I to publish

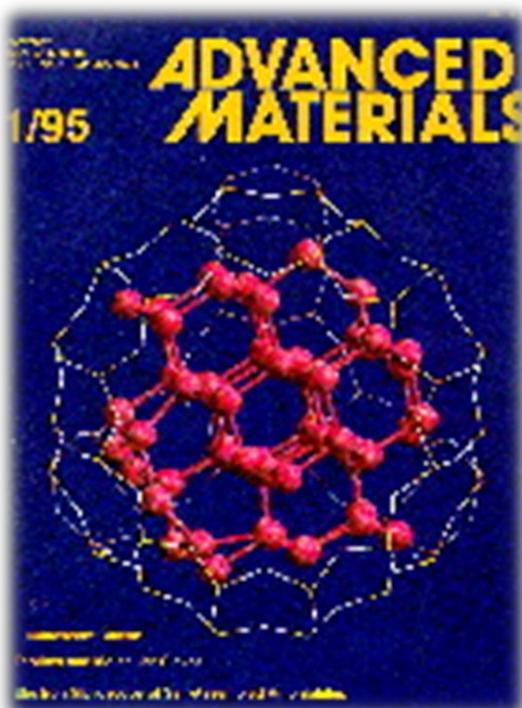
my work? There were no suitable chemistry journals in which to publish my materials chemistry research other than tired, old, solid-state chemistry journals.

We needed a champion, we needed a savior. The rest is history because Peter Goelitz and Peter Gregory recognized the gigantic void that existed in the materials chemistry publishing world. They appreciated the need for a new type of journal to showcase the breakthroughs that were beginning to appear from chemistry research groups who dared to venture across the boundaries of traditional chemistry, condensed matter solid state physics, materials science and engineering, into the emerging field of materials chemistry.

The birth of the journal *Advanced Materials* had a monumentally positive effect on the growth of the field of materials chemistry and its *young bride* nanochemistry, which have blossomed into two of the most scientifically significant and technologically relevant fields of the 21st century. The creation of *Advanced Materials* enabled the career development of millions of academic, government and industrial researchers across the globe in the fields of materials chemistry and nanochemistry, without whom we may not have many of the technologies we enjoy today, and which promise to shape our lives in the future.

Really, if you think about it, what journals did we have before *Advanced Materials* to showcase the amazing breakthroughs emerging from the world of

materials chemistry? The answer is simple, none! Now we have *Advanced Functional Materials*, *Journal of Materials Chemistry*, *Chemistry of Materials*, *Small*, *Nano Letters*, *ACS Nano*, *Nature Materials*, *Nature Nanotechnology*, *Nano Research*, *Nanoscale*, and the list continues to grow!



On a personal note, my group was lucky enough to contribute the inaugural cover of *Advanced Materials* back in 1995. We are proud of that, and we have tried to publish their regularly ever since. I was fortunate enough to have Peter Goelitz recognize my group's work in the fledgling field *Advanced Zeolite Materials Science* in 1989 and Peter Gregory to identify my group's work on Nanochemistry – *Synthesis in Diminishing Dimensions* in 1992. These papers earned my research group a lot of recognition and hopefully

helped just a little to make the journal and the field the success story that it enjoys today.

And do you know something? Materials scientists and engineers, physicists and biologists, biochemists and medics have read the materials chemistry and nanochemistry published in every issue of *Advanced Materials* since its inception, and they have been inspired by what they have read and they have become involved worldwide, and the world has benefited!

What an exciting time it is for the global materials chemistry and nanochemistry family. We should all be proud to be part of this family and I thank *Advanced Materials*, the *Two Peters* and their able staff for helping to make this happen. Cheers!

2. Is the Nano-Bubble about To Burst?

What are we going to do with all these nanomaterials – when is enough, enough?

It is a nagging question that has been asked before in other areas of chemistry when the rate of production of molecules or materials reaches what is perceived as a saturation point in the supply chain.

I think this is a question on most of our minds these days as we try to wrestle which way to go scientifically and technologically with the exponentially growing bank of nanomaterials and ponder the gigantic efforts and funding levels devoted to the discovery and utilization of these nanomaterials in diverse areas of nanotechnology.

To me it seems that these tiny pieces of matter are the *new materials proving ground* of chemistry and physics, materials science and engineering, biology and medicine for pure unadulterated basic research, and play an unquestionable central role in the multidisciplinary quest for discovery and development of new and improved products and processes.

Aside from all the good stuff we all know about, I sense something is rotten in the state of nanomaterials. With more than four decades of research under my belt beachcombing for exciting new materials in many different fields, I am sufficiently long in the tooth scientifically, to have witnessed the rapid rise and fall of all sorts of exciting new classes of molecules and materials. I have that sinking feeling that nanomaterials might suffer this fate unless some strategic changes in direction are implemented pretty soon.

This boom and bust phenomenon is most often driven by scientific oversell and overproduction of molecules and materials by enthusiastic practitioners of their art, hyped expectations that cannot be realized and promises that cannot be fulfilled. This rise and fall of new classes of molecules and materials is often accompanied by loss of interest by funding bodies in continuing to support the work and the flight of top notch researchers from the area not keen to keep the flame alight and looking for something better to keep them occupied.

Recall after the heydays of organometallic and cluster chemistry, researchers in the field turned their attention to the use of organometallics and clusters as reagents and catalysts in organic and polymer synthesis, and precursors in materials chemistry from which blossomed a new genre of pharmaceutical chemistry, organometallic polymer chemistry and solid state chemistry, as well as a host of new journals to cater to their publication needs.

Historically there has been a critical point of boom and bust in most branches of chemistry when granting agencies switch off the money supply, industry loses interest in supporting the work and researchers wind down their activities and redirect their efforts to more fertile and productive pastures.

I sense this situation looming with all the nanomaterials being thrust upon us in far too many papers and in far too many journals from every conceivable corner of the world.

This is not to say that amongst the mass of nanomaterials being reported every day there are not a few distinctive ones that can change the prevailing view in the field. These are few and far between and suffer the danger of their significance being overlooked and their impact under appreciated in the Tsunami of irrelevant reports. Often quality falls as hoards of researchers jump on a bandwagon like scientific sheep. The effect of this is to muddy the waters and diminish the visibility of the work of black swans with a need to distinguish themselves, so they lose interest and move on to what they perceive as bigger and better things with more satisfying scientific rewards and the field dies.

After roughly two decades of observing the appearance of nanomaterials with every imaginable organic and inorganic composition, size, shape and surface, it is disturbing that we still are unable to make them truly monodispersed on demand. We still only know the single crystal X-ray structure of less than a handful of nanomaterials and the cytotoxicity of the majority of them still remains unknown!

These days I have been wondering what should we be doing with all these nanomaterials? We are reaching a point where we will soon have as many nanomaterials as molecules but without the perfection trademark of molecules.

It seems to me that to give nanomaterials the status of molecules and approve their long-term survival as the building blocks of myriad nanotechnologies we have to start a discussion on what are the really big questions, both intellectual and practical, and hopefully encourage young scientists to take a risk with more challenging problems in their chosen field instead of wasting their time working on trivia that nobody cares about.

I believe young researchers should be encouraged, without penalty, to tackle big and important problems even though there is a greater chance of failure rather than forcing them to play safe in a field and continue to turn the handle of incremental technical improvements, when it is clear enough is enough. A change of attitude towards young researchers would inspire creativity and enable science, technology and society to move forward faster and further.

I am of the opinion that we have reached a point in the development of nanochemistry where we have an oversupply of nanomaterials and unless we assume the scientific responsibility to take the field to a higher level of development it will loose ground around the world as both students and stake holders will see nanomaterials as a just a means to an end rather than an exciting platform for new science with identifiable technology's.

I imagine most would agree that nanomaterials will have a recognizable impact in healthcare, clean energy and water, and all things related to the environment and sustainability. And while new nanomaterials will likely underpin these technologies surely it is time to ask, do we really need to keep on churning out more and more nanomaterials to solve these problems?

I think it is now time to improve the basic and directed science for making, understanding and utilizing what we have already banked in our vault of nanomaterials and in the list below I have taken the liberty of offering up ten recommendations, not set in stone, to begin a discussion on what is next:

- (i) learn how to make them more perfect and elucidate means to define the degree of perfection,
- (ii) delineate metrics that demarcate the boundaries between molecular, nanoscale and bulk forms of matter,
- (iii) establish situations when perfection is beneficial and when imperfection can be tolerated,
- (iv) understand better their surface and bulk chemistry,
- (v) devise synthetic methods and characterization techniques for composition tuning and doping,
- (vi) control and characterize surface and bulk defects
- (vii) improve control over their self-assembly and disassembly,
- (viii) report information on their shelf-life in dry and humid air and under vacuum, their colloidal stability in different solvents, and how long they live when stimulated thermally, electrically and photolytically,
- (ix) reduce-to-practice prototype devices, products or processes for your pet nanomaterial and if successful figure out how to scale up its production to industrial proportions in an economical and safe manner,
- (x) facilitate the transition of your idea to innovation that works and helps humankind

Maybe in another NanoChannel we can contemplate a future in which nanomaterials can be made atom precise and structure perfect to order, and can be chemically and physically manipulated in ways we handle molecules. I think by perfecting imperfection and with a treasure chest of ideal nanomaterials the field of nanochemistry will return to its chemistry roots!

3. Good Nano Stuff – Where's It Going?

After a century or more of traditional materials research, which in one form or another ended up in products and processes that influence our everyday lives, there has for the past twenty five years been an intense global effort to remodel these materials through chemistry from the macroscopic scale where they display conventional bulk properties to the nanoscale where materials properties, chemical and physical, are often defined by quantum mechanical scaling laws and show anything but conventional behaviour.

This intermediate state of spatially confined nanomatter lies in the fuzzy regime straddled on one side by molecules with their chemistry and molecular orbitals and on the other side by materials with their physics and electronic bands. It is still not very clear how to demarcate these three regimes!

All of today's effort in nano is directed towards a search, understanding and exploitation of chemical and physical phenomenon that are unique to this small scale, a key phase in the drive to re-invent the world of materials, products and processes, a means to gain a competitive edge in a knowledge based, high technology, rapidly expanding, global marketplace.

These days, all sorts of nanomaterials are being synthesized and self-assembled into new structures over multiple length scales in much the same way atoms and molecules have been coerced through chemistry to form new compounds for over a century. And just as the library of known molecules today has reached countless millions it looks like nanoscale materials are well on the way to match their molecule scale brethren in proportion. But it is not quite as simple as that.

While molecules are atom precise and structure perfect and offer predictable properties and function, nothing can be further from the truth for most nanomaterials.

Yet even imperfect nanomaterials with respect to inhomogeneity of size, shape and surface, offer more than just a length scale advantage over bulk analogues. We tend to be impressed with the effects of quantum and spatial confinement on the electronic, optical, magnetic and mechanical properties of nanomaterials yet surface physicochemical phenomenon can be where the real action in synthesis and structure, property, function and utility lies. The surface advantage of nanomaterials lies in their disproportionately large surface area compared to its volume (S/V). The surface challenge is to control, understand and exploit structure and chemistry, defects and reconstruction of nanomaterials surfaces at the atomic and molecular scale.

Beneficial surface effects at the nanoscale can for example be seen in enhanced electron and phonon scattering in nanothermoelectrics, conduction electron resonances in nanoplasmonics, fast-ion transport in nanoionics, chemical activity and selectivity in nanocatalysts, molecule recognition and detection in nanosensors, ion and molecule diffusion in nanofluidics, mechanics of nanometals and nanoalloys, electron-hole separation and charge transport in nanophotovoltaics, and electroluminescent quantum yield in nanooptoelectronics.

The surface advantage of nanomaterials also provides notable benefits when used as precursors in a solid state materials synthesis through larger contact area and smaller diffusion lengths, which synergistically reduce reaction temperature, increase reaction rate and boost product yield and purity. In a heterogeneous materials synthesis involving solid nanomaterial and solution phase precursors the surface advantage is manifest as a slow and steady release of reactants, which can facilitate controlled nucleation and growth of a product nanomaterial. The surface advantage is also appreciated in novel ion-exchange, galvanostatic and Kirkendall reactions used to tailor the composition, modify the structure and make hollow capsules for storage and release of pharmaceuticals.

But as we walk the nano path into the future it is important to ask, where is it taking us? Is our present mindset stifling the true potential of nano? Can we still take what we have and perfect and utilize it to develop nanotechnology that works for the greater good of science and society? Or is the field about to self-destruct (see [link to article 1](#))?

I think the gradual transition of century old colloid chemistry to today's nanochemistry has provided us with better and better size and shape control of metal, semiconductor and insulator based colloidal particles. It has provided us with the know how to modify their surfaces and create stable dispersions of these colloids, so vital for the reliable and reproducible production of *colloid morphology* exemplified by colloidal films, multilayers and patterns as well as other colloid forms like sheets and spheres, rods and wires, made from these colloids. These are key milestones in the quest for cost-effective and safe manufacturing solutions through the processing of colloids.

But we are *not there yet* with respect to the degree of perfection of these colloids (e.g., size and shape specific synthesis and size and shape selective separation), single crystal X-ray structures of archetype colloids (e.g., nanocrystal crystals or superlattices), the quality of colloid organization (e.g., self-assembly, co-assembly or directed assembly) into hierarchical constructs by design, and the monumental task of scaling well-defined colloids (e.g., hundreds of kilograms) for industrial manufacturing of colloid based *good nano stuff*.

These are important challenges for bottom-up nanomaterials, for nanochemistry and for nanoscience, because the performance of a wide range of solid-state products will depend on how well we are able to manipulate and control, electrons and holes, photons and excitons, phonons and plasmons, and electron and nuclear spins in periodic or aperiodic assemblies of colloidal nanocrystals, at least as well as it is done in the parent solid-state bulk materials.

And the success of this endeavour will be predicated not just upon how perfect we can make our nanocrystals and how well we can organize them into predetermined forms but also on *how well we can chemically command that teeny-weeny space between nanocrystals*, which controls their collective interactions and their translation into the electrical, optical, magnetic and mechanical properties so central to the function and utility of any nanocrystal-based product exemplified by nanostructured solar cells and batteries, light emitting diodes and lasers, photodetectors and sensors.

A closing thought to express my optimism about recent developments in the field of Nanochemistry. I have said in my paper, Nanochemistry: Synthesis in Diminishing Dimensions (*Advanced Materials*, 1992, 4, 612), and expressed in two recent graduate and undergraduate textbooks on the subject of Nanochemistry (*RSC and Wiley VCH*, 2009), that synthetic chemists pride themselves on being able to synthesize perfect objects having nanometre scale dimensions. They have worked hard for over a hundred years to hone their skills at making incredibly beautiful and important atom and structure perfect molecules, clusters and polymers.

And just to put things in perspective, they have been working equally hard for just the past twenty years or so to match these molecule scale accomplishment at the nanoscale but now learning how to achieve comparable fidelity over the size, shape and surface, and self-assembly of myriad new nanomaterials.

Making nanomaterials through nanochemistry is a large and important field, there is still much to do and we have taken the first step!

4. Nano Silicon Samurai?

One thing that has caught my eye in the last few years is the burgeoning activity and potential technological impact of research on new kinds of nano silicon, made from one of the most abundant and green materials on earth.

I am not talking about the utilization of top-down nano silicon for integration as electrical components in the incredible shrinking world of *M(o)re* powerful and faster microelectronics.

I am rather referring to the notable intensification of research on bottom-up nano silicon for everything other than microelectronics!

Nano silicon materials and structures fashioned into almost every conceivable size and shape, chemically functionalized surface and overall form, is beginning to play a prominent role in the bottom-up assembly and top down fabrication of a cornucopia of nano stuff exemplified by chemical and biological sensors, fluidic field effect transistors and flow monitors, printed ink backplane thin film transistors, computer memories, radio frequency identification tags, proton conducting membranes for hydrogen-oxygen fuel cells, high capacity lithium ion battery anodes, photocatalysts, solar cells, solid state lighting, optical interconnects, ultrahigh frequency oscillators, photonic crystal optical cavities and waveguides, electronic eyes, bioinspired self-cleaning anti-reflection coatings, nutrients in functional foods and beverages to enhance bone health, biodegradable luminescent porous drug delivery systems, and biocompatible implantable medical devices. This overly long list just names a few prominent reports for nano silicon that one can easily search in the 2007-2010 scientific literature.

Curiously nano silicon has even been invoked to explain the origin of the observed extended red emission (ERE) from interstellar dust. And the purported non-toxicity and biocompatibility of nano silicon allows it to be marketed as a “Green” material in medical theranostics!

As a self-confessed proponent of nanochemistry I note that many of these new applications for nano silicon are enabled by bottom-up synthetic strategies. These are providing increasingly impressive command over the size and shape, dopants and defects, surface structure and surface functionalization of nano silicon and the self-assembly of these nano silicon forms into purposeful constructs. And the ultimate success of most of these applications will depend on the scalability and processibility, cost effectiveness and manufacturability of nano silicon in these varied forms.

It is a truism that chemistry is the beginning of the nanomaterials food chain and we are now seeing this in creative synthetic routes for preparing silicon in

a range of forms beyond those documented for the usual nanocrystals, nanorods and nanowires. These syntheses include gas, solution, liquid and solid phase chemical, photochemical, thermochemical and electrochemical pathways to nano silicon with self-assembled architectures often directed by templates and lithographic patterns.

Using these methods one can gain access to all-silicon-based amorphous nanoscale colloids, zig-zag, buckled and porous nanowires, straight and buckled nanoribbons, nanotubes, nanosheets, nanospheres, nanoshells, nanocrystal nanospheres and periodic mesoporous materials. And at slightly larger yet submicron length scale we find a treasure trove of silicon based macroporous crystals, meshes and membranes, two and three dimensional folded thin film shapes, and even replicated biomineral and geomineral shapes like diatom microskeletons and opals.

Of course evoking light from indirect bandgap silicon has always been and continues to be a challenge for light emitting diodes and lasers. And then along came brightly emissive porous silicon in the late eighties and the rest is history. For the new nano silicon forms to display bright tuneable wavelength photoluminescence arising from quantum and spatial confinement effects, at least one dimension of the nanostructure has to be below the dimensions of the 5 nm exciton in silicon. In this context, it has been recently shown that the color of nano silicon can be tuned across the visible spectrum in an entirely different way involving the strong resonant scattering of white light from silicon nanowires with different diameter. And as expected, the main challenges for successfully handling, processing and exploiting the unique properties of nano silicon in this tiny size regime are long term control of its surface oxidation and its colloidal stability. *The electrically pumped silicon laser is a still a holy grail!*

One can appreciate from the above that while the reign of the Silicon Samurai is still the computer chip there is a flood of opportunities for fundamental research on Nano Silicon that could give birth to the Nano Silicon Samurai spawning exciting new nanotechnologies potentially able to change the world as we all experienced with the silicon transistor.

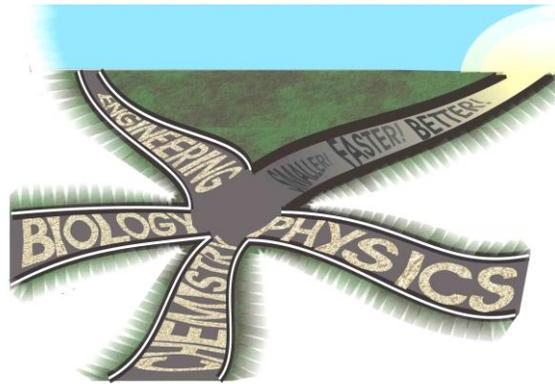
5. Who Needs A NanoScientist?

In the year 2000 the University of Toronto launched the world's first undergraduate degree program in nanoscience, an initiative spearheaded by Nanoengineering as a specialization in the Engineering Science program (Nature 2000, 408, 623).

This multidisciplinary degree program is taught by faculty from the materials science, physics, chemistry, chemical engineering, and mechanical and industrial engineering departments, and the institute for biomaterials and biomedical engineering. The emphasis of the first two years is on a solid grounding in mathematics, chemistry and physics and in the final two years on allowing students to tailor their program of lectures, laboratories and final year thesis research by drawing from any of the aforementioned subjects to allow them to satisfy their individual interests and aspirations in nanotechnology.

I offered courses in materials chemistry and nanochemistry as part of this nanoengineering degree program and was also involved in delivering nanoscience lectures to students who were potentially interested in pursuing the nanoscience degree. I recall students asking me why they should train for a career in nanoscience when the field might not survive. Was this not a huge risk to take? I answered with conviction that the field certainly was going to survive, and that a student who was considering not being involved was taking a bigger risk than a student who was eager for a slice of the nanopie.

Fast forward a decade, and I can't help but question whether I was justified in my unwavering promotion of nanoengineering science and belief in it as a field with a rosy future which, due to strong government and industrial ties would lead to great career prospects for any young scientist who chose to apprentice in it. Although we have had our great successes, the field has perhaps not reached the full potential I envisioned, and I'm compelled to ask: who needs a nanoscientist?



One of the main arguments used back in the good-old-days for encouraging students to specialize in nanoscience was its interdisciplinary nature; its promise to provide an education that criss-crosses the borders of the traditional scientific disciplines to gain as broad and deep an appreciation of the subject as possible. This is a lot to ask of a student but the core nanoscience principle is that with the right role models and the right mix of factual, conceptual and analytical thinking, students can transcend the

traditional model of a scientist who is an expert in one subject area at the expense of the others, and instead manage to have a good understanding of all, or, if that is not realistic, at least many areas of science.

Indeed maybe one of the greatest contributions of nanoscience is its success at encouraging bands of scientific specialists from disparate disciplines, to work together as integrated and harmonious units on big problems that require more than a single speciality for their solution. Together we are strong!

This new found interdisciplinary approach to solving research problems in information technology, biotechnology and nanotechnology is something of a recent development for the majority of university researchers who traditionally have felt more comfortable working alone or only with their closest coworkers in the speciality in which they feel scientifically secure and strong. To best take advantage of the nanoscience approach to research, one must be willing to expose their weaknesses in a multidisciplinary team environment and this is not every scientist's cup of tea! However, those with the confidence to do so usually benefit enormously from the experience of working in a stimulating multi-expert environment with the free-flow of ideas directed to solving a problem of mutual interest that is far beyond the capability of a single expert, or even a single discipline. Of course, having teams of scientists from different disciplines collaborating on the same problem is nothing new: it took scientists from many disciplines working together to put a man on the moon. What is new, however, is that we now have a new breed of scientist who, when faced with such a problem, aims to understand not just his small section of it, and those to which it is directly related, but also to understand the nature of the entire problem itself. For this reason, the nanoscientist is ideally positioned as a central player in these interdisciplinary problems. Accordingly, nano degree programs need to evolve from the 'nano for the sake of nano' philosophy to one where nano is a means to an end within a well-defined future technology. This is what students and employers recognize.

This leads me towards the answer to my question. We are now beginning to understand some of the great issues facing our species. We're running out of energy. We're poisoning our atmosphere, our water, and ourselves. We're slowly cooking our planet. Many of the most important recent advances in tackling these problems "particularly in the alternative energy sector, which promises to be the centrepiece of our ultimate solution" have come from scientists whose research draws from the broad range of knowledge that an education in nanoscience aims to provide. Indeed, I believe that some of the greatest progress that we are seeing in tackling some of the greatest issues we have ever faced is coming from nanoscientists.

*My answer then, to the question: 'who needs a nanoscientist?' is that we **All** do!*

6. What Can Nanochemistry do for Hydrogen Storage?

I was intrigued by a paper that David Antonelli and coworkers published in JACS 2010, 132, 11792 earlier this year on a new generation of enhanced performance hydrogen storage materials. They reported a fascinating new class of metal hydrazide porous gels that instead of storing hydrogen through the usual metal-dihydrogen physisorption or metal-hydride bonding mechanisms of trapping hydrogen in solids, instead works through the well known Kubas metal-dihydrogen chemisorption bond.

I spoke at length to David about the innovation, significance, timeliness and potential technological relevance of his breakthrough and because of my perceived view of the importance of his work in the highly competitive field of hydrogen storage I decided to integrate his thoughts and mine on the matter in this NanoChannel perspective with an eye on the role that nanochemistry can play in the hydrogen storage challenge.

The story of hydrogen storage in solid begins with hydrides that hold more hydrogen per unit volume than liquid hydrogen – some close to twice as much. This sounds promising because hydrogen liquefies at 20 K and it is both expensive and inconvenient to cool to these temperatures. But there is a catch and a big one at that!

While the slow release kinetics of these compounds can sometimes be overcome with a little trickery such as ball-milling and additives, the fact that the thermodynamics of the uptake and release are problematic is something that still remains a challenge, perhaps too large to overcome. The reason is that for those hydrides and hydrogen-containing compounds that reversibly absorb and release hydrogen, an enormous amount of heat is released on uptake and an equally enormous amount of heat is required to liberate the hydrogen for use as fuel. This necessitates complex engineering solutions that cut into the efficiency of the system in ways that make them unusable.

Because of these difficulties many materials researchers have explored nanochemistry ways of absorbing hydrogen, such as on the surface of metal organic frameworks called MOFs and various forms of nanoporous carbon. These nanomaterials can physisorb up to 7 wt% hydrogen at 77 K and 65 bar which is a feasible pressure considering that everything up to 200 bar is considered safe and convenient from the standpoint of building conformable tanks that can be bent around the design of an automobile chassis.

The aesthetic structures of MOFs and their gigantic surface areas, some even approaching the extraordinary gas adsorption limit of 7000 m²/g, seemed to

offer the potential of high weight percentages of hydrogen with no kinetic barrier on release and this opportunity was enough to ignite the imagination and efforts of some of the world's best academic scientists and chemical industry giants. However these materials have the innate problem that hydrogen binds so weakly to the surface that temperatures of 77 K were necessary to keep the hydrogen intact. Moreover, and this is possibly an even bigger blow, the volumetric densities are far too low for practical use. Even when you include the compressed gas in the pores in addition to that adsorbed to the surface the best materials hold about 50 kg/m³, which is 20 kg/m³ less than liquid hydrogen. So you lose whatever advantage that you had over liquid hydrogen.

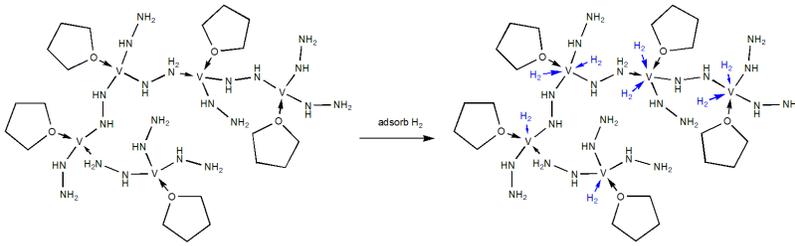
But the troublesome question still remains, how do we better store the hydrogen?

As it turns out, nanochemistry may provide an answer to this dilemma. The key to storing hydrogen effectively is to tailor the highest density of spatially accessible binding sites of the correct energy into a solid state material. The irksome point is that hydrides have enthalpies that are too high (ca. 70 kJ/mol) and MOFs have enthalpies that are too low (ca. 8-10 kJ/mol). Calculations show that the optimal for room temperature storage without any kinetic barrier or heat management problem is 20-30 kJ/mol. This is exactly where the Kubas interaction mentioned above falls – a molecular hydrogen chemical binding mode discovered in organometallic compounds in the 1980s by Gregory Kubas.

A challenge for nanochemistry is then to find ways to tailor Kubas binding sites at a high density into nanoporous solids with a very low molecular weight.

While nanochemistry has made great strides to control size, shape, porosity and surface functionality of solid state materials, in this application it is necessary to discover ways and means to also control the coordination sphere about a metal center to allow the maximum amount of Kubas binding in an extended solid while maintaining hydrogen diffusion properties. This is quite a difficult task because transition metal solids and compounds almost always have filled coordination spheres with an average of six ligands per metal, which would not allow room for molecular hydrogen to bind. The only exceptions to this are compounds with very sterically bulky ligands that allow such reactive and unstable coordination numbers lower than six to be stable. The key then is to find a way to jump from the trapped low coordination number in these low-coordinate complexes to a similar coordination number in an extended solid full of accessible space for dihydrogen like nanopores.

I was intrigued to discover that Antonelli and coworkers seem to have found a solution to this problem. In using metal alkyl complexes with low coordination numbers and bulky alkyl ligands as precursors they have found a way to preserve these low coordination numbers through a polymerization reaction



involving hydrazine to lead to nanoporous metal hydrazide gels with elimination of the alkyl sheaths by reaction with the hydrazine protons the concept of which is

illustrated in the figure (permission Journal of the American Chemical Society). Hydrazine was chosen because it is light weight, and just big enough to bridge the transition metals together without causing clustering. It also has four available protons that can react with the alkyls, which stay on the metal just long enough to protect the low coordination sphere during the reaction. The final compounds have formulas of the type MN_xH_y and molecular weights of around 70-80 g/mol with extended open frameworks comprised of metal sites connected by M-NH-NH-M and M-NH-NH₂→M bridging groups, creating thereby a random network of nanopores. This means that binding 2 H₂ per metal, which is more than possible, would result in weight % numbers over 5 and volumetric densities close to 100 kg/m³.

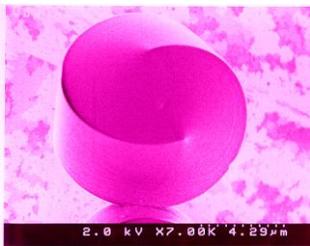
In discussions with David my thoughts on the matter were first and foremost that the materials are pretty sensitive and can ignite in air. As hydrogen and fire do not sit well together it will be necessary to develop synthetic pathways to less oxygen sensitive metal hydrazide gels. I thought it might also be advantageous to find ways to make nanoscale metal hydrazide gel particles to reduce diffusion lengths for adsorption-desorption cycling to improve the kinetics and energetics of the system while at the same time minimizing sensitivity to air. Efforts to enhance the porosity of the metal hydrazide gels, which is currently around 200 m²/g, might also prove beneficial as easy access of dihydrogen to Kubas-type metal binding sites may enhance the storage performance. This possibly could be achieved by integrating porogens into the synthesis of the metal hydrazide gels.

While the work described is just a first step for Antonelli and coworkers they have already made materials with as high as 3.2 wt% and 41 kg/m³ volumetric density at pressures under 200 bar with no kinetic barrier and what promises at this early stage to be little heat management issues. These materials already hold about four times as much hydrogen as compressed hydrogen per unit volume at any given pressure and temperature and are totally compatible with compressed gas technologies, as pressure is the toggle switch. This is advantageous given the fact that the industry is currently moving towards compressed gas anyway as a short-term solution.

7. Natural Nanochemistry: Artificial Petrification

Materials and structures in nature have successfully evolved, adapted and survived over a 3.5 billion year learning experience. Humankind has always admired and been inspired by the aesthetics of *natural form*, the visual perception of a class of objects with structural features associated with biological shapes, every one of which has a function and a purpose.

Through reverse engineering of nature's life forms, materials chemists, scientists and engineers have learned how to employ design principles and building strategies that abound in nature's organisms to find materials solutions to a wide range of scientific and technological problems, from the architectural wonders of the filigree Eiffel tower, Buckminster Fuller's geodesic dome and Stuttgart airport's metal tree roof to practical achievements of bone replacement, dry adhesive and military armour.



Morphosynthesis – Biomimetic inspired liquid crystal templated mesostructured silicate with a form reminiscent of a Brancusi sculpture in the New York museum of modern art – permission Canadian Journal of Chemistry.

This is the field of biomimetics (bios: life, mimesis: to imitate, synonymous with bionics, biomimesis, biomimicry, biologically inspired design) and many practical examples now exist of learning from nature's materials secrets and applying them to solve practical problems for society. The motivation in biomimetics is couched in the question: why reinvent the wheel when nature has spent billions of years finding materials engineering solutions to related problems in biological systems?

In this context, well known bottom-up materials synthesis examples taken from nanobiology include keeping surfaces dry and clean using nanoscale structured bas-relief patterns analogous to those found on the Lotus leaf, making full color reflective displays based upon the interference of light from a nanophotonic crystal similar to the periodic dielectrics found in butterfly wings, peacock feathers and beetle cuticles, and developing fracture-resistant ceramics by employing layered inorganic-organic nanocomposites of the kind found in the tough calcite-protein laminated architecture of the abalone shell.

I have been ruminating: rather than imitating life forms using nature's marvels as a blueprint for synthesis from scratch in the incessant search for materials solutions by pursuing biomimicry, why not instead use constructs that abound

in the natural world as structure-directing templates for creating copies in synthetic materials selected for particular applications?

In the language of templating these copies of natural forms can be co-assembled composites or template-free inversions thereof. An exquisite natural example of this is petrified wood where all the organics comprising the hierarchical architecture of wood have been infused with and replaced by silicate minerals (silicification) while maintaining the overall structural integrity of the wood. This is not to be confused with a fossilized impression of wood; rather, it is a three dimensional representation of the entire internal structure and external form of wood replicated in silicate from the bottom up.

In natural petrification wood is turned into stone using what might be called Medusa chemistry. This kind of morphosynthesis inspires the paradigm of artificial petrification for chemically transforming natural forms into functional inorganic structures with purpose.

Enter artificial petrification, whereby biological structures are employed as templates for making inorganic replicas with purposeful form and function. Laboratory prototypes of this process are beginning to emerge in the literature for solving problems in optics, energy and the environment. Recent demonstrations include the use of siliceous diatom microskeletons as templates for making nanocrystalline silicon diatom replicas with porous lacelike structures conducive to enhanced light harvesting in solar cells, the use of proteinaceous periodic microstructured wing scales of the iridescent blue *Morpho* butterfly for templating alumina photonic crystal replicas able to reflect and guide light in miniaturized optical devices, and the use of the hierarchical structure of the green leaf for templating nanocrystalline anatase-platinum replicas for improving the photocatalytic efficiency of splitting water into hydrogen and recycling carbon dioxide into solar fuels like methanol.

Imagine bacteria shapes assembled from silver nanowires and facsimiles of virus cages made of cobalt nanocrystals, calcite coccoliths in graphene and echinoderms in gallium nitride, mosquito eyes in silver and sponge spicules in gold, radiolaria microskeletons in yttrium barium copper oxide and marine diatoms made of copper indium selenide, and the hierarchical structure of Haversian bone in titanium. What would you make out of these?

8. Nanochemistry: Who Owns It?

What isn't chemistry? Nearly everything in the world around us is made from chemicals and chemistry pervades the physical, life and applied sciences and is often termed "the central science". Synthetic chemistry is certainly playing a central role in modern nanochemistry, the hallmark of which is a bottom-up synthetic approach to nanoscale building blocks made from inorganic, organic and polymeric materials and composites thereof. And nanochemistry is playing a central role in nanoscience and nanotechnology as evidenced by the disruptive effect it is having on basic and directed research emerging across the disciplines of physics, materials science, engineering, biology and medicine.

But is there anything "really" new about nanochemistry? Is it just the next chapter in the long and illustrious history of colloid chemistry, the centerpieces of which are the same tiny pieces of matter and the forces between them that occupy much of nanochemistry research today?

So who owns nanochemistry? Should "all" the credit be given to chemistry pioneers of the past 20-30 years or were the foundations of nanochemistry already laid in the field of colloid chemistry, the origin of which can be traced to a century earlier?



The term colloid (Greek word kola meaning glue-like) was coined by Thomas Graham in 1861 and used to describe the distinctive behaviour of any form of matter, soft to hard, with a physical size in the 1-1000 nm range and with properties intermediate between that of a solution and a suspension (e.g., slow diffusion, difficult crystallization, scattering light, sol-gel formation). While Graham (1805-1869) is often credited with founding colloid chemistry, Wolfgang Ostwald (1883-1943 seen in the portrait – not to be confused with his Nobel Lauriat father Wilhelm Oswald (1853 – 1932) renown for catalysis, chemical equilibria and reaction kinetics - permission Journal of Chemical Education) is given credit for propagating the field of colloid science, the physicochemical principles of which are expounded in his classic book "The World of Neglected Dimensions, 1914".

Colloid science owes much to the pioneering contributions of early researchers like Aldar Buzagh (1895- ??) and Ernst Hauser (1896- ??) who came to the realization that all matter with at least one of its physical dimensions in the colloidal domain will display colloidal properties and it was also noted how colloid science impacts many fields of science and technology crisscrossing the boundaries of science from chemistry and physics to biology and medicine to geology and mineralogy. *This is very similar to the nanosheets, wires, and dots*

which occupy much of modern nanochemistry research and is echoed by the multidisciplinary nature of the field of nanochemistry today. Herbert Freundlich (1880-1941) noted how the colloidal state of matter can be accessed through what he called “two doors” either from a molecularly dispersed system whereby the size of a dissolved species is increased continuously until the colloidal chemistry regime is reached or by constantly reducing the size of matter to the colloidal state until it can be continuously dispersed in another one. *Today we refer to these as the bottom-up and top-down approaches to nanomaterials.* In 1903 Richard Zsigmondy (1865-1938 - Nobel in chemistry) was the first to observe the colloidal state of matter in an optical microscope, which becomes visible when illuminated from one side despite the gold particles he was studying being smaller than the resolving power of the microscope. The work of Gustav Mie (1869-1957) on the scattering of light by metal colloids complements the optical studies of Zsigmondy and provided a theoretical foundation for the plasmon resonance of colorful gold colloids, originally observed by Michael Faraday (1791-1867). *Now days, we routinely use absorption and scattering of light for studying the structure, stability and dynamics of gold nanomaterials and how they interact with each other and their environment which underpins exciting breakthroughs in nanoplasmonics and photonic metamaterials, as well as diagnostics, therapeutics and imaging in nanomedicine.*

It is worth noting that in the early days of colloid science the unit name “nanometre” did not exist. In optical spectroscopy it was referred to as a millimicron. Pieter Harting (1812-1885) a Dutch biologist and geologist and early pioneer of optical microscopy, invented in 1845 a new measure of length, the micron as the millimetre millimetre (mmm), later denoted μm , to study microscopic objects. In order to handle colloidal length scales Zsigmondy introduced a system with three size regimes, denoted in German, “Mikron, Amikron und Ultramikron”. *The Ultramikron, translated as submicron, can be regarded as today’s nanometric ruler for defining the size of nanomaterials.* The 1926 chemistry Nobel awarded to Theodore Svedberg (1884-1971) for his work on the analytical ultracentrifuge also cited colloid science research. This was followed soon after by the 1932 Nobel to Irving Langmuir, largely for the development (with Katharine Blodgett) of monolayer surface chemistry. *So this was the high point in terms of recognizing colloid and affiliated surface-science research as core areas of chemistry, as opposed to industrial chemistry.*

By 1959, when Richard Feynman delivered his after dinner speech on the future of miniaturization, “Plenty of Room at the Bottom”, colloid science was pretty well grounded as a field and colloid chemistry was the premier method to synthesize colloids, made for example of metals, metal alloys, metal oxides or metal chalcogenides, dispersed on the surface or within the spatial confines of supports, such as alumina, silica, clays, zeolites and polymers. These colloids were often targeted at the time for applications in the burgeoning field of

heterogeneous catalysis. Precursors from inorganic, organometallic, cluster and metal vapor chemistry were employed for synthesizing and controlling the nucleation and growth of unimetallic and multimetallic catalytic colloids and it was well recognized that the catalytic activity and selectivity of the colloidal particles depended on their size and shape, accessible crystal surfaces and crystallographic sites, as well as electronic and steric effects associated with interaction of the colloidal particles with the support.

The “perfect colloid” was always a holy grail in the field of heterogeneous catalysis as this was seen as one of the best ways to control catalyst performance and many creative ways were devised to make single size and shape colloids, on and in a range of supports, expressly for this purpose. *These days, we are still pursuing the perfect colloid, although now we call them monodispersed nanoparticles, no matter how they are made and what they are made of.*

And simultaneous with the emergence of heterogeneous catalysis, a multi-analytical approach, including X-ray diffraction, electron microscopy, extended X-ray absorption fine structure, photoelectron, laser Raman and Fourier transform infrared spectroscopy was being developed and used to establish the structure and chemical reactivity of catalytic colloids. *These analytical methods are amongst the major tools used for characterizing nanomaterials produced by nanochemistry today.*

Yet in all of this early research employing colloidal particles particularly catalytic colloids in heterogeneous catalysis, to the best of my knowledge, the nano word was never used. The prefix “nano-“ was of course used in “nanosecond”, from the 1960s onward, because pulsed laser flashes had durations that were conveniently expressed in that unit.

Norio Taniguchi (1912-1999) is credited with the first use of the term “nanotechnology” in 1974 in reference to “production technology to get the extra high accuracy and ultra fine dimensions, i.e. the preciseness and fineness on the order of 1 nm (nanometre), 10^{-9} meter in length”. Whilst he was initially concerned with top down semiconductor fabrication techniques, his term and its descendents have come to be used across all branches of modern science.

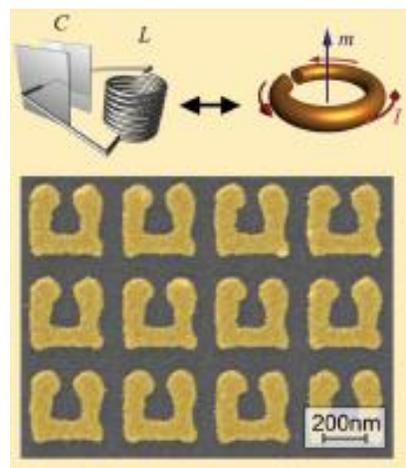
So: who gets the credit for nanochemistry ?

9. What can Nanochemistry do for Photonic Metamaterials?

Many exciting chapters in the annals of twentieth century chemistry are traceable to breakthroughs in experimental and theoretical physics like the discoveries of X-ray diffraction and electron optics that revealed the geometric arrangement of atoms in molecules and materials, and the formulations of quantum mechanics, molecular orbital theory and band theory which enabled our understanding of the structure, bonding, optical, electrical and magnetic properties of molecules and materials.

Nowadays, one of the hottest areas of physics research is photonics: the control of light by structures fabricated at the wavelength and sub-wavelength scales. The field of photonics really took off with the theoretical prediction of an omnidirectional photonic bandgap in certain three dimensional periodic dielectric lattices, now known as photonic crystals. Chemists and materials scientists have been involved in efforts to fabricate photonic crystals for over a decade and their main successes have been with the self-assembly of spherical colloids into opals, and the use of these structures as starting points for replicating other, more complex, materials. Chemists working in the field have made contributions to many of the current and emerging applications of these materials, such as full colour reflective displays, security devices, and sensors.

Now I am wondering what chemistry can do for the rapidly emerging and intriguing field of metamaterials? This new class of materials provides a platform for tuning optical space through command of local electric and magnetic fields in ways not previously imagined possible. The first example of a metamaterial with designed structural properties was the split-ring resonator (a miniature LC circuit wherein an electromagnetic field can induce a circulating and oscillating electric current making it act as a miniature planar electromagnet in which the electric dipole and magnetic dipole moments are respectively disposed within and normal to the plane of the split-ring - (see illustration – permission Martin Wegener, KIT) that was first demonstrated in the microwave region but with advances in nanofabrication techniques can now be applied to near-IR frequencies. The ability to fabricate optical metamaterials, that is, metamaterials operating at or near to visible frequencies, also referred to as photonic metamaterials, has excited enormous interest in the optical physics community not just because of the potential to discover new physics but also the opportunity to reduce to practice some of the promises of metamaterials



that operate at visible wavelengths, such as the perfect lens, the invisibility cloak, and the perfectly absorbing optical black hole.

All of this excitement in physics makes me wonder, *what's in this new class of photonic metamaterials for chemistry?*

To understand this, we need to answer a number of fundamental questions which include:



First, what is it that is so amazing about metamaterials? Although the term 'metamaterial' in its broadest sense refers to any material displaying optical properties not readily available in nature, its most common association is with materials having negative refractive indices. The simplest physical manifestation of a negative refractive index would be that when light enters a negative index material the resulting refracted beam would appear as the reflection of the

refracted beam for a material of positive index of the same magnitude (see illustration – permission Martin Wegener, KIT). Although it may be difficult to immediately see how these effects could be of practical value and not just cute physics demonstrations, it turns out that they actually have extremely powerful applications to the control of the flow of light.

Second, what material properties do metamaterials need to have in order to display their incredible optical properties? The refractive index of a material may be written as $n = \pm(\epsilon\mu)^{1/2}$ where ϵ is the material's relative electric permittivity and μ its relative magnetic permeability – terms which describe a material's response to imposed electric and magnetic fields. In order for a material to possess a negative refractive index it turns out that both ϵ and μ must be simultaneously negative. Achievement of this poses a significant challenge, and has only been possible in recent years, firstly with the split ring resonator in the microwave region, albeit with a slightly different double-ring configuration, as opposed to the single ring design shown in the illustration, used for the visible region.

Achieving negative ϵ , even at visible wavelengths is not difficult. Metals are the typical example of materials displaying this property. Negative μ and n are typically achieved by fashioning a material with negative ϵ , such as gold, silver, or copper into a structure which displays negative μ . In the split ring resonator the size of the metal ring is designed to be resonant with electromagnetic radiation of the target frequency, that is, the frequency at which we intend to demonstrate a negative index. The slit in the ring allows it to resonate on exposure to radiation whose wavelength is much larger than the size of the ring

– this is critical because when we design such a material we want the radiation to have uniform optical properties at the frequency of interest, which requires that the spatial period of the material be much less than that of the radiation. The optical physics analysis is complicated but it turns out that a properly designed split ring resonator can display a negative permeability at its resonant frequency, and thus can be used as an element in fabricating negative index materials. Since the advent of the split ring resonator other structures have been shown to function as metamaterials, such as gold helices.

Photonic crystals can provide control over the electric component of light while photonic metamaterials can control both electric and magnetic components of light.

Third, and a central feature of this editorial, how does one make photonic metamaterials? All reports so far of photonic metamaterial fabrication have relied on top down methods such as electron beam lithography, direct laser writing and nanoskiving on rigid and flexible inorganic and polymeric substrates. As nanochemists, is there a way for us to bring the same bottom up techniques that we successfully applied to photonic crystal fabrication to the world of metamaterials? What molecular or materials structures and compositions should be synthetic targets for photonic metamaterial building blocks and their arrays besides gold? Also what properties of photonic metamaterials should be sought after and what are the best ways for evaluating these properties? And what properties of photonic metamaterials can be usefully exploited in chemistry and biochemistry, biology and medicine?

As far as I can judge, a bottom-up approach to photonic metamaterials is proving to be quite a challenge. Gaining synthetic access to building blocks with complex shapes like split-rings and spirals, antenna and fishnets, having sub-100 nm dimensions and self-assembling them into periodic arrays with predefined geometries is not easy. It is at the cutting edge of nanochemistry!

In this context, a couple of bottom-up inroads to large-area split-ring arrays could make use of multi-tip dip pen nanolithography coupled with metal electrodeposition or template directed self-assembly using nanodroplet wettability arrays and metal nanocrystals. Imagine split rings made of collections of metal nanocrystals whose nanocrystal separation, non-metal-metal transition and hence photonic metamaterials properties, can be controlled through self-assembly chemistry.

With respect to possible applications one can seek to exploit the unique properties of photonic metamaterials, namely that conduction electric and magnetic resonances both become observable at optical wavelengths. This in principle provides an extra degree of analytical freedom beyond that offered by plasmon resonance spectroscopy for monitoring local changes in the

environment of split-rings caused by chemical, biochemical, thermal, photochemical and electrochemical stimuli.

In this context one can imagine dynamic tuning of the photonic properties of gold metamaterials by selective chemical etching or galvanostatic reconstruction of the split-ring units in an array to change the optical resonant frequencies. One can also envision gold metamaterial arrays coated with self-assembled monolayers based upon alkanethiolates with terminal groups designed to recognize DNA, proteins and peptides, viruses, bacteria and cells through changes in the electric and magnetic optical resonances of the metamaterials that might outperform straight plasmonic probes. Gain materials like dyes, polymers and quantum dots chemically tethered to metamaterials could help ameliorate optical absorption losses that plague metals like gold. Another interesting study would be to gradually bend a gold nanorod into a split ring configuration to see when the diagnostic transverse and longitudinal plasmon resonances of the nanorod transform into the electrical and magnetic resonances of the metamaterial? And as it is well documented that gold nanorods can be functionalized on their ends and sides with different kinds of self-assembled monolayers one can imagine the same being accomplished with the gold split-ring and this attribute used to selectively tune the electric and magnetic resonances through end and side selective chemical recognition or by altering the capacitance across the ends of the ring?

Also what materials besides gold are useful for other photonic metamaterials objectives? Can one for instance build solid state properties like piezoelectricity, ferromagnetism or photoconductivity into photonic metamaterials to create a whole new world of multifunctional photonic metamaterials? It is interesting to ask, of the many perceived applications of metamaterials which one could make it first as a real product to the marketplace? *How about the perfectly absorbing optical black hole solar cell?*

If some of these ideas could be reduced to practice it seems to me that nanochemistry has a lot to offer photonic metamaterials.

10. Nanochemistry Pores for Thought

Have you ever paused to think whether there are more materials being reported these days filled with regular arrays of holes than materials with close-packed lattices?

Not so long ago it was thought that thermodynamics would dictate how atoms, molecules and clusters would pack in the lattice of crystals to minimize the occurrence of energetically unfavourable open space. With the discovery more than half a century ago of large families of naturally occurring and synthetic zeolites with crystalline microporosity this view soon changed and was replaced by the realization that kinetic stability can dominate over thermodynamic stability with respect to pore collapse. The trick to creating voids in nominally dense materials was to find a synthetic pathway to metastable phases with chemically and mechanically robust open frameworks.

In this context, research conducted over fifty years ago aimed at understanding the mode of formation of zeolites led to the concept of *templating* in which a structure-directing, space-filling and charge-balancing, hydrated inorganic or organic cation, was used as a template for the co-assembly of tetrahedral silicate and aluminate building blocks, causing them to organize and polymerize around it and leading to porosity after its subsequent removal.

Sounds simple enough but the mechanistic details of zeolite self-assembly are still not fully understood and research into it continues to this day.

It is worth mentioning at this point the recommended nomenclature for porous materials, from the International Union of Pure and Applied Chemistry (IUPAC), that micropores have free diameters less than 2 nm and mesopores are in the range of 2-50 nm while 50 nm and above are macropores.

Knowledge of how to introduce voids into solids ignited an intense global effort aimed at understanding the rules of zeolite templating in order to gain control over the structure of the crystalline microporous framework, the pore size and shape and the silicon : aluminum ratio, which determined the ion-exchange capacity and the acidity or basicity of the pore surfaces; properties that enabled a range of applications like molecule size and shape selective catalysis, gas separation, humidity control, sequestration and storage of radioactive waste, heat pumps working on adsorption-desorption cycles, and replacement of environmentally unfriendly phosphate water softeners in detergents with “green” zeolite ion-exchange substitutes.

The aluminosilicate zeolite and all-silica molecular sieve eras were followed by the expansion of the composition field of microporous materials to include a large portion of the periodic table most notably being the crystalline microporous aluminophosphates, AlPOs and element substitutions thereof such as the metal aluminophosphates, MeAPOs.

At the time this was celebrated as a great breakthrough and enormously expanded opportunities for microporous materials not only in traditional areas like catalysis and separation but also for advanced technologies that could benefit from holey materials with large internal surface areas and voluminous pore spaces: chemical sensors, solar cells, fuel cells and batteries, controlled chemical storage and release vehicles, and nanoreactors for host-guest inclusion dubbed “ship-in-the-bottle” chemistry. The latter avenue notably provided a structurally well-defined confining space for the nucleation and growth and stabilization of quantum size effect mediated, brightly luminescent semiconductor nanocrystals and plasmonic metal nanocrystals.

Early research aimed at the synthesis of semiconductor and metal nanocrystals within the nanometre voids of zeolites and molecular sieves inspired analogous studies of arrested nucleation and growth of nanocrystals in solvents that were also ligands, where in the case of zeolites the capping ligand was the zeolite cage.

Research that was beginning to stretch the traditional boundaries of zeolite and molecular sieve materials science raised the possibility that crystalline microporous metal chalcogenides might be accessible. The rules developed for templating turned out to work quite well when applied to metal sulfide building blocks and this research revealed a whole new world of porous metal sulfide semiconductors. The pioneering archetypes were made of tin and germanium sulfides with impressive open-framework structures. Some of these materials displayed flexibility of their open-frameworks with respect to the adsorption and desorption of molecular guests, and some were reported as seasonal because their structures changed depending on relative humidity.

So the holey genie was out of the bottle and soon thereafter it proved possible to make crystalline microporous metal selenide analogues and the first example of electronic bandgap engineering - traditionally applied to bulk semiconductors - applied to these materials was demonstrated by the synthesis of crystalline microporous thioselenides and their verified composition-tuneable properties. This led to the possibility of building molecule discriminating electronic and optical devices out of microporous semiconductors, and an early example of an electronic nose was demonstrated.

The discovery of coordination frameworks nowadays considered synonymous with metal organic frameworks (MOFs) was inspired by earlier work on

crystalline microporous metal oxides and metal sulfides. In these holey materials, metal ions or metal ion clusters are linked together through organic ligands the choice of which controls the size, shape and dimensionality of the pores and their gas adsorption-desorption behaviour.

The surprisingly large pore surface areas of coordination frameworks, some able to withstand pore collapse on removing imbibed solvent and/or template, have turned out to be especially pertinent with respect to a number of environmental problems facing our planet today, such as the challenge of safe storage of large amounts of H₂ under practical temperature and pressure conditions for clean power generation and the greenhouse gas conundrum that requires the sequestration of large quantities of CO₂ from our atmosphere to prevent further global warming.



Half a century of research on the synthesis of a periodic table of crystalline microporous materials created the impression that pore sizes above the 2 nm limit in this class of materials would be impossible.

The above doctrine proved to be wrong with the discovery that periodic mesoporous silicas (PMS) and periodic mesoporous organosilicas (PMO) with pore sizes in the

2-50 nm range could be synthesized using supramolecular templates comprised of surfactant or block copolymer micelle or liquid crystal assemblies, rather than having to synthesize larger-and-larger organic molecule templates to direct the formation of pores bigger than 2 nm.

This breakthrough led to intense global research activity on a periodic table of mesoporous materials, to accompany the microporous materials which had been studied for over five decades. This discovery provided new opportunities for materials scientists as a great many solid state materials that had been engineered into advanced technologies were now accessible in mesoporous form. As a result, research and development began in earnest to discover whether this new class of materials filled with regular arrays of mesoscale channels and pores could improve the performance of existing products or facilitate the development of new products in application areas including, electrodes and electrolytes for fuel cells, photovoltaics and batteries, photocatalysts, low dielectric constant film for smaller more powerful microelectronics, more efficient antireflection coatings in optics, efficacious chromatography stationary phases, drug delivery and drug removal vehicles in medicine, and pesticide/herbicide release platforms in agriculture.

Pore control was taken to even greater precision with the realization that crystal lattices of self-assembled micron scale silica and polymer spheres, called opals, could also be used as templates for replicating inorganic materials. One of the first major breakthroughs for these kinds of periodic macroporous materials involved inversion of an opal template in silicon to create the world's first three-dimensional silicon photonic-bandgap material, potentially useful for controlling light in all three spatial dimensions. Research of this genre established opal optical materials not just as photonic platforms for controlling light (e.g., guiding, switching, localizing and amplifying photons at sub-micron length scales) but notably through Bragg diffraction also for the creation of structural color with myriad uses from electrically tuneable reflective full color displays to effective authentication technology to color sensors.

So where will we see the next downpour? One thing that struck me as truly unexpected was the very recent report that a chiral nematic liquid crystal composed of cellulose nanocrystals can function as a soft template to cast a hard replica in silica. And free-standing films of this material devoid of template were shown to behave as chiral photonic crystals. As a result of this astonishing discovery we can expect to see light-scale chiral porous silicas explored for chiral separations of biological molecules and as hard templates for double inversions of myriad replica materials with imprinted photonic chirality.

All these materials filled with regular porosity over multiple length scales, from nanometers to microns are enough to make one pause for thought and ponder the old adage: when it rains it pores!

11. Powering the Planet with Energy Nanomaterials?

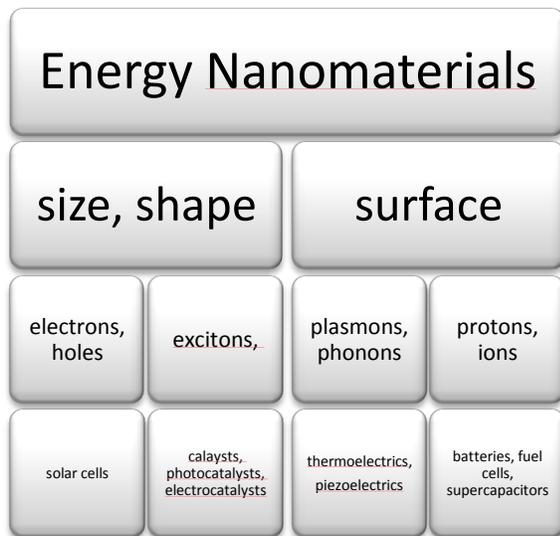
How can nanochemistry help solve the energy problems that our world faces today? How can nanomaterials make a difference in the grand challenge: efficient and green global scale production, storage and use of energy?

It turns out that depending on how energy is generated; by making or breaking chemical bonds; exciting electrons or holes; creating excitons or multiple excitons; using plasmons or phonons; the physical size of materials involved in the process can make a big difference as below a critical dimension the chemical and physical properties of materials are subject to quantum mechanical scaling laws. So why is small often good for many kinds of energy materials and devices?

To answer this question we must understand the special properties of different classes of energy materials fashioned at the nanoscale and the role their size plays in energy or storage. A primary consequence of diminished size is to amplify surface effects and morphology will determine the crystal faces available for surface reactions. By reducing the physical dimensions of energy materials to the scale of nanometres the surface to volume ratio and number of active surface sites increase, which enhances the efficiency of any heterogeneous catalytic process whether thermo-, photo- or electro-catalytic.

For energy materials, with physical dimensions smaller than the wavelength of electrons, holes or excitons, the beneficial effects of spatial and quantum confinement on electrical, optical, thermal and mechanical properties are becoming apparent in the fabrication of solar and fuel cell, lithium ion battery, supercapacitor, piezoelectric and thermoelectric energy devices. At these tiny scales, enhancing the absorption, diffusion and scattering lengths and strengths of all the various particles and quasi-particles which contribute to energy generation processes are of paramount importance in the production of efficient energy materials and their implementation in energy devices.

I am really impressed by the many ways in which the unique properties of nanomaterials are being creatively applied to help solve today's energy problems.



To amplify on the above with some representative examples, the intense electric fields associated with plasmons in silver and gold nanoparticles are being employed to enhance the harvesting of light, production of electrons and holes, and performance of metal oxide water splitting ($\alpha\text{-Fe}_2\text{O}_3$ nanoparticles) and carbon dioxide recycling (TiO_2 nanotubes) photocatalysts for the production of hydrogen, methane and methanol solar fuels. Noble metal nanoparticle plasmons are similarly being used for improving the light absorption and photon to electron conversion efficiency of different kinds of

photovoltaics from silicon to dye sensitized solar cells.

In semiconductor nanocrystals, the effect of confinement of electrons and holes in a three-dimensional potential well is to transform the continuous energy levels of the electronic bands of the bulk semiconductor into discrete energy levels in the nanocrystal, whose energy spacing can be tuned by controlling the nanocrystal's physical size. This so called 'quantum size effect' in semiconductor nanocrystals can be usefully exploited in the construction of different kinds of solar cell, which take advantage of size tuneable electronic band gaps to optimize the harvesting of solar photons; size controllable electronic coupling between nanocrystals to enable efficient transportation and collection of charge; and multiple exciton generation from absorption of a single photon to maximize power conversion efficiency.

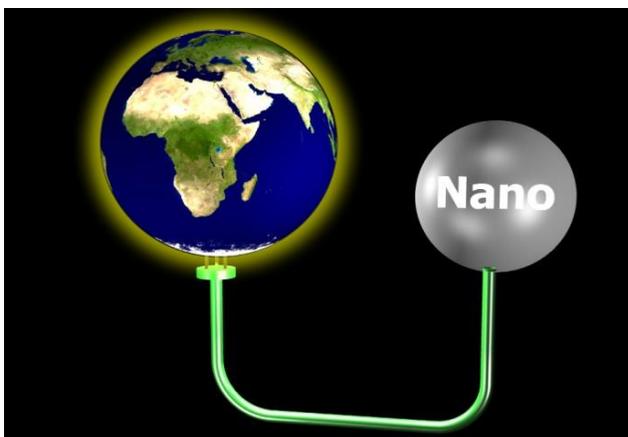
Colloidally stable dispersions of semiconductor nanocrystals have the additional advantage that they can be readily combined with organic polymers, dyes or other nanocrystals and processed into thin films and multi-layers on rigid or flexible substrates such as metals, transparent conducting oxides or polymers, all key attributes for the development of third generation solar cells.

In this context, the integration of photonic crystal architectures, such as those formed from multi-layers of colloidal nanocrystals, into solar cells has provided another means of improving their light collection and overall efficiency by increasing the effective path length and hence absorption of photons in the active semiconductor region of the device.

In lithium ion batteries, metal oxide nanoparticles based on titania, silica or alumina are replacing organic plasticizers in polymer-salt electrolytes because of their ability to stabilize the room temperature high ionic conductivity amorphous phase of the polymer and at the same time render the system less

prone to explosion hazards during recycling. In this context, the deleterious charging-discharging volume swings of lithium ion battery anode and cathode materials, which occur due to intercalation of lithium ions at the negative electrode during charging and at the positive electrode during discharging, can be ameliorated by reducing their scale to nanometre dimensions with the additional benefit of improved cycling times. A notable accomplishment in this regard is the development of high capacity silicon based-batteries which accommodate the substantial fourfold silicon anode volume changes on lithium insertion by fabricating the anode as an array of silicon nanowires, which provide small lithium ion diffusion lengths for rapid charge-discharge, nanowire conduits for transporting charge to current collectors as well as sufficient space in between nanowires to contain their volume expansion and contraction recycling requirements.

The development of high performance super-capacitors as electrical energy storage devices can also benefit from the use of high surface area electroactive nanomaterials. While the power density of super-capacitors is higher than that of batteries their energy density ($E = 1/2CV^2$ where C = capacitance and V = cell potential) needs to be improved for them to be widely deployed in electronic devices and industrial electrical systems. In this endeavour a notable research target is the high energy density asymmetric super-capacitor comprised of a high surface area carbon cathode and a metal oxide anode. A recent promising example is an interpenetrating porous network of vanadium pentoxide nanoribbons and carbon nanotubes, which enables easy accessibility of an organic electrolyte and facile charge transport into the electroactive nanomaterial network.



Powering the Planet with Energy
Nanomaterials – Graphic Illustration by
Wendong Wang

Reducing the scale of thermoelectric materials to the nanoscale provides a means of boosting the figure of merit ($Z = \sigma S^2 / \kappa$ where σ = electrical conductivity, κ = thermal conductivity, and S = Seebeck coefficient) to values in the range $Z = 3-4$ that make their use in power generating systems a realistic prospect. Bismuth based nanomaterials - metal and metal chalcogenides in the form of dots, wires, sheets and assemblies thereof - can simultaneously display high electrical conductivity enabled by quantum size effects that enhance the electronic density-of-states and low thermal conductivity enabled

through amplified surface phonon scattering effects.

Exploiting piezoelectric materials like zinc oxide, which generate electricity from the application of pressure, notably from tiny movements of easily deformable nanowires grown on different substrates (fibres, meshes and films), allows them to be fashioned into new kinds of mechanically actuated nanogenerating power systems targeted for mobile, implantable and personal electronic devices. Here the electrical energy to drive the device is created by some form of physical motion of the zinc oxide nanowires, human or otherwise, originating in for example, sound, wind, heartbeat, muscle contraction and blood flow.

It is the nanochemical techniques which have been developed and refined over the past two decades, which have led to our ability to produce these potentially groundbreaking energy materials and devices. Nanochemists have strived to produce nanoscale materials with controlled size and shape and surfaces and well defined compositions, which are necessary for tackling these challenges. Although there is still a great deal of work to be done, we have come a very long way in a very short time. Now the challenge is to make the leap from nanoscience to nanoengineering; from the simple quest to discover and characterise new energy materials to the true goal of applying them in the solution of global energy problems, illustrated in the futuristic scheme of *nanomaterials powering the planet!*

In the emerging field of enhanced energy nanomaterials it has been the increasing application of nanochemistry synthetic strategies which has provided the enabling nanoscience that has led to the realization of improved performance energy nanotechnologies.

12. Nanospheres and Solar Cells – On a Roll

It seems like the whole world is working on solar cells; trying to make them better, cheaper and safer to cope with the looming global energy drought.

Solar cells today come in three main flavours: Generation I – high efficiency, high cost; Generation II – low efficiency, low cost and Generation III – high efficiency, low cost. Most of the market activity seems to be concentrated around Generation I and II while Generation III remains mainly in the laboratory research phase awaiting a big breakthrough.

Crystalline silicon, expensive to produce but exhibiting high efficiency, stands aloof and alone in Generation I, with its performance capped by the thermodynamic Shockley-Queisser 33% limit, defined by sub-electronic band gap energy and hot electron losses. Despite its high cost, crystalline silicon makes up the vast majority of cells being employed in real-world applications today.

Vying for market dominance and accepting lower efficiency in exchange for lower cost are Generation II thin film solar cells utilizing semiconductor materials such as amorphous silicon, cadmium telluride, copper indium gallium selenide, nanocrystalline titania, organic molecules and polymers.

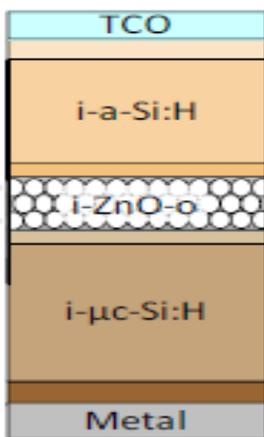
Generation III solar cells are attracting a lot of research activity these days and can be considered to synergistically integrate electrical, optical and photonic (nano)materials chemistry, materials science and engineering approaches to create low cost and high efficiency solar cells designed to beat the Shockley-Queisser limit. Despite all of the attention Generation III solar cells have received, they are still a very long way from achieving their target efficiencies.

Different solar cell architectures and strategies currently being explored to achieve Generation III cost and efficiency goals include multi-junction tandem, multi-exciton, up-and down-conversion, texturing, intermediate band states, intermediate reflectors, photonic crystals, and plasmonic and optical concentrators.

Generation III is proving to be a (nano)materials playground for creative bottom-up chemistry ways to simultaneously enhance solar cell performance while keeping the cost down.

One thing I have noticed in recent Generation III solar cell research is the increasing use of self-assembled monolayer or multilayer films of nanospheres with diameters from nanometers to microns. These nanospheres may serve a number of purposes, for example as templates for texturing semiconductor surfaces using the patterning technique of nanosphere lithography. Texturing causes multiple scattering of light and so increases the optical path length of light inside the active semiconductor material, thus increasing its absorption while using a smaller thickness of material, saving on cost.

Sphere films are also being employed to enhance the harvesting of light and boost the generation of electron hole pairs using different kinds of optical and photonic effects.

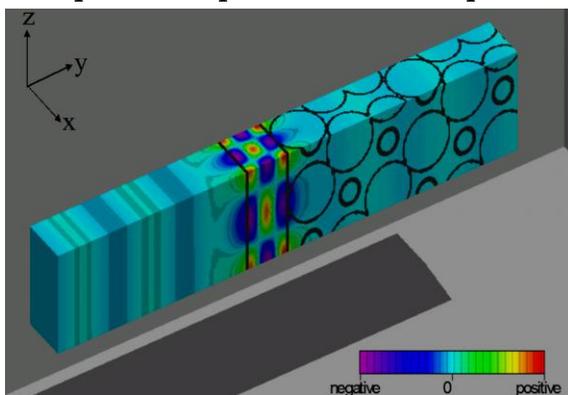


(a)

Noteworthy in this respect is the use of optically transparent and electrically conductive zinc oxide inverse colloidal crystal film as an intermediate reflector in a silicon tandem solar cell to enhance its performance, using the cell architecture illustrated in the Figure. The role of the intermediate reflector layer between the a-Si:H ($E_g = 1.7$ eV) and μc -Si:H ($E_g = 1.1$ eV) junctions shown in the Figure is to return incident photons of energy greater than 1.7 eV to the upper a-Si:H cell, where they have a second chance to be absorbed and where more of their energy will be available than would be to the 1.1 eV layer due to thermalization losses. To optimize the operation of this tandem solar cell the goal is to obtain the same current in the top and bottom components of cell. The

aforementioned intermediate reflector is designed to boost the current generated in the upper cell while transmitting photons of lesser energy to the underlying μc -Si:H cell.

Another approach to boost performance involves the placement of spheres with encapsulated plasmonic nanoparticles on an electrode of a dye sensitized solar cell, whereby trapping of light occurs



through a combination of multiple light scattering and local electromagnetic field enhancement that serve to amplify the absorption of light by the dye and enhance the photogeneration of electrons and holes.

A colloidal crystal film made of silica spheres has also been utilized as a back reflector optically coupled to a silicon or

nanocrystalline titania thin film in a silicon or dye sensitized solar cell. The idea of this cell architecture, illustrated in the Figure for the case of a thin silicon film (centre) sandwiched between silica colloidal crystal film (right) and a glass substrate (left), is to enhance the effective optical path length of light in the active semiconductor. This occurs through a combination of transverse reflected and longitudinal diffracted modes, which enable the localization of light and its absorption in the semiconductor and hence the efficiency of generating electron hole pairs, manifest as an amplification in the photoconductivity compared to the case where a silver mirror or air replaces the silica colloidal crystal film.

Colloidal crystals assembled from nanospheres have also been used in solar cells for their ability to control light by slowing it down as Bragg standing waves as well as simply reflecting it. Silicon inverse colloidal crystals can be synthesized in both intrinsic and extrinsic n-doped and p-doped forms. The intrinsic inverse silicon colloidal crystal has been used as i-layer, in a p-i-n amorphous silicon solar cell, to exploit slow light amplification of the absorption of incident light in i-layer in an attempt to improve cell performance.

Nanospheres have also been used for their ability to individually confine light: whispering gallery modes associated with spheres in a monolayer sphere film located on the electrode of a dye sensitized solar cell have been used to enhance the coupling of incident light to the absorbing dye in an effort to improve the performance of the solar cell.

While there is still much research to be done to understand how to improve the efficiency of Generation III architectures it seems to me from all this recent activity that nanospheres and solar cells are on a roll!

13. What can Nanochemistry do for Chemical and Biochemical Sensing?

It seems these days that if one's "pet nanomaterial" does not live up to initial expectations for use as an active component of a solar cell, photodetector, light emitting diode, laser, field effect transistor, battery, display, chromatography stationary phase, water splitting or carbon dioxide recycling photocatalyst, hydrogen storage or gas separation open framework, drug delivery or detoxification system, medical imaging or therapeutic device, then for sure it will respond in some way to some stimulus and thereby function as some sort of chemical or biological sensor.

Is this the nano graveyard for our beloved nanomaterials? A kind of nanoscience 'booby' prize often claimed by researcher's who discover that their materials are unsuitable for their initially intended uses? Or is it rather a valid scientific and novel application, and is nanochemistry the place to look for the sensors of the future, or will it only provide us with a stream of barely adequate also-rans?

The glass pH electrode invented by W.S. Hughes in 1922 is the first recorded chemical sensor. Here the pH of a solution is detected through chemical exchange signals in a thin glass membrane. This breakthrough was followed by a stream of other kinds of sensors for detecting a variety of chemicals from oxygen to glucose. Developments in the semiconductor microelectronics industry led to the miniaturization of circuits and sensor arrays in the 1980s that were able to exploit signal pattern recognition for differentiating different chemicals and biochemicals.

Around this time nanochemistry was beginning to produce myriad examples of nanocrystals and nanowires with controlled size and shape with surfaces that could be chemically modified to make them function as new sensor platforms for monitoring chemical and biochemical contaminants in water, air and food, as well as biomedical and security applications.

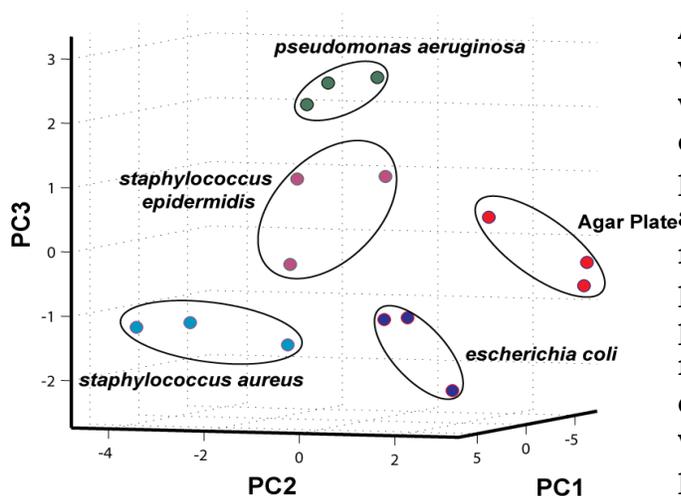
The large surface to volume ratio of these nanomaterials meant that minute changes in their environment could trigger a detectable response to just a single molecule; exemplified by surface enhanced Raman spectroscopy, Förster resonance energy transfer and whispering gallery optical microcavity techniques. Additionally, these materials' small size meant that they could provide a unique opportunity to sense the environment in nanoscale spaces like that found in a living cell or even a cell nucleus. Through intelligent design of chemical and biochemical molecular recognition events between receptor and analyte at the surface of a nanocrystal or nanowire, coupled with large optical and electrical responses to these events, it has proven possible to

develop a wealth of new highly selective and sensitive sensors able to monitor heavy metals in drinking water, detect bacteria and viruses in our hospitals, indicate when food has spoiled and identify chemical and biological agents in acts of war and terrorism.

But the search for nanochemistry-inspired sensors is often the pursuit of last resort that researchers adopt with their nanomaterials platform when they have run out of ideas. This is because pretty well any nanomaterial will show a response to a stimulus and therefore function as a sensor – is it the death of imagination?

A genuinely novel nanomaterial sensing mechanism is worthy of exploration but too much effort goes into trying to improve sensor performance by a few tenths of a percent rather than to searching for real breakthroughs. Unfortunately this same situation is present in many other areas of science, such as much of today's energy nanomaterials research.

So what is next for nanochemical and biochemical sensor research? Should we not be trying as hard as possible to find something absolutely outrageous to do? Something crazy that might just work? Shouldn't we be trying to find the next glass electrode rather than trying to squeeze that extra fraction of a percent out of our tried and tested materials?



An example of a new type of sensor, which is close to my heart and which certainly falls into the crazy category and is showing great promise for actual commercial application, is a pixelated nanoparticle one-dimensional photonic crystal chip in which each pixel is functionalized with different molecule recognition sites that display diagnostic color changes when exposed to different vapor phase analytes; a 'photonic nose', if you will. The overall photonic color

response of the chip to the headspace atmosphere of bacteria, recorded with a simple digital camera color image with automated principal component (color image change) analysis, enabled distinct strains of bacteria to be distinguished. This breakthrough was achieved by Leonardo Bonifacio, a recently graduated

coworker in my research group, who is actively involved in commercializing the P-Nose platform at the University of Toronto. The next stage of development will allow for a portable, versatile and low-cost sensing platform with potential for applications that span from environmental monitoring to food safety to disease diagnostics.

Another amazing and ‘crazy’ (and I mean that in the best possible way) - sensor, from the laboratory of Shana Kelly, also at the University of Toronto. She is also commercially developing an array of on-chip nanostructured palladium sensing nanoelectrodes. The location of these nanoelectrodes is defined by top-down nanolithography, their growth is enabled by bottom-up nanochemistry and their surfaces are functionalized with biomolecule recognition agents using thiol chemical anchoring strategies. Attomolar sensitivity in a proof-of-concept nucleic acid assay has been realized with finely-structured highly-branched nanoelectrodes that provide to analytes high surface area coral, cauliflower and snowflake like nanoscale “natural” forms. The impressive sensitivity of these tiny electrochemical sensors seems to be related to their nanostructuring and their capacity for genetic analysis of cancer cells, as well as detection of proteins, RNA and DNA, bodes well for their implementation in high-throughput, high-performance medical diagnostics.

How about getting nanomaterials smarter and a bit crazier? That is what Mike Sailor at UC San Diego has been doing by developing a ‘smart dust’. Also based on photonic crystals, these platforms are strong competitors for remote detection of threat agents and toxic chemicals. The grains of ‘dust’ are actually tiny particles composed of nanoporous photonic crystals usually made of silicon that change color in the presence of certain compounds. The material can be sprayed onto a surface and the color change can be monitored remotely by use of a portable laser source with an integrated detection system. In this way, a hazard can be detected at a remote location even before anybody has entered the space.

These are just a few examples of technologies based on nanochemistry that are going beyond academic curiosities. They are actually getting closer and closer to real world applications. Some nanomaterials are really learning how to navigate the rough path towards the sensing market!

Now that’s really crazy and pretty impressive too!!!

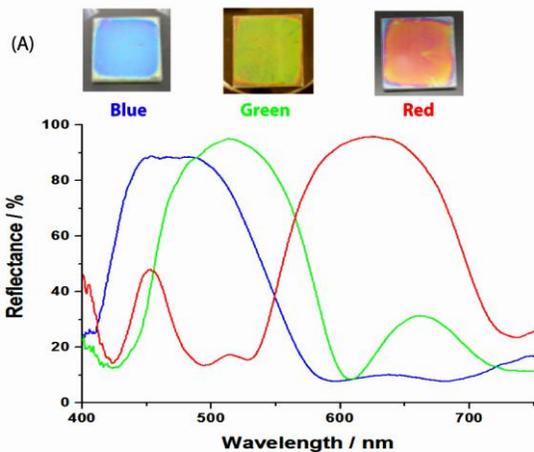
14. Bragging about Nanoparticles

There is a lot to brag about these days in the field of nanoparticles. Control of their composition, size and shape, surface chemical and physical properties, and self-assembly into a myriad of forms are notable contributions of a nanochemistry approach to their study. They are attracting increasing interest for integration into advanced materials and biomedical devices.

Colloidal stability enables the formation of thin films of nanoparticles by simple techniques such as spin and dip coating. Thin films can be formed from many types of nanoparticles, regardless of whether they are mono or polydispersed in size and spherical or non-spherical in shape. By stacking multiple nanoparticle films of different refractive indices on top of one another it is possible to create superlattices with photonic properties that are dependent upon the geometrical thickness and refractive index of the component layers. This kind of multilayer architecture has an interesting history.

Lord Rayleigh in 1887 first studied the interaction of light with this kind of periodic multilayer film and recognized that the interference of light reflected at the interfaces of the constituent layers could give rise to strong reflection of certain wavelengths by constructive interference of reflected waves, and zero reflection of others by destructive interference. This was the first work on what are now often referred to as Bragg mirrors (after W. Bragg and W. H. Bragg who performed extensive work on diffraction and are nowadays probably best remembered for pioneering X-ray crystallography) or one-dimensional photonic crystals. These mirrors, which are ubiquitous in modern optics labs, can easily be designed to exhibit a large spectral range of intense (commercial Bragg mirrors with reflectivities above 99% are available – exceeding that available from any metallic mirror) reflectivity known as the stop-band. As well as finding their way onto optical tables in physics departments around the world, many scientists are pursuing applications that exploit the ability of Bragg mirrors and other photonic crystals to manipulate light by means of functional defects and amplify light by the use of the slow photon effect, finding utility in enhanced efficiency solar cells and light emitting diodes, as well as highly reflective cavities in lasers and fiber Bragg gratings for reflecting a particular wavelength of light while transmitting all others.

These devices typically employ Bragg mirrors made of non-porous layers of materials like silicon nitride, magnesium fluoride, aluminum and silicon oxides, deposited by top-down methods such as plasma enhanced chemical vapor deposition (PECVD). The resulting dense layers with no intrinsic possibility for active reflectivity tuning, means that these materials form passive optical components.



On the other hand, via the introduction of porosity, a Bragg mirror can be made active and display broadband tuning of its reflective properties through externally stimulated physically, chemically or biochemically induced changes in the thickness or refractive index of the component layers. Nanoporosity can be introduced into the layers of a Bragg mirror through colloidal assembly of intelligent nanoparticles such as metal oxides, clays, mesoporous materials and zeolites

into multilayer thin films, exemplified in the Figure for three npTiO₂-npSiO₂ Bragg mirrors with stopbands at the wavelengths of the primary red, green and blue colors. The internal surface area and porosity of this new generation Bragg mirror can be very high reaching 200-500 m² g⁻¹ and 50% porosity, enabling the housing of all sorts of encapsulated guests like dyes and polymers (an architecture which has been shown to function as a laser – quite an achievement for something which at a glance appears rather crude) as well as allowing the adsorption and desorption of many kinds of analytes into and out of the voids, which has been exploited for chemical sensing directed towards a color sensitive photonic nose and a color coded drug delivery device.

Many types of smart nanoparticles can be readily integrated into the nanoparticle layers of Bragg mirrors including ones with photocatalytic, plasmonic, photoluminescent, photoelectrochemical, photosensitization and up-converting properties designed to improve the efficiency of light driven processes and devices including antipollution coatings, water splitting and solar cells. The range of opportunities for nanoparticle Bragg mirrors can be further enriched and expanded by making hierarchical architectures that enable light to be managed in these devices over wider spectral ranges, even to create a white light Bragg mirror. This can be achieved by introducing multiple stop bands into Bragg mirrors through tandem and gradient arrangements of constituent nanoparticle layers.

Now that's something to brag about!

15. Artificial Photosynthesis *versus* Greenhouse Gas

Discovering and understanding chemistry that enables the transformation of atmospheric O_2 and N_2 into useful materials has been an area of intense scientific and technological interest for more than a century. There have been numerous successes, perhaps the most notable of which are abiological mimics of nature's hemoglobin (oxygen transport iron containing protein) and nitrogenase (nitrogen fixation iron-molybdenum containing enzyme) both of which serve to sustain life on earth but there are still many natural processes that we are unable to successfully replicate in the lab, perhaps the most fundamental and challenging of which is photosynthesis.

Nature's photosynthesis apparatus housed in plants, certain algae and bacteria, utilizes atmospheric $CO_2 + H_2O +$ sunlight to provide humanity with oxygen to breath, food to eat, and fuel to satisfy the world's energy needs, however a catalyst that can produce fuel at a globally meaningful efficiency from sunlight and atmospheric carbon dioxide and water has not yet been discovered.

The invention and development of a practical artificial photosynthetic machine is perhaps humanity's most important 21st century grand challenge.

To amplify in the context of learning nature's secrets and transforming them in the laboratory into useful technologies, it is impressive that atmospheric CO_2 can be so efficiently converted by plants into energy rich sugars, yet efforts to devise similar reactions in the laboratory have had limited success. The driving force for accomplishing this is now greater than ever in the face of the present energy and climate crises, which threaten the very existence of humanity.

Indeed the greatest mission facing humankind in the 21st century will likely be to discover a straightforward, scalable, safe, and cost-effective means to reduce our dependence on fossil fuels and to curb the release of greenhouse gases into our atmosphere from burning these fuels.

Recall the old adage "nature did it first"; In the case of photosynthesis this is certainly apt with respect to the energy and climate problems facing humanity today. If we could learn how to mimic the way green plants make energy rich fuels from $CO_2 + H_2O +$ sunlight by inventing an artificial leaf made of earth abundant elements that recycles atmospheric CO_2 to energy rich fuels at rates and efficiencies equal to or greater than photosynthesis and can be manufactured economically as solar fuel machines for integration into homes,

buildings industrial plants and non-arable land, then we could be weaned off our reliance on fossil fuels that currently power our world and eliminate the negative effects of greenhouse gas emissions on our planet – sounds like a magic bullet!

You can imagine this idea it not new and not surprisingly has grown in importance recently as governments around the world panic over the energy and climate crisis. In a valiant attempt to “save the planet” billions of dollars are being invested globally on research programs and centers that purport to be working on artificial photosynthesis.

It seems to me however, that much of the work in this area is actually focused on sunlight-powered electrolysis of water to create H_2 as an energy rich transportable fuel for making electricity, and, to the best of my knowledge, photoelectrochemical splitting of H_2O into H_2 and O_2 driven entirely by sunlight does not occur in nature, but requires an additional fuel input (i.e. glucose), ultimately leading to the production of CO_2 as an undesirable byproduct. This process occurs in certain species of algae and cyanobacteria under anaerobic conditions using the hydrogenase metalloenzyme and its optimization through genetic engineering is actively being investigated. While these activities are undeniably very important and could help realize the dream of a green hydrogen economy, they differ fundamentally from the photosynthetic leaf where the only required chemical feed-stocks are CO_2 and H_2O , which is desirable both economically and environmentally as it consumes CO_2 rather than producing it.

Surely nobody can deny that an artificial leaf able to conduct photosynthesis must at the very least have certain features in common with the natural leaf, such as its ability to efficiently trap, guide and absorb sunlight, successfully generate and separate electron-hole pairs, and effectively drive the multi-electron redox reactions responsible for the conversion of $CO_2 + H_2O +$ sunlight into an energy rich fuel. While we can learn much by understanding the scientific principles governing the natural photosynthetic processes, without doubt a realistic mimic of the leaf is one that combines $CO_2 + H_2O$ to make an organic fuel such as CH_3OH rather than one that just divides H_2O into H_2 .

All we have to do is invent the right material with the right structure and the right properties to achieve this goal.

Sounds simple enough, so why is it taking us so long? It's all about designing and making the right photocatalyst in the correct form that exhibits sufficient reactant activity and product selectivity to do the task. This is not a simple problem to solve because management of the energetics and control of the dynamics of sunlight generated electron-hole pairs have to be finely tuned through material composition and structural engineering to optimize multi-

electron oxidation and reduction reactions of H_2O and CO_2 that underpin the formation of a specific organic product.

This is where the strengths of a nanochemistry approach to nanoscale materials are likely to come into play, with all the advantages of synthetic control over their size and shape, bulk and surface composition, porosity and surface area, and their ability to self-assemble into constructions with structure, property and function relations designed to mimic the photosynthetic solar fuel machinery of plants as imagined in the graphical illustration of an artificial leaf made and powered by nanochemistry – image courtesy of Dr. Wendong Wang.



If this could be accomplished at a globally significant rate at a globally meaningful scale and at a globally competitive cost there would be nothing artificial about the magnitude of this scientific and technological achievement and humankind would be able to turn over a new leaf and enjoy the benefits

of having learned from nature's solar fuel factories a much better way to power the planet and keep it safe and clean!

16. How “Green” Does Your Nano Materials Garden Grow?

After more than a century of colloid chemistry, now rebranded ‘nanochemistry’ we only know the single crystal X-ray structure of one nanoparticle, Au₁₀₂(SR)₄₄!

The atom-precise knowledge of the structure of the gold core and alkanethiolate surface ligands of Au₁₀₂(SR)₄₄ caused a complete re-evaluation of years of acceptance of how alkanethiolates bind to the surface of gold in both nanoparticle and bulk forms.

The reality is that even though size selective separations of nanoparticles have recently developed to a high level of sophistication, exemplified by density gradient ultracentrifugation, size exclusion chromatography, gel permeation electrophoresis and solvent-antisolvent size selective precipitation techniques, all nanoparticle samples prepared by nanochemistry approaches are polydispersions with a characteristic nanoparticle size distribution. This is complicated even further by the difficulty of controlling the ratio of nanoparticle core atoms to number of capping groups resulting in a heterogeneous distribution of ligands - be they ions, surfactants, polymers or biomolecules - on the nanoparticle surface. This means that, aside from that one example all nanoparticle properties measured and reported to date, whether chemical, physical or biological, refer to an ensemble average.

Unfortunately, this makes the quantitative evaluation of their toxicity, whether *in vivo* or *in vitro*, precarious at best as one never can be absolutely sure whether it is a specific size, shape or surface property of a nanoparticle or a certain group of nanoparticles or every nanoparticle in an ensemble that is responsible for a positive test result and may therefore pose a health and safety hazard to researchers, manufacturers and consumers. The same uncertainty applies to the behavior, fate, bioavailability and effects of nanoparticles that escape into the environment.

Currently many major companies and about 1500 spin-off companies around the world are involved in nano R&D and there are now about 600 nano-based products on the market!

In 2005, the International Organization for Standardization (ISO) and the International Electrotechnical Commission (IEC), with 30 collaborating

countries, launched initiatives to facilitate the safe and responsible development, production, use, transportation and disposal of nanoparticles in existing or emerging nanotechnologies.

It is ironic that while nanoparticles are gainfully exploited in nanoscience and nanotechnology and celebrated for their exquisite size, shape and surface tunable properties, it is precisely these attributes that are potentially problematic in health and safety matters when trying to quantify the toxicity of a polydispersion of nanoparticles where it is impossible to decide whether it is the size, shape or surface of all, some, one or none of these nanoparticles that we have to be concerned about.

Could one atom difference in size and shape or disparity of one capping group on the surface of a low abundance nanoparticle in an ensemble of nanoparticles make a difference between being safe or unsafe to human health?

So how do we handle this grand challenge? And I believe it is a “grand” challenge because it is simply not possible to make every nanoparticle polydispersion into a true library of monodispersions, in which every nanoparticle is really single size, single shape and with a single kind of surface, and only then with detailed studies of the fate, transformation and transport in living organisms and our ecosystem, would it be possible to establish the toxicity of every member of the polydispersion to determine if one, some, all or none are rogue nanoparticles. Not to mention the possibility that a combination of different particles may exhibit synergistic toxic effects that the individual nanoparticles on their own do not show.

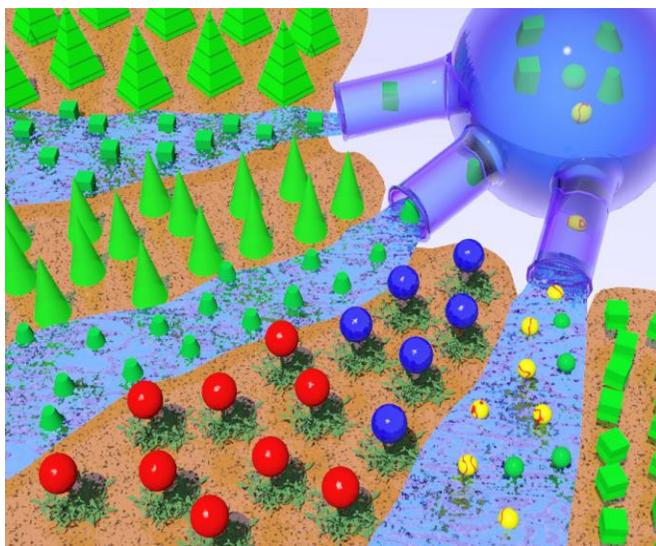
It seems best to approach this problem from two angles. Firstly, like the way we have treated chemicals, to always consider any nanoparticle to be hazardous until proven otherwise and operate according to the ISO and IEC recommendations for safe handling of nanoparticles, and to bear in mind that no matter what has been shown in another laboratory for a nanoparticle with the same chemical formula that some quirk of your synthesis may mean that the nanoparticle polydispersion you create is toxic due to its particular distribution of nanoparticle sizes, shapes and surfaces. Secondly, we must make the assumption (it may turn out not to be a very good one, but it is the most practical starting point) that there is something to be learnt of nanoparticle toxicity from the toxicity of the corresponding bulk.

With this in mind it makes sense to intensify the global research effort of the nanochemistry community on the synthesis and study of nanoparticles that are purportedly “green”, such as TiO_2 , ZnO and Fe_2O_3 , which are targeted for use respectively as nanocrystalline photocatalysts for air and water purification, nanowire piezoelectric nanogenerators for powering mobile,

implantable and personal electronic devices, and nanomagnetic agents for medical diagnostics, therapeutics and imaging, rather than the current overwhelming focus on toxic heavy metal nanoparticles, such as CdTe, PbSe, InAs and $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ that are increasingly targeting many consumer products like solar cells, detectors, light emitting diodes, lasers, sensors and displays.

The newest collection of “green” nanoparticles to have caught my attention recently and which seem to be most promising candidates in this context are C, Si, Ge whose appealing energy storage, optical, optoelectronic, photonic and biomedical attributes are gaining much attention and Bi (known as the new ecologically green metal which is significantly less toxic than other heavy metals) chalcogenides are attracting a lot of interest due to their thermoelectric properties and also because some of them are part of the exotic class of 'topological insulators'. And interest is growing in bismuth chalcogenide nanoparticles as contrast agents in medical imaging using X-ray computed tomography where superior image quality is enabled by the high electron density of bismuth-based nanoparticles.

Recent developments on the synthesis, structure, property and function relations, of carbon quantum dots, diamond nanocrystals, graphene nanosheets, silicon and germanium nanocrystals and nanowires, and bismuth sulfide quantum dots and rods, ultrathin wires and plates, have provided a myriad of remarkable observations that speak well for the expanded use of this latest generation of “green” nanoparticles in a number of areas currently dominated by their toxic heavy metal cousins.



While the same polydispersity criticism can be voiced against these ostensibly “green” nanoparticles it will be interesting to see how “green” they turn out to be from deeply analytical toxicity studies that I anticipate are under active investigation around the world as I write.

So when contemplating growing your nanomaterials garden for pleasure or profit, think “green”!

Image “Nanomaterials Garden” courtesy of Dr. Wendong Wang.

17. What Is My (Nano)Material Good For ?

Whatever happened to curiosity-driven research aimed at the creation of fundamental knowledge without the need for immediate application, a business plan and commercialization of the technology?

Throughout the history of science, many of the discoveries which have proven to be the most important and influential for humanity have arisen out of nothing more than a scientist pursuing his curiosity. Electricity, X-rays, lasers and semiconductors are classic examples of this and pretty well every great scientific discovery would not have been made if the research had been driven by applications and economic impact, which tend to encourage unoriginal research and reduce the likelihood of discovering things that did not exist before, the very essence of research.

Nowadays, in the area of materials research however, scientists have to pin applications on their materials which aren't ready for them. It's not enough to just study an interesting material – now you must put it into a solar cell (and probably not a very good one because it takes years to develop these things) or claim that it is good for 'drug delivery' or a 'sensor' or a 'battery' or a 'white light emitting diode'.

Although the taxpayers who fund our research naturally deserve to see it applied to a problem that affects them, we often spend too much time on trying to dress up science, which is at a very early stage and from which it will realistically take many years for practical applications to come, as something which will save the world next week. Just come up with a nice new nanomaterial? You'll be making 70% efficient 'third generation' solar cells from it by the end of the year, \$1bn production in two years and climbing exponentially. You'll have simultaneously averted climate catastrophe and saved your country's floundering economy. At the very least you'll be feathering your research treasure chest!

When I was beginning my academic career as a young assistant professor at the University of Toronto in 1969 my research was directed towards pure, unadulterated, knowledge generation geared towards making an original and important contribution in my chosen area of interest. My work at the time involved experimental and theoretical studies of nucleation and growth of ligand-free metal clusters from the atom up and how these metal clusters interacted with ligands.

The goal of this work was to throw light on the transition of metal atoms to metal clusters to bulk metal and to explore localized bonding models of chemisorption of the aforementioned ligands on metal surfaces, work inspired by the challenge at that time of trying to understand the basic science that underpins metal cluster catalysis, and as it turns out these were embryonic steps in the field of bottom-up nanomaterials.

Today it is virtually guaranteed that any attempt to have fundamental materials research published in a top rank peer reviewed journal will result in you being told by referees and editors that while your results are hopefully of high scientific quality you have not shown practical utility and that unless this is demonstrated the work is not acceptable for publication in our journal and you should try a more specialized one. How many scientists striving to do basic research in the field of (nano)materials have been faced with this dilemma? Perhaps my experiences over a four decade career can throw some light on the origin of this change from ideas driven research to one progressively and possibly irreversibly based on application.

On arriving at the University of Toronto to begin a program of research and teaching in materials chemistry in the chemistry department I was faced with what seemed like an insurmountable problem. Pretty well all materials research in this era was conducted in materials science and engineering departments. This had always been the tradition and I soon realized that trying to convince my materials science and engineering colleagues otherwise was going to be met with powerful opposition and to persuade my colleagues in chemistry that I was a worthy partner who belonged in their department was going to be a struggle.

My main argument was that new classes of materials and not one's based on incremental improvements of existing materials, are invented by chemists who are trained to devise synthetic pathways to novel compositions of matter. On these grounds after much debate my case was accepted by materials science and engineering and I initiated a materials chemistry program of research and teaching for the first time in the chemistry department at the University of Toronto in the early seventies.

This is how my materials chemistry and nanochemistry activities began and these were the heydays of curiosity driven research in the field mainly driven by synthetic inorganic, organometallic and polymer chemists transitioning their careers to this emerging and exciting new field and as a result funding began to flow from granting agencies worldwide to power basic research efforts. As the promise of the cornucopia of new materials and nanomaterials being produced by synthetic chemists became clear a number of important changes transpired that led people to wonder and to ask: 'what are all these new (nano)materials going to be good for?'

First, granting agencies, presumably influenced by government policy and pressure from industrial leaders began to demand relevance as a prerequisite for successful funding of materials and nanomaterials research. Academic researchers who were focusing on curiosity driven scientific questions were now being coerced to think beyond synthesis, structure, and property to include utility, which was often not their strength.

Second, as a result of this change of focus from ideas to application in (nano)materials chemistry, practitioners of the art sought collaborations with physics and materials engineering colleagues, very few of whom were, at the time, prepared to step outside of their specialized area of expertise and take a risk working with chemists on their new-fangled (nano)materials to try to help them determine what they might be good for and in the process helping them survive the pressure from granting agencies who had imposed this requirement on funding.

This in my view is where the interdisciplinary approach to (nano)materials chemistry that flourishes today originated, and this is one thing that we can be thankful for when it comes to the change in emphasis of research – in order to show potential applications, even if they may not be quite so realistic as is frequently claimed, we must seek out broader collaborations and expand our networks beyond the confines of our own labs.

Initially very few materials physicists and engineers bought into this thrust towards collaborative teamwork with chemists but as interest grew in the profusion of new (nano)materials with a plethora of novel, important and potentially technologically relevant breakthroughs, critical mass was achieved and the field changed its character forever from one that was powered mainly by curiosity driven basic science to one directed by applications and technological consequence.

I suppose we should not be surprised that this change has occurred because the materials physics and engineering community eventually recognized the potential of this new wave of (nano)materials being produced by chemists, and all those brave collaborators who believed in the revolution in (nano)materials chemistry research refocused their attention on non-traditional materials rather than the materials that had underpinned their field for more than a century and had provided them with the building blocks for engineering the needs of the human race.

There is no going back to just pure (nano)materials research and nowadays your pet (nano)material has to be presented as having a potential application. You can see this first hand in the way the content of the top (nano)materials science journals has transformed from a (nano)chemistry approach to nanomaterials to a (nano)engineering focus heavily driven by practical utility. This philosophy is also being promulgated by funding agencies with

government and industry support leaving little space for a chemistry approach to nanomaterials to maneuver.

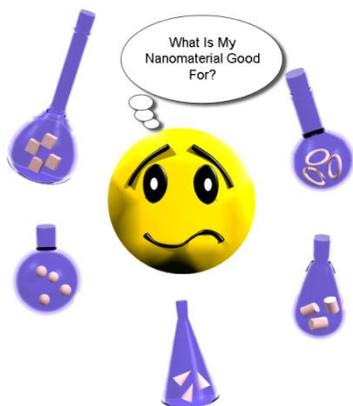


Image: "What Is My Nanomaterial Good For?"
courtesy of Dr. Wendong Wang.

I am not going to reiterate on my recently published views on Nanochemistry - What Is Next? (Ozin and Cademartiri, *Small* 2009, 5, 1240-1244) and From Ideas to Innovation – Nanochemistry a Case Study (Ozin and Cademartiri, *Small*, 2011, 7, 49-54), other than to say that without great patience, dogged perseverance and sound investment in the future of curiosity driven (nano)materials research the natural progression from the breakthrough to the new products will be in great jeopardy. It is not in anybody's interest to try to control the

unpredictable fruits of fundamental research in the exciting area of (nano)materials chemistry!

In my opinion it's not all about whether your favorite (nano)material is good for a better performing lithium ion battery, a hydrogen storage reservoir, a dye sensitized solar cell, a water splitting or carbon dioxide recycling photocatalyst, a full color display, a white light emitting diode, a photodetector, a drug delivery or biomedical imaging system and so forth, which everybody in the world is working on to satisfy government expectations and industry needs, but rather is it interesting in a way that others aren't? Does it teach us something new and unexpected? What is the Nano Advantage?

If you want it to be the great idea, which changes the world then surely you're aiming for application, which seems contrary to the point!

18. Nanochemistry Nostalgia 2011

As we enter 2012, inspired and captivated by a myriad of exciting discoveries in the field of nanochemistry, with new world records for bottom-up synthesis of inorganic materials fashioned as the narrowest nanowires and thinnest nanosheets, largest nanopores and smallest nanogaps, biggest supracrystals and most extensive superlattices made of nanocrystals and nanorods, nanoplatelets and nanooctapods, it seemed like a good idea, as the year draws to a close, to look back at some influential 2011 papers with a common theme that by any measure would be considered 'surprising' by an experienced materials research community with respect to the high level of creative thinking, skillful inventiveness, extraordinary scientific impact and widespread technological implications.

In this vein I would contend that a potentially revolutionary new paradigm in nanochemistry is 'nanolocomotion' where the power source for the propulsion of a nanoscale object such as a rod, tube, sphere or sphere dimer, is drawn from a chemical reaction of an energy rich fuel localized on a specific region of the nanoscale object.

A requisite for this kind of chemically powered motion is the creation of an anisotropic force on a nanoscale object, which can be generated by constructing the object with an asymmetric structure, like a Janus sphere, a tapered nanotube or a bimetal segmented nanorod.

The work of the PennState groups of Tom Mallouk and Ayusman Sen and the University of Toronto group of Geff Ozin is notable in this respect who first demonstrated the use of hydrogen peroxide as a fuel to induce linear and rotary motion of asymmetric bimetal nanorods made of Pt-Au and Ni-Au in an aqueous environment. To create nanorod motion, forward thrust has to overcome viscous frictional forces and the power to achieve this was derived from the catalyzed decomposition of hydrogen peroxide $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ localized at the Ni or Pt ends of the nanorods.

The early challenge in this field was to establish a fundamental understanding of the physicochemical principles that underpin nanorod motion and with this knowledge devise ways to control the velocity, direction and trajectory of the nanorod, in order to be able to rationally design and build nanomachines that perform a useful task with acceptable speed, reliability and efficiency.

With this brief background on chemically powered nanomotors in what follows I will highlight some spectacular advances recorded in 2011 that take this budding field of research to even greater heights.

In a significant departure from the 'fixation on hydrogen peroxide' as a fuel to generate locomotion of nanomotors, the group of Ayusman Sen described an innovative bimetal copper-platinum nanorod motor where thrust was generated through a self-electrophoresis mechanism induced by battery-type coupled redox reactions of an aqueous bromine solution localized at the ends of the nanorod.

The motion originates from anodic oxidative dissolution of the copper segment induced by the bromine which occurs concurrently with cathodic reduction of bromine or hypobromite at the platinum segment according to the short-circuited battery equations:



The origin of the nanorod motion is explained in terms of electro-osmotic fluid-flow of a positive electrical double-layer of ions along a negative (metal oxide passivated) surface from the copper positive anode towards the platinum negative cathode ends of the bimetal nanorod. This occurs simultaneously with electron transport from the anode to the cathode, which in accord with the concept of 'Galilean inverse' causes the nanorod to translate in the opposite direction, led by the copper end.

While neither hydrogen peroxide nor bromine are environmentally friendly reagents they are currently the only efficient transducers of stored chemical potential to mechanical energy, however for nanomotors to establish their usefulness in real world applications a challenge for future work is to discover alternative fuels that are environmentally benign and biocompatible.

Another innovative contribution from the group of Ayusman Sen that expands and enriches the scope of catalytic reactions for powering nanoscale motors, involves the development of thrust from the catalytic polymerization of an organic monomer localized on one side of a Janus microsphere. The basis of the motion is a ring-opening polymerization reaction of norbornene using a Grubb's catalyst.

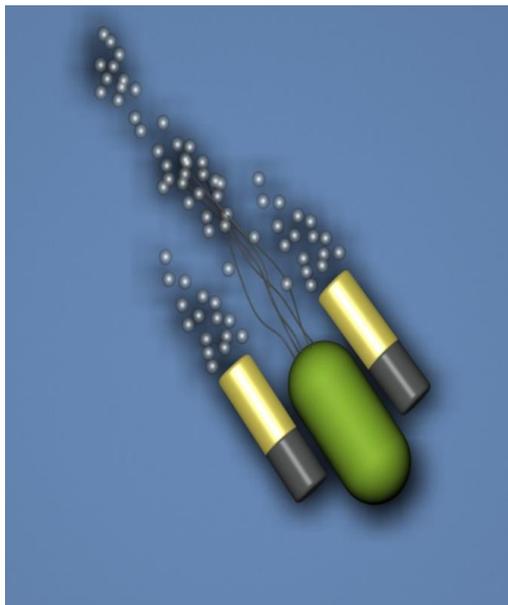
The principle of operation is based on a Grubb's catalyst that is chemically tethered to the silica side of a gold-silica Janus microsphere. Because of the lower monomer concentration developed in the proximity of the silica polymerization zone, fluid transport to the opposite gold side of the microsphere occurs, which causes it to translate in the opposite direction. This prototype laboratory polymerization nanomotor can be viewed as a biomimic of

Listeria monocytogenes, a bacterium whose motion stems from the polymerization of the protein actin.

In this context, chemically powered nanomotors have been explored as vehicles for delivering biologically relevant payloads, such as pharmaceuticals as well as for biosensing through motion detection. They have also been shown to exhibit dynamics characteristic of nature's chemotaxis, namely directed motion of a nanomotor stimulated by a concentration gradient of fuel.

The technological relevance of this work is witnessed by the recent appearance of patents that describe methods for fabricating nanomotors with different shapes as well as potentially useful applications of nanomotors, such as a novel way of patterning surfaces by spatially localized delivery of precipitating or etching reagents and motion based biodetection for *in vivo* analysis.

The concept of an on-board bioactive cargo has recently been taken to a higher level of biological sophistication and relevance with the impressive demonstration by the Arizona State University group of Joseph Wang that chemically-propelled nanomotors functionalized with single strand DNA can selectively and efficiently capture and isolate target nucleic acids 'on the fly' from untreated biological samples, such as serum, urine, saliva and lysate of *E. coli*, and transport them to pristine locations for *in vivo* analysis, without the requirement of pre-processing steps. A noteworthy attribute of these bionanomotors is their enhanced target hybridization efficiency, which was traced to motion induced turbulence of the local environment.



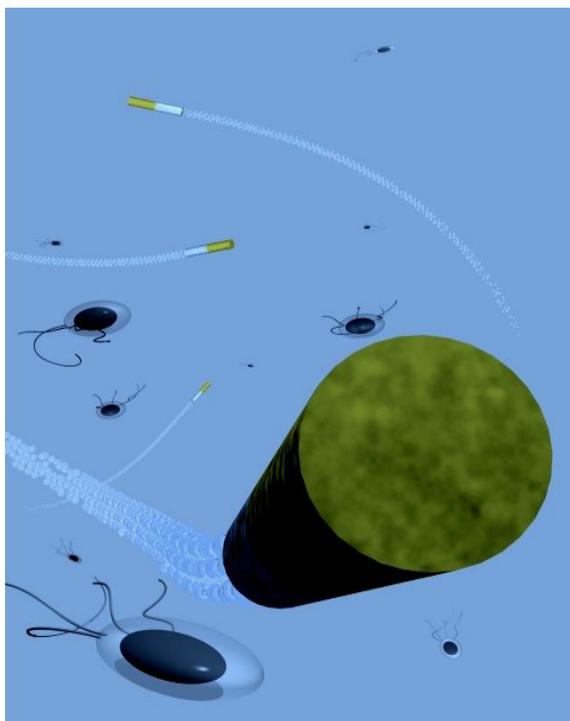
In another creative development of this paradigm the group of Joseph Wang has demonstrated that by functionalizing microjets with lectin receptors that recognize polysaccharide bacteria surfaces, they are able to scour, capture and isolate *E. coli* bacteria from complex milieu. The arrested bacteria can subsequently be liberated from their microjet captor by dissociation in an acidic environment. The true theranostic potential of these microjets was established by the capture and transport, of both a target bacteria and drug carrier, an accomplishment which speaks well for their ability to discover and destroy pathogens in contaminated food and water.

One can imagine further exciting applications of these self-propelled nanoscale motors for making 'house-calls' in biomedical diagnostics and cancer

theranostics as well as functioning as nano inspectors for environmental monitoring and nano investigators for forensic analysis.

Meanwhile the race continues for induction into the 'Guinness Book of Nanomotor World Speed Records' through new engine designs and new catalytic materials to increase their velocity beyond those of the fastest moving bacteria and thereby enable self-powered nanomotors to facilitate long distance transport of heavy payloads or respond faster to emergency tasks or even cooperate or compete with bacteria in interesting ways as envisioned in the graphical illustration (image credit: Dr. Tihana Mirkovic).

In this context two advances towards enhancing the efficiency of nanomotor engines for transforming chemical to mechanical energy while minimizing the consumption of fuel are worthy of note.



One entry into the race involves the catalytic titanium-chromium platinum tubular bubble propulsion microjet engine from the IFW Dresden group of Oliver Schmidt. These hollow cylindrical microjets are slightly tapered internally to facilitate thrust from nanobubbles formed on the catalytic internal platinum layer. They are made by a sophisticated multi-layer, thin-film, stress-induced roll-up nanofabrication process.

By making a slight increase in the temperature of the surrounding aqueous hydrogen peroxide fuel supply to physiological warmth of 37°C it was reported that as little as 0.25% H₂O₂ is enough fuel to boost the nanomotor speed to 140µm.s⁻¹, which corresponds to movement of 3 body lengths per

second. At 5% H₂O₂ superfast speeds were achieved of 10mm.s⁻¹ with trajectories that changed from linear to curvilinear in accordance with computer modeling of the nanomotor motion (image credit: Dr. Ludovico Cademartiri).

The other competitor in the race is a tapered tubular polyaniline-platinum microjet entry from the group of Joseph Wang. They are conveniently synthesized on a large scale using template-directed bilayer electrodeposition of polyaniline-platinum conical-shaped microtubes localized within a polycarbonate conical-shaped nanochannel membrane. The so-formed

microjets are subsequently released into solution by sacrificial etching of the polycarbonate template. These bubble microjets achieved an ultrafast speed of 350 body lengths per second at 0.2% H_2O_2 even in biological milieu, which bodes well for applications in biomedicine where rapid response to a stimulus and fast action to a task is a matter of urgency.

In an imaginative expansion of these high-speed, conical-shaped, polymer-metal microjets, the group of Joseph Wang has side-stepped the use of H_2O_2 fuel by making the inside surface of the microjet out of zinc and used hydrogen bubble formation, from the dissolving reaction of Zn with mineral acids like HCl, H_2SO_4 and H_3PO_4 , to provide the thrust with the observation that microjet speed depended on the pH. One can envision acid fuelled microjets operating in a number of extreme environments such as the human stomach and sulfuric acid pools and geysers where acidophiles, bacteria that thrive in acidic media, thrive.

Based on the incessant flow of impressive ideas and innovations in the burgeoning 'nanomotor industry' it looks like the field of nanolocomotion has the horsepower to keep on advancing for the foreseeable future!

19. Ode to CO₂

Oh small molecule

Friend or foe

To love or hate

To understand you better

Before it's too late!

Geoffrey A Ozin, April 2012

Of the three small molecules that dominate the composition of our earth's atmosphere, it is the minor component, CO₂ that we are beginning to fear because of the looming Armageddon global warming scenario arising from the accumulation of *green house gas* in the troposphere. While O₂, N₂ and CO₂ brought about and maintain life on our planet, CO₂ the combustion product of the human race now threatens its demise.

It is the innate ability of humans to recognize and react defensively to danger and in doing so learn how to survive that has inspired a global effort to understand how to transform CO₂ into a *clean house gas*!

While these days CO₂ might be considered the molecule to hate there are many reasons why our relationship with it could be transformed into an eternal love affair. In this article I will take a look at how CO₂ emerged into our scientific consciousness, how it became the molecule of choice for numerous products and processes, how its abuse and misuse are becoming a looming ecological, environmental and sociological nightmare, and how this fear of the consequences of global warming is driving a scientific and technological revolution aimed at making CO₂ into a friend rather than a foe, by learning how to capture and recycle it back into a useful fuel rather than simply capture and store it, the latter considered an unsafe practice and banned in some countries.

Jan Baptista van Helmont (1580–1644) a Flemish chemist, physiologist and physician, whose research was contemporary with Paracelsus, remembered for his neologism of the word gas (Greek *chaos*), is given credit for the discovery in 1630 of carbon dioxide, as an off-gas in the combustion of wood, which he named *gas sylvestre*, wood gas.

The Scottish chemist Joseph Black (1728–1799) in 1756 first proved carbon dioxide occurred in the atmosphere and called it fixed air. He also showed it is a product of human and animal respiration and microbial fermentation and that it has a fascinating chemistry exemplified by the precipitation of limestone (calcium carbonate) by bubbling carbon dioxide into aqueous lime and reversed by heating the resulting limestone. He showed carbon dioxide to be denser than air and can extinguish both flames and life.

Joseph Priestley (1733–1804) could be considered the father of the soft drink industry with his discovery in the mid-1700's that carbon dioxide evolved from the action of oil of vitriol (sulfuric acid) on chalk (calcium carbonate) could be dissolved in water to produce a pleasantly flavored fresh sparkling soda water.

Imagine what these CO₂ pioneers would say today if they had known in addition to CO₂-driven photosynthesis in plants to produce carbohydrates which feed humans and animals and the beneficial effects of natural CO₂-based climate control of the planet to stabilize it at the right temperature for maintaining life, that if allowed to increasingly accumulate in the atmosphere, CO₂ could also cause long term harmful effects to the human race and life on earth.

Our love affair with CO₂ is seen in its many uses, including soft drinks, dry ice solid refrigerants, ingredients in frozen food, cooling bunches of grapes in wine making, atmosphere for reactive welding, capsules for air guns, extinguishers for electrical and oil fires that cannot be put out by water, supercritical solvent for the environmentally friendly and safe removal of caffeine from coffee to help the old to be put in the coca cola to help the young, the first infrared gas laser, and an enabler for enhanced oil recovery.

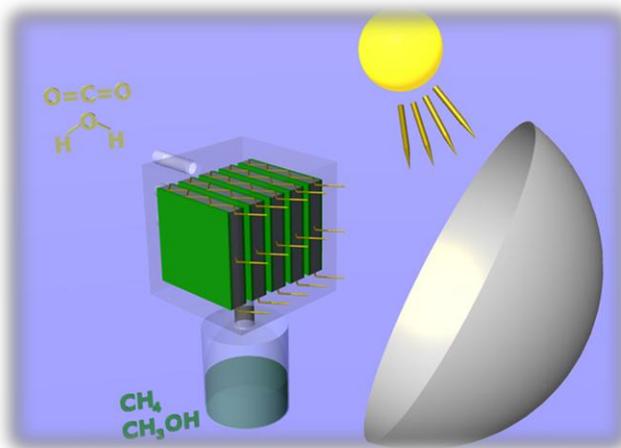
This affection is also found in chemically bound CO₂, pervasive as carbonate minerals with wide ranging uses that include construction, pharmaceuticals, food, glass, polymers, paper, coatings, pigments, paints, pottery and jewelry manufacture.

In the natural world carbonate biominerals are omnipresent in calcareous forms such as calcite and aragonite coccolithophores, sponge spicules, echinoderms, corals and the molluscan shell, the shapes and patterns of which continue to visually impress and intellectually challenge our understanding of morphogenesis, the origin and control of natural form.

The manufacture of chemicals and pharmaceuticals, fuels, and polymers from CO₂ using well established technologies is growing in importance but is currently having only a minor impact on the roughly 10 Gt of yearly anthropogenic CO₂ emissions. It has been estimated that the implementation of these chemical technologies in large scale industrial processes could reduce CO₂ emission by as much as 350 Mt yearly however this only represents about

3-6% of annual anthropogenic CO₂ emissions even when added to the corresponding reduction in fossil fuel usage as a result of these kinds of CO₂ processes.

In this context, a promising area for research and development is the sunlight driven conversion of CO₂ and H₂O to energy rich and transportable fuels like CH₄, CH₃OH and HCO₂H but to achieve steady state in atmospheric CO₂ this will have to be implemented in a process that utilizes earth abundant, low cost, and non-toxic materials operating at globally significant rates and scales in order to stand a chance of making a real impact on the problem of anthropogenic CO₂.



While there are currently around half-a-dozen approaches competing for this CO₂+ H₂O + sunlight grand prize including solar thermal, homogeneous and heterogeneous catalysis, biomass, electrocatalysis and photoelectrochemistry, it is likely that the most practical and economically viable programs for large-scale CO₂ capture and recycling (CCR) to chemical fuels will involve gas-phase flow-based photocatalytic reactor units. They

will likely work alongside CO₂ capture, purification and storage (CCS) technologies, possibly based on metal organic frameworks, frustrated Lewis pairs or amine resins, integrated into CO₂ emitting fossil fuel power plants and iron, steel, cement and aluminum production facilities, working at low pressures and temperatures and driven by sunlight (image credit, Dr Wendong Wang).

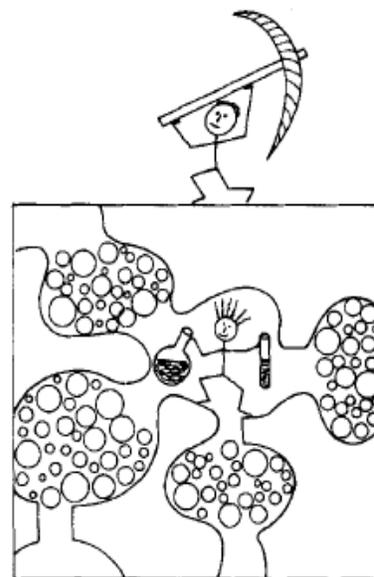
One can also imagine personalized versions of these CCS+CCR units installed in homes and buildings, generating from CO₂ + H₂O solar fuels like methanol or methane used for heating and lighting as well as for powering cars.

So what will it take for CO₂ + H₂O + sunlight photocatalysis to outperform photosynthesis? Simple, the right (nano)material!

20. Nanochemistry: Prescience?

It is the 20 year anniversary of the 1992 Advanced Materials paper “Nanochemistry – Synthesis in Diminishing Dimensions”. I thought it would be an interesting exercise to see how the promising future I imagined for this fledgling field back then, is working out in practice today. Pertinent to my thoughts on this matter is my opening statement in the paper and a graphical comparison of the top-down nanophysics and bottom-up nanochemistry philosophy’s of making nanomaterials:

“Nanochemistry, as opposed to nanophysics, is an emerging sub-discipline of solid-state chemistry that emphasizes the synthesis rather than the engineering aspects of preparing little pieces of matter with nanometer sizes in one, two or three dimensions. Currently there is considerable interest in nanoscale objects, since they exhibit novel material properties, largely as a consequence of their finite small size. The nanochemist can be considered to work towards this goal from the atom “up”, whereas the nanophysicist tends to operate from the bulk “down”. Building and organizing nanoscale objects under mild and controlled conditions “one atom at a time” instead of “manipulating” the bulk, should in principle provide a reproducible method of producing materials that are perfect in size and shape down to the atoms. A cartoon of this comparison is shown in the illustration. These little objects can be made of organic, inorganic and/or organometallic components. Their structure-property relationships are designed to yield new materials with novel electronic, optical, magnetic, transport, photochemical and electrochemical, catalytic and mechanical behavior. Areas of application that can be foreseen to benefit from the small size and organization of nanoscale objects include quantum electronics, nonlinear optics, photonics, chemoselective sensing, and information storage and processing”.



Questions: Has nanochemistry emerged as a new field, a discipline, a branch of knowledge in its own right, has it gained mainstream acceptance as opposed to just being a sub-section of materials chemistry? Is activity in synthesizing and organizing nanoscale objects with novel size and shape tunable properties increasing? Is the accrued fundamental scientific knowledge of nanomaterials enabling applications envisioned for nanochemistry in information technology, biotechnology and nanotechnology?

Is nanochemistry a field? Some metrics and information to help think about whether nanochemistry has achieved this status include the following: a Google search on nanochemistry raises about 50,000,000 hits on a cornucopia of topics that crisscross the borders of the science, engineering, biology and medical disciplines; stunningly beautiful microscopy and graphical 'ArtScience' images of nanomaterials made through nanochemistry pervade the internet; nanochemistry has entered the pages of Wikipedia (<http://en.wikipedia.org/wiki/Nanochemistry>) where it is acknowledged as a new branch of nanoscience concerned with the preparation and reactions of nanomaterials in the size range of 1-1000 nm; intensive research in nanochemistry is underway by top rank scientists in most of the world's university, industrial and government research laboratories; nanochemistry centers, institutions and networks have been established in different corners of the globe; prestigious international prizes are being awarded to nanochemistry pioneers including the Nobel, Millenium, Bower, Albert Einstein, Kavli, Wolf, Kyoto, King Faisal, Lemelson and Feynman; new and well established scientific journals publishing nanochemistry papers have appeared and grown in number across the disciplines; undergraduate and graduate textbooks on nanochemistry are continuing to appear; nanochemistry is taught in universities around the world; billions of dollars are being invested annually to fund basic and applied research in nanochemistry on the grounds that new nanomaterials will drive new nanotechnologies; nanochemistry breakthroughs in nanoscience and nanotechnology are frequently reported in the popular press and scientific magazines; the general public is becoming aware of goods and services in their lives enabled by nanochemistry; national nanotechnology research strategies around the world have been initiated to grapple with the complex and urgent task of establishing the effects of nanomaterials prepared using nanochemistry on human health and the environment.

Based on this information I contend nanochemistry is a field and we can all look forward to 'better living through nanochemistry'.

Is interest in the size and shape of nanomaterials made by nanochemistry increasing? The search for the atom-perfect nanomaterial whatever its size and shape and growing single crystals thereof suitable for obtaining a single crystal X-ray structure continues to be a challenge for nanochemistry. This situation is improving with the growing interest in chemical and physical methods for separating and characterizing the structure and properties of nanomaterials with different size and shape, notably size selective crystallization, gradient and analytical ultracentrifugation. The composition field of nanomaterials has increased to more-or-less encompass the periodic table of materials and properties, almost every size of nanomaterial from nanometers to hundreds of nanometers is now accessible, many shapes of solid and hollow nanomaterials from cubes to

spirals, wires to plates to poly-pods have been realized experimentally with impressive control of their chemical nature. Control and understanding of defects and dopants in nanomaterials is showing impressive progress, a broad spectrum of hierarchical architectures is emerging from self-assembled clusters to superlattices to chains, and a mounting library of nanocomposite architectures is arising from core-corona spheres, cubes and rods to binary heteronanostructures, a veritable ‘periodic table of nanomaterials’.

There is still much interest in nanomaterials made by nanochemistry aimed at expanding and enriching the pool of knowledge upon which future nanotechnologies will be founded.

Is nanochemistry delivering nanomaterials with interesting size and shape tunable properties?

Returning to the idea of a ‘periodic table of nanomaterials’, it is probably fair to say that there is no important bulk material chemical or physical property which has not been touched in some positive way by reducing their scale to nanometers through nanochemistry, examples being the metal-nonmetal transition, surface plasmon resonance, photoluminescence, Seebeck effect, melting point, phase change, water splitting and hydrogen storage. The driving force for the majority of work in this endeavor has been to understand how the chemical and physical properties of materials synthesized at the nanoscale change with size and how to exploit these size tunable properties in a wide



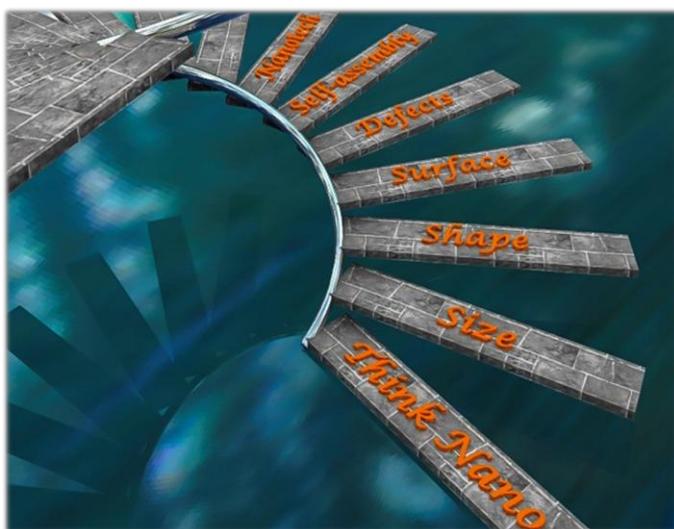
range of technologies to realize the Nano Advantage.

To comprehend the revolutionary impact of the ‘materials to nanomaterials’ paradigm shift, one must go to the source of how purposeful materials of the last century have been created from the chemical juxtaposition of a ‘periodic table of the elements’ and how this *modus operandi* metamorphosized into nanomaterials fashioned from a ‘periodic table of materials’.

How did this happen? It can be traced to a universal operating principle that has guided the development of a century of materials science. This principle is expressed as synthesis to structure, structure to properties, properties to function, function to utility. This materials operating principle can be expanded and enriched through a ‘stairway’ of the six fundamental nanochemistry concepts of size, shape, surface, defects, self-assembly and the interface with

the 'ologies', information technology, biotechnology, nanotechnology, over 'all' length scales, from nanoscopic to macroscopic.

Building upon these ideas, without chemical synthesis, there would be no new materials. Without structure determination, there would be no knowledge of the atomic make up and arrangement in materials. Without properties measurements, the behavior of these structural arrangements of atoms would be unknown. Without a knowledge of the properties of materials their functionality and performance would be undefined and ultimately materials utility would not materialize until their role for different tasks is elucidated. These are the five key operating principles of solid state chemistry upon which the fields of materials chemistry and nanochemistry are founded.



Classic examples where these concepts all come together and lead to a purposeful application for a nanomaterial are graphite to graphene electronics; zinc oxide to zinc oxide nanowire piezotronics; gallium nitride to gallium nitride nanowire ultraviolet-blue laser lab-on-a-chip and high-density data storage coherent light source; silicon to silicon nanowire battery; titania to nanocrystalline titania solar cell; lead selenide to nanocrystalline lead selenide

near-infrared photodetector; silver to nanocrystalline silver antibacterial; silica to nanoparticulate periodic mesoporous silica targeted drug storage delivery and release vehicle; iron oxide to nanocrystalline iron oxide cancer therapy; gold to gold nanorod tumor imaging.

This paradigm has spawned the 'nanomaterials movement', the driver of the 21st century nanotechnology revolution. What we are talking about in nanochemistry is controlling the physical scale of a material through chemistry, not any scale but a specific scale, one that is neither molecular or microscopic nor macroscopic matter, but a 'fuzzy' regime somewhere in between; an intermediate length scale, called 'mesoscopic'. This mesoscopic scale provides a known material with new properties that through quantum mechanics can be shown to scale with its physical. Essentially, it offers a new way of thinking about creating new materials beyond variations in composition and structure from a 'periodic table of nanomaterials,' rather than a 'periodic table of elements.'

Through nanochemistry a vast array of materials can be sculpted as nanomaterials with synthetic command over their size, shape, surface, defects and their self-assembly into purposeful matter. The number of possible materials combinations of the elements of the periodic table when coupled with these concepts of nanochemistry are mind boggling and one can immediately see how through nanochemistry it is possible to discover an 'infinity of nanomaterials for an infinity of scientific investigations for an infinity of technological opportunities', limited only by one's imagination, providing enough inspiration to keep the materials science community busy and content for the next hundred years.

One can experience the aforementioned Nano Advantage, for example over a platform of materials energy systems, where they may be engineered for solar cells, fuel cells, batteries, supercapacitors, thermoelectrics, piezoelectrics and where the enhanced performance relative to their macroscopic counterparts always looks to the Nano Advantage. Take nanorods, nanowires and nanotubes: They are all one dimensional nanoscale constructions and can, for example, be comprised of almost any element or element combination in the periodic table such as carbon, gold, silicon, zinc oxide, titania or gallium nitride. But they are not the materials as we know them in the bulk form. Their tiny size endows them with vastly more surface area and surface active sites with respect to their volume than our experience of normal size rods, wires and tubes. And their optical, electrical, magnetic, photonic, plasmonic and mechanical properties can be engineered to be distinct from those of their parents.

These are nanomaterials attributes that provide them with the ability to speed up the rates of chemical and photochemical processes, like the production of gasoline from oil, hydrogen from water and methanol from carbon dioxide. These are the qualities that enhance the efficiency of physical processes exemplified by better generation, storage and delivery of electricity in lithium ion batteries, fuel cells and supercapacitors. These are the characteristics that serve to increase the harvesting and conversion of light to electricity in solar cells, and enhance the transformation of mechanical and thermal energy to electricity in piezoelectric and thermoelectric devices. These are the traits that often make for brighter luminescence and more efficient light emitting diodes.

That's the Nano Advantage for energy nanomaterials, a catalyst for change through the nanochemistry experience!

Is innovation in nanochemistry birthing nanotechnology?

Experience has shown over the last century that the time to nurture a breakthrough in materials research through to a product or process can be 10-20 years. Since the emergence of nanochemistry as a field there has been exponential growth of research activity in the area globally and

the record shows that many Fortune 500 companies are exploring nanochemistry as an engine for innovative nanotechnologies, thousands of spin-off companies have sprung up attempting to develop, manufacture and commercialize nanochemistry based products, thousands of nanochemistry based goods have entered the consumer market place, and to allow nanotechnology to bear fruit without harm to human health and the environment, protocols are being actively formulated by government agencies to regulate the safe handling, storage and disposal of nanomaterials.

Nanochemistry has done a lot of birthing!

A Nanoscale Future On closing it is worth noting the concluding statement of my 1992 Nanochemistry paper:

“We are entering an era of solid-state chemistry and physics in which there will be increasing demands for structured nanophase materials with stringent requirements of size, shape and dimensionality, as well as the type and concentration of dopants, defects and impurities. In such a world of tiny objects, processes and devices, the undisputed production workhorse of the nanophysicist over the next decade or so will be sophisticated forms of planar deposition and lateral engineering techniques. The practical limit of these methods appears to be about 100Å. Beyond this size, the nanotips of scanning probe microscopes will continue to be developed towards achieving the ultimate in miniaturization, namely atomic and molecular scale devices. This promising technology could show some practical utility in the 21st century provided that the huge challenge of rapidly and reproducibly moving matter at the atomic level can be surmounted. Meanwhile the elegant patterning and templating methods of the chemist for producing spatially controlled nanophase materials are likely to receive increasing attention in the exciting nanoscale world of the future.”

Clearly top-down and bottom-up approaches to nanostructured materials has burgeoned beyond my wildest expectations. A portfolio of innovative hard and soft lithography methods are pushing the spatial resolution envelope towards 10 Å for practical information technology, biotechnology and nanotechnology devices; thousands of hard and soft nanotips are pushing molecules and materials around into functional constructs at scales smaller than what would ever have been imagined possible; chemists have learned how to reconstruct almost every known material through chemistry into nanoscale versions with precision of size and shape honed towards the degree of perfection only dreamed about twenty years ago; and interest in applications of nanomaterials, touted (as well as debunked) as the trillion dollar industrial revolution has gone global, which has focused keen attention on approaches for safely and economically scaling the production of nanomaterials in different forms concurrently with the development of ‘green nanochemistry’ manufacturing methods for making ‘green nanomaterials’.

21. Nature's Nanomaterials – To be or Not to be Bioinspired?

Some old adages in the field of biomimetics include, “Nature did it first”, “if it exists, it can be synthesized”, and “bioinspiration from Nature”.

The word “biomimetics” derives from Greek bios, "life" and mimetic, "competency for mimicry". Since the word was coined in the 1950's biomimetics has become a vibrant field and today is associated with the design, synthesis and fabrication of materials and machines whose structure and properties, function and utility derive inspiration from biological systems.

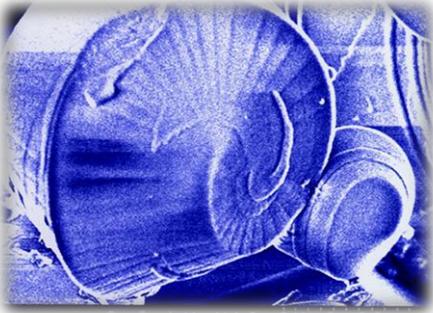
This bioinspiration comes from efforts to understand the chemical, physical, and biological principles that underpin Nature's marvelous constructions. Their very existence is predicated upon perfected and optimized change that has been fine-tuned over evolutionary time scales enabling endurance of the fittest materials, honing of the most efficient processes and survival of the top performing devices and systems.

For scientists working within the field of biomimetics the overarching goal is to learn and purposefully exploit Nature's secrets to solve materials problems and thus enable the development of new materials technologies.

Some practitioners of the art have, however, said that biomimetic materials would have been invented without any knowledge or inspiration from Nature while others have argued that it would have simply taken longer to invent these materials without that insight. This debate still smolders amongst academic researchers, and the controversy keeps government and industrial scientists, policy makers and funding agencies on their toes!

Nanochemistry has received much inspiration and benefit from trying to understand morphogenesis; the origin, growth and form of nanomaterials that abound in nature, exemplified by the structure, properties, and function of tough mollusk nacre, colorful butterfly wings, iridiophores and beetle cuticle; porous diatom, radiolarian, echinoderm and coccolithophore micro-skeletons; spicules and spines of sponges and stinging nettles, sticky gecko's feet and self-cleaning lotus leaves, hierarchical architecture of wood and bone, and the photosynthetic solar fuels machine.

This insight into Nature's morphogenesis has enabled “morphosynthesis”, the development of bottom-up auto-construction strategies, such as self-assembly, co-assembly, directed-assembly, shape-assembly, oriented-assembly and hierarchical-assembly, for making new classes of nanomaterials with tailored form in the laboratory: nanocomposites and nanostructured surfaces, nanocrystals and nanoporous solids, nanomotors and nanomachines.



Synthetic sea shells

Knowledge of the structure and properties of Nature's nanomaterials over "all" scales from the lowest to the highest level in the structural ladder, from nanoscopic to macroscopic constructions, has spawned new science, and engineering aimed at understanding new problems such as organic template-directed nucleation and growth of inorganic nanomaterials; mesocrystals, nanocrystal oriented growth, organic-inorganic epitaxy and interface engineering; formation of periodic micro-, meso- and macroporous inorganic

particles, fibers and films, morphology control of inorganic materials with natural form, exemplified by the surfactant-templated sea-shell mimics having patterns and shapes reminiscent of the natural world shown in top Figure; and chemically powered locomotion at the nanoscale, exemplified by catalytic nanorods, a futuristic playground poised to perform purposeful tasks in nanotechnology, and challenge conventional forms of diagnostics and theranostics in nanomedicine, illustrated in bottom Figure.

This gathering nanomaterials knowhow and momentum is providing numerous technological opportunities that embrace many fields of use, including adhesion and wettability controlled surfaces, food packaging and food quality control sensors, antireflection and high transparency glasses, self-cleaning and antibacterial coatings, tough corrosion resistant ceramic films, energy storage and conversion devices; porous solids for hydrogen, methane and carbon dioxide storage as well as pesticide, herbicide and pharmaceutical targeted release systems; solar fuels catalysts, bone, cartilage and spinal cord analogues for regeneration and replacement, augmentation and repair, structural-color for security devices, displays, paints, cosmetics and chemical sensors, and nanomachines for seek-and-destroy missions, oil spill clean-up tasks, cargo pick-up and delivery, the holy-grail being targeted cancer therapy.

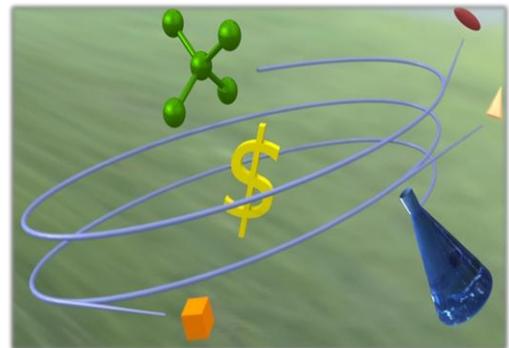


Chemically powered nanorods outswim flagellated bacteria

Nanochemistry in Nature continues to prove itself as an inspiration for Nanochemistry in the laboratory - it has been responsible for many incredible birthings!

22. Spin of a Nanotech Spin off

Innovation in advanced technology often springs from ideas birthed in universities yet the attitudes of professors and their students towards entrepreneurship and their stance on the collision between fundamental research in the pursuit of knowledge and applied research directed to the creation of intellectual property, inventions, companies, jobs, products and wealth, is not that well appreciated either inside or outside our universities. In this article I will explore this interesting issue and try to gain some insight into the challenges faced by professors confronted by the challenge of transforming basic science and engineering knowledge into products in the market place, using nanotechnology as a case study. While the specific focus of this article is on nanotechnology, more generic issues are also raised that relate to transformational business development and entrepreneurship in society and universities in a larger sense.



Introduction

Materials devices and systems built of 1-100 nm components have been shown to have unique structures, properties, and functions relative to molecular and bulk forms of matter because of their scale. The newly established ability to exploit variations in the physical scale of materials rather than the traditional use of materials composition provides cross-disciplinary potential to improve the performance of a myriad of industrial products and processes that utilize electronic, optical, photonic, magnetic and mechanical components.

Furthermore, manipulation of the scale of materials enables radically new technologies for a sustainable future in energy, climate, water and air in our environment as well as revolutionary solutions to improve human health through new paradigms in medical diagnostics, drug delivery, therapeutics and imaging.

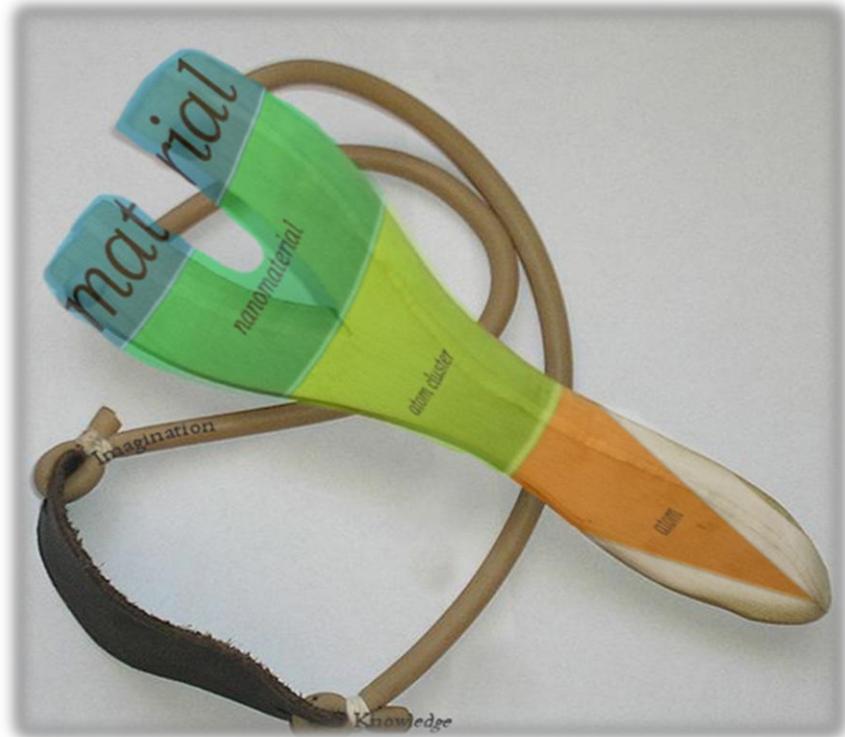
The consensus amongst industrialized nations is that nanotechnology holds great promise for creating substantial economic growth through the creation of new markets, providing incentives for large investments in nanotechnology developments with anticipation of great returns. It has also been acknowledged somewhat facetiously that nanotechnology is an advertising term designed to stimulate the injection of additional funding into the natural sciences and engineering disciplines to ensure scientific, military and economic advantage over international competition.

To expand and quantify, BCC Research, a market research firm, reports that nanotechnology is poised for considerable growth and the four countries most able to commercially exploit the transfer of ideas to innovation are the United States, Germany, Taiwan, and Japan. They have assembled the necessary scientific expertise, competitive technology companies, highly qualified workforce, and access to public and private equity, to ride the wave of success in the development and commercialization of nanotechnology. It is estimated that the global market for nanomaterials, nanotools and nanodevices will grow to \$26.7 billion in 2015 from \$11.6 billion in 2009 and Global Industry Analysts estimate nanotechnology products across the automotive, chemicals, electronics,

cosmetics and healthcare sectors will reach \$2.41 trillion by 2015. It is noteworthy that nanotechnology activity has intensified in Russia, Saudi Arabia, and China who judge its development as crucial to its future.

RusNano Corporation, created to commercialize developments in nanotechnology, has garnered billions of dollars from the Russian government, nanotechnology scientists are being head-hunted by

Saudi Arabia from all corners of the globe, and China has made a heavy enough financial commitment to nanotechnology research and development to be internationally competitive.



Creating this integrated bottom-up and top-down slingshot (atom to atom cluster to nanomaterial to material) for the transfer of nanoscience to nanotechnology is one great innovation - knowing what you are targeting and how to hit your mark is another - Todd Siler and Geoffrey Ozin, ArtNano Innovations©.

With all the excitement about the transformative potential of a 21st Century nanotechnology revolution, in which Canada has made a significant investment relative to the U.S. on a per capita-basis, I have been trying to understand the underperformance of Canada in transforming its world-class home-grown

nanoscience into nanotechnology spin-off companies thriving in an innovation ecosystem.

I have identified five main issues, which I believe can help to explain this underperformance:

1. A lack of available funding from the likes of venture capitalists and public programs
2. A lack of a suitable physical infrastructure and environment that would support the growth of world-class nanotechnology start ups
3. The unique challenges facing nanotechnology as a result of the often broad applications of its innovations
4. The attitudes and in-grained ways of Canadian university faculty
5. A pervasive fear of failure and excessive risk aversion within the minds of Canadians

In addition to discussing these five issues from my own perspective and with the input of some fellow academic colleagues, this article will also present viewpoints from the perspectives of both graduate students and entrepreneurs.

A lack of available funding from the likes of venture capitalists and public programs

While it is true that on a population basis Canada is doing as well as the U.S. in creating spin-off companies from university-based research, many of these are software and digital-media firms, which do not need much start-up capital and have a relatively short development time. Another issue is that Canadian investors tend to be more conservative than U.S. investors and U.S. investors don't often invest outside the U.S. although this may be starting to change. An entrepreneurial academic colleague of mine echoed that this is a serious issue in Canada, across all disciplines. PARTEQ Innovations in Ontario has been trying to build a VC network for Canada, to make it easier for VCs to work in Canada.

An academic-entrepreneurial colleague who specializes in corporate law and finance with a particular interest in venture capital and small firm financing pointed out that there has been a trend in recent years for U.S. venture capitalists to do more and more business in Canada. The 2011 industry statistics show that for the past 6 years, foreign VCs (mostly U.S.) have invested about 20% (on average) of all VC money invested in Canada. When they invest in companies in Canada, they typically invest more money than Canadian VCs do. In 2011, the average amount invested by U.S. VCs was more than double that of Canadian VCs - \$3.1 million versus \$1.3 million. This is because U.S. VCs typically have more money available to them than their Canadian counterparts and can therefore afford to make larger investments with the expectation of larger returns. Because of this, U.S. VCs are also generally more capable of investing in follow-on rounds, which tend to involve

larger amounts of money and can be critical to keeping a company afloat when it starts to grow. In Silicon Valley, the VC firms have pretty much ceded investments of under \$10 million to angel investors. In addition, the U.S. is big enough that VCs can specialize in a narrow part of the technology spectrum (i.e. there are economies of scale). In Canada, VCs are generalists and resource-based, and so are not as good at assessing potential tech investments, or providing mentorship to entrepreneurs in particular segments.

In addition to the lack of available private capital, Canada also lacks large-scale government support for new ventures; and indeed one attempt to provide such support. Labor Sponsored Venture Capital Corporations (LSVCCs) has proven to be highly misguided. These LSVCCs require a union sponsor and the only investors who can invest in them are individuals. There have been very generous tax credits offered on investments by individuals in **these companies**, and as a consequence billions of dollars have poured into them. The downside is that they are often run by people who don't have any experience at all in VC investing, but are attracted by the fixed fees that they can charge investors every year even if the fund makes no money. LSVCCs as an asset class have earned no better than GICs. To top it all off, because they have huge amounts of money and a lower cost of capital than private funds, the LSVCCs have been able to outbid more efficient private funds on promising investments resulting in far less growth in the private fund sector than would otherwise have been the case. Governments are now realizing that these LSVCC funds were a mistake, and Ontario (where most of them are incorporated) will reduce its tax credit to zero next year. But the situation is still dire: the Business Development Corporation (a federal Crown Corp that invests in small and medium-sized enterprises) put out a report last year saying that the Canadian VC scene was "broken". They are quite right. And without an effective VC sector, it is difficult for start-up firms and later stage firms to get funding. An issue facing nanotechnology in particular, because of the breadth of its potential markets is that it has tended to fall between the cracks in many funding programs, and the government has been slow to recognize this issue. On this last point, an entrepreneur experienced in pharmaceutical startups commented: this breath coupled with the newness of the technology can be an impediment for investors as focused developments are in the throws of being defined and saying that nano can do everything does not provide confidence that nano can do something.

Thus far, nanotechnology companies in Canada do not have as strong a success story as those in the U.S. which seems more adept at transforming public nanoscience to nanotechnology spin-offs, through the pipeline of a well-integrated network of university, government, military and industry laboratories, large manufacturing companies, venture capital and private equity firms, to innovative products and processes in the global market place.

In the context of military support the U.S. defense industry has played a huge role. DoD and the military have a long history of being the implementer and enabler of technological innovation and this remains true with nanotechnology. DoD has taken a keen interest in budding nanotechnology startup companies being high cost buyer or buyer of last resort in addition to well-funded supporter of university and national laboratory research centers seen by their injection of around 28% of all federal funding to exploit nanotechnologies potential. MITs Institute for Soldier Nanotechnologies is a good case in point where nanotechnology is being explored for its impact on future warfare (e.g., military performance objectives, command and control, modern machines), some targets being pathogen and explosives personal sensors, super-explosive bombs, tougher lighter materials, and adaptive camouflage. Technologies birthed in the bowels of the military determine the progress and nature of a technology that may spill over to benefit civilian society while others remain classified and never see the light of day except in espionage and conflict.

The U.S. Navy has been a “first adopter” of many new technologies and they also actively fund high-risk but potentially very innovative nanotechnology projects through “DARPA” - Defense Advanced Research Projects Agency”. The Department of Energy’s “ARPA-E” (Advanced Research Projects Agency - Energy) has modeled itself on DARPA, and seeks to fund high risk potentially “disruptive” technologies in the energy field where nanotechnology is expected to play a major role. They expect a failure rate of above 90% for their funded firms.

Canada currently lacks the massive public investments in high-risk nanotechnology spin-off enterprises that exist in the US through agencies such as Department of Defense (DoD), Department of Energy (DoE), ARPA-E and Small Business Innovation Research (SBIR) and the vast infrastructure network of public universities, advanced materials national laboratories and firms exploring the commercial potential of nanotechnology. Start-up companies in the U.S. may be fueled by these public grants, which are relatively easy to get and provide real funding especially in phase 2 of a start-up. Canada simply does not have this investment firepower; the NSERC I2I and CIHR POP programs are nice but are an order of magnitude too low in funding, and the limitation to a single year is a show-stopper. Without a vibrant SBIR program funding innovation, Canadian entrepreneurs will always lag behind those in the U.S.

It is worth mentioning that the SBIR program does two things. One is grants the other is to require that all federal agencies with extramural research budgets over \$100 million set aside at least 2.5% of that money for contracts with small businesses. This makes the federal government a "first adopter" or at least an "early adopter" of many new technologies. The Canadian federal government has a similar program which is not nearly as ambitious as the

SBIR program and it is difficult to determine how much money has actually been spent on contracts with small firms with "pre-commercial innovations".

A 2011 Lux Research report on government spending on nanotech ranked nations for three consecutive years through 2010, on a per capita-basis. Canada is on par with the U.S. (1/9th population, comparable fractional spending). A knowledgeable colleague observed in this same report that Canada's corporate spending on nanotech lags way behind the U.S., even on a per capita basis. But, then again, so does that of all other nations except Japan and Germany. The trouble is there are not enough big wealthy companies in Canada that can comfortably invest in nanotech, as do the GE's, IBM's, 3Ms, Intel's, HP's, AT&Ts, Motorola's, DuPont's, Toyota's, Sony's, Hitachi's, BASF's, Philips' and Merck's of the world.

Part of the cause here likely is, in the words of the Alberta Centre for Advanced Micro Nano Technology Products (ACAMP's) CEO, that "there are far too many small hobby companies in Canada." He believes that there does not seem to be enough Small Medium Enterprises (SMEs) in Canada that have a serious drive to work hard enough and long enough to earn even \$10 million in revenue, never mind \$100 million or a \$1 billion, thus ultimately limiting the number of major (multinational) corporations in this country, beyond the financial institutions and companies in the traditional natural resources sector. If technology companies in Canada really look good they often get bought out by the U.S. and moved south. This becomes clear when one compares the sectors of the top 20 U.S. vs. top 20 Canadian companies where one can conclude that Canada is sliding in innovation because there is not enough emphasis on growing the size and quality of SMEs, rather than just their number. And, of course, starting small nanotech businesses can lead to big innovation and thus ultimate success.

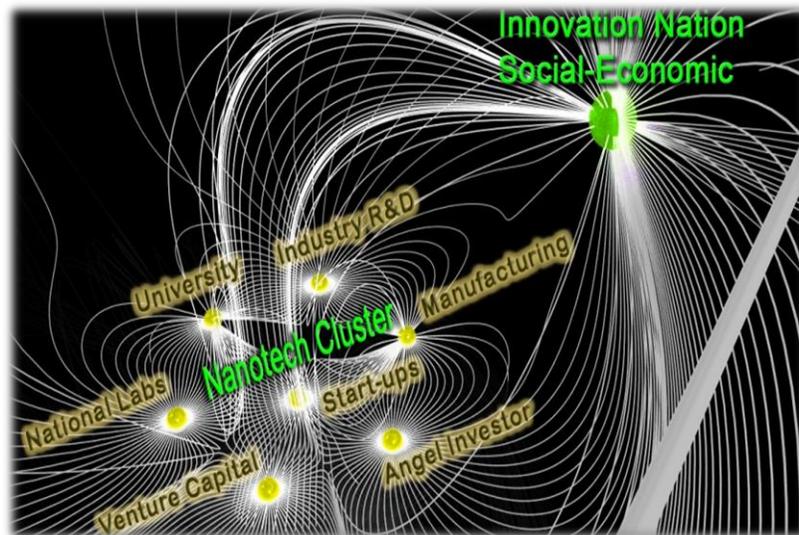
It is instructive to look more closely at the distribution of the global investment in nanotechnology between governments, corporations and venture capitalists described in a 2011 Lux Research report. The U.S. government outspent all others with \$2.1B in 2010 and Russia overtook Japan to gain second place with \$1.05B and Canada took tenth place with an investment that on a population basis was proportional to the U.S. However, the U.S. and Japan dominated in corporate spending on nanotechnology having invested \$3.8B and \$2.8B respectively with Canada in nineteenth place. Of all venture capital investments in Nanotechnology, 89% was captured by U.S. companies.

A lack of a suitable physical infrastructure and environment that would support the growth of world-class nanotechnology start ups

To foster a successful innovation environment it is important to have a place that is physically conducive to the founding of successful companies. Within this environment clusters are important, composed of a critical mass of start-up companies, university, national and industrial research and development

laboratories in a given region. Key to the success of such a cluster is having at least one large company that anchors a region and then several small companies can form and grow-up around this with public and private investment providing financial support and employment supplied by a highly qualified workforce, all together building the local and national economy. In Canada, Ottawa and Nortel, Waterloo and RIM are examples of telecommunication and wireless network companies that in their prime were globally successful and worked well; these can serve as models for how to make nanotechnology work in Canada.

In addition to the presence of other large companies which can provide support, it is important to have venues in which would-be entrepreneurs and investors and free to meet up and discuss their ideas. A Canadian researcher who did post-doctoral research at Harvard commented that the one thing that struck him in Boston was not the prowess of the IP offices and the supporting bureaucracy; it was the fact that there are bars on Massachusetts Ave whose only reason for existing is to provide a space where MIT and Harvard students can meet investors, talk about ideas, develop elevator pitches. In Stanford, as he heard, it is the same. In this environment entrepreneurs are completely normal and not outliers as they are in Canada. Young scientists and engineers need channels to understand the nature of the questions that will be asked by industry and investors and to begin to understand how to answer them. While there are vast numbers of invention disclosures from academics and their students, essentially none of them make a serious effort to understand and predict cost competitiveness. It's not obvious that they even know where to start! Of course there are causality issues here but still one cannot dismiss the importance of external factors that must at least co-evolve with entrepreneurial faculty.



Anatomy of a living nanotechnology cluster - graphic illustration courtesy Dr. Wendong Wang

An experienced Canadian academic entrepreneurial colleague remarked: While a spin-off is one route to commercialization, it is not the only way to commercialize IP and have very significant economic impact. I would argue that licensing technology allows for several specific benefits: 1. Immediate and

realistic assessment of commercial viability of technology by those who know the market. 2. More rapid integration in to production/marketing and sales. 3. Immediate and on-going financial benefit for inventors and 4. It allows academics to focus on what they do best: explore and invent. My view is that this is of course true if those companies existed in Canada, which in advanced materials technologies they generally do not - oil and gas yes but what do they do other than pipe crude and natural gas to others for them to burn, make products and create jobs - is this really the future for Canada ?

The unique challenges facing nanotechnology as a result of the often broad applications of its innovations

A comparison of emerging nanotechnology spin-offs with established biotechnology and microelectronics firms, all three being materials technologies, has indicated that the nanotechnology transfer model may be different to the one responsible for biotechnology evolution, where small and medium size companies play a major role in the industrialization of research ideas. Instead the model of nanotechnology development may be more akin to that of the microelectronics sector where the translation of ideas to innovation may be enabled by larger companies and often has a longer time to market commercialization phase which consequently reduces that amount of time that an invention can be on the market whilst under patent and therefore reduces its profitability potential.

Because of the wide range of potential applications for their products, nanotechnology start-ups can play multiple roles as primary engines of technological change in diverse high technology sectors by bridging the gap between universities and large enterprises as well as providing specialized services and products to both. This uniquely heterogeneous and multifaceted trait of nanotechnology needs to be recognized by managers of university technology transfer, policy makers of public investment and private equity firms who endeavor to understand and facilitate the successful creation, growth, profitability and survival of university nanotechnology spin-offs.

This wide range of potential applications and target customers contrasts with patterns commonly observed in other industries. For example, if a biotechnology company can develop this family of drugs and discover one candidate that cures cancer, then it can produce it, push it through clinical tests, and sell it via prescribers. Many technologies already have a customer identified, and this makes it a lot easier to start a company, easier to get investors - it's high risk, but the potential payoff is very clear.

Nanomaterials are different in many ways. While we can come up with some potential applications, there are some substantial barriers - will it be better than a competing product, can it be scaled and manufactured and is it safe, could it easily displace another technology? When you start looking at which company might be interested in being a customer of your nanotech product

when you produce it, it's really hard to identify a Canadian company to involve in the transfer process. And it is much more challenging to get things off the ground unless you already have that connection or at least a clear application for the nanomaterials you are developing. So, one of the major impediments to spinning off companies in nanomaterials is having a critical mass of companies lined up to take new materials that we might develop to the market as a range of products, so most strategic alliances are with foreign owned firms.

The attitudes and in-grained ways of university faculty

While it is true that appreciation of this important issue involves a complex mix of country-specific political, economic, social, environmental, and educational factors, in my opinion an important and generally unrecognized flaw in the system lies at the beginning of the innovation supply chain, where an invention shows the potential to begin the journey down the long, winding, and arduous road to the market place. This has existed all around me every day of my more than four decades of working in the field of advanced materials – the professor and a more than century old culture in which academics like to function and thrive - the Ivory Tower, teaching, research and the creation of knowledge.

Yes it is true that academics have plenty on their plate with research, teaching, and helping to manage their department and service their university and community and are happy doing so with their job security, pension and academic freedom safely in their pocket (at least for those with tenure). Typically the professor tends to be risk averse, for example reluctance when exposed to the uncertainties associated with lack of control in the business venture, additional time commitment, business inexperience, conflict of interest, legal and financial liability, fear of failure and stress related health issues. This is even more of a conundrum in Canada, which has few industries in the advanced materials nanotechnology space to which the professor can license their nanoscience inventions let alone expect them to be able to hire students when their graduate/post-graduate training is completed.

One way to address this complacency which exists within the academic community may be to consider changing the metrics for judging the performance of a professor and figure out how to justly reward them for entrepreneurship as one of the mandates upon which they may be awarded tenure and promotion, along with their contributions to research, teaching, and/or service to the university and community. Professors should be given a choice how and where to direct their creative energies and their entrepreneurial contributions should be appropriately recognized and compensated using an appraisal model that will have to be defined and which is fair to all. I recall one academic colleague who remarked when I asked for advice on how to spin-off my first start-up company that this was 'not a scholarly and gentlemanly pursuit for a professor'. Fortunately, I did not listen to this perspective and the company was founded and is still in business; unfortunately, I would opine that many of my academic colleagues still support that view.

There are of course issues which arise when trying to judge the merits of an entrepreneurial endeavor. There is the mismatch in timing, for one thing. Suppose the tenure decision is in a professor's 7th year, and they start up a company in their 4th year. Whether the company is a success or not will often not be known until after the tenure decision – or that decision will have to be postponed, something that most professors will not like. Perhaps more serious, the majority of tech start-ups ultimately fail. But failure or success may not be a good measure upon which to evaluate someone. A start-up may fail for reasons totally beyond the control of the entrepreneur, such as the economic climate, the environment for angel, VC, and strategic-partner funding, or the arrival of a newer and better technology. Patents are probably not a good measure of success since some fields require patents, while others like software do not. Moreover, patents are not peer reviewed, and there are lots of patents out there that will never earn a penny and many are abandoned. Some of these may contain extremely useful ideas but not ideas that are readily commercialized. In addition, commercialization is a group project; it involves a team. Success (or failure) may be attributable to other members of the team. Many angels and VCs will say that the most important thing about a start-up is not the idea or product, but the management and marketing. This raises the question of how one evaluates a professor's contribution to the venture, particularly given that the most important actions and decisions may be taken by others. Figuring out how to reward commercialization may be the biggest nut to crack in diverting professors down the commercialization path. A colleague questioned, that couldn't a very similar argument be made about academic research? Sometimes it can take a long time to build up an area of expertise and become successful at researching it.

In addition to judging a professor's candidacy for tenure based on their efforts to commercialize their research, it is also important to provide them and their students with excellent training opportunities to equip them with the necessary skills to embark upon such a project. It is my contention that if professors better understood the steps that underpin the idea to innovation entrepreneurship pathway they could advise and help enable their students to walk the path from lab to market while the students with this guidance from the professor will make it happen as they are often only too pleased to take the risk because they are young, well trained, fearless, need a job and have nothing to lose but everything to gain with enormous rewards if the company succeeds and a great experience even if the company fails, valuable knowhow which will enable them to be successful with their next spin-off adventure. Student founders of spin-off companies cannot do it alone and will also need founder partners who are seasoned business managers who have learned key business and technology skills in companies and then started a business that is well-thought out, qualities not often found in angel investors. That is true for professors too. Many VCs and angels will not invest in a start-up if the professor is also management. They want to see a management team with some experience.

If Canada is to be a world class player in nanotechnology and reap the long term socio-economic benefits of their investment in students and education in this area then more professors both young and old have to rise to the challenge through entrepreneurship and business courses and get busy understanding the idea-to-innovation supply chain so that they can properly support and encourage their highly creative, energetic, and motivated students to succeed in entrepreneurship. I think that there is a role for the business schools to play in this respect. I know first-hand that there is a gigantic pent-up frustration amongst hoards of talented Canadian students who want to do this and often take entrepreneurship courses to help them get a career underway and in doing so help their nation but in my view they often lack supervisory role models.

On this point, an entrepreneur experienced in the Canadian, U.S. and European technology startup scene commented that the real problem with students isn't a lack of business skills but critical thinking skills to make decisions, how and when to change course, independent thinking, adaptability, efficiency in effort toward a commercial goal, analytical problem solving skills. Experience helps but it's either innate or learned by being around people that are driven. You get that from a school that is full of people who are driven like MIT/Harvard, Stanford/Berkley.

A pervasive fear of failure and excessive risk aversion

Another issue that I have identified – fear of failure, is an issue that can affect all people with a stake in the entrepreneurial process, but the biggest problem arises when the trait is possessed by professors – whose duty should be to encourage their students to take the risk of founding their own company – and potential funders, who must recognize that only by accepting and exposing themselves to higher risks will they have access to greater rewards. A tenured colleague commented that it is important to have enough companies try and fail in order for there to be successes, and it seems that Canadians are too frightened to fail - the U.S. has many more start-ups, many more sources of funds and many more failures, which is why they have successes, and in particular why they have such grand successes.

It seems that the Canadian philosophy is to try to consistently pick sure returns, rather than use the 'shot gun' approach to innovation and entrepreneurship by investing in many different companies at many different levels of risk. This approach only works, however, if they actually can consistently pick the winners otherwise it is better to spread the risk more thinly and hope that one hits however thin money cannot be shot gun and deep at the same time. A common issue, particularly in the case of publicly funded ventures is that bureaucrats don't have the expertise to make well-informed decisions about which projects to fund. Moreover, they aren't looking for disruptive technologies – rather, it is low risk "photo op funding" that they aim for. Again, the metrics by which these public employees have their job

performance measured could perhaps also be changed in line with the suggestions I outline above for factoring in entrepreneurship as a measure of the success of a professor.

As well as discussing these issues from my own perspective as a veteran professor of nanochemistry, it is also important to hear perspectives of current students and entrepreneurs, and I present these viewpoints in the following sections.

Students' Perspectives

Talking to a recent Canadian PhD graduate who worked on a nanoscience problem, I asked, look back on your work and consider the question why did you not try to commercialize your research or perhaps more insightfully what would need to have been different in order for you to do so?. The graduate said there were three things that would need to have been in place to consider a spin-off based around the PhD research: a good idea, access to funding and personal expertise. In addition, he commented on the importance of having a mentor in the shape of a professor who is willing to support entrepreneurial ambitions.

Returning to the first point, the student remarked that scientific projects typically fall into two categories: so-called 'basic or fundamental' work and 'applied' work which seeks to address a real need and propose a real solution to a real problem. Within the latter group there are two sub-categories: projects that are cognizant of the real-world requirements for the solution to their chosen problem and that genuinely seek to address these, and projects that claim to address a real problem but in reality are only using these claims to boost the apparent importance of their work. Unfortunately, the vast majority of research falls into this latter category. What is needed is for the 'applications' of a piece of work to be truly tested and justified by real market demand, not merely claimed as a way to artificially boost its apparent relevance. If a researcher claims to have discovered a new technology that will be of use for drug-delivery, display technologies, or solar power, they should perform a full cost/benefit analysis of their technology, compare it to the competing technologies, both in the marketplace and in development, and also discuss the likely target customer segments. Students should be encouraged to truly test the applications of their projects and to discuss them frankly and honestly. If a technology seeks to solve a particular problem then researchers working on that technology must understand not just the scientific barrier which must be overcome, but also any relevant political and economic issues so that they can truly understand the implications of their proposed solution.

On the second point the student said much research in Canada is funded by the Natural Sciences and Engineering Research Council (NSERC) which has a yearly budget in the region of ~\$1B CAD. A sizable portion of this goes to awarding scholarships to graduate and postdoctoral researchers so that they

may conduct academic research. In particular, the flagship Vanier scholarship program accounts for approximately \$25M CAD/year. As a graduate student he often received notice from his department about looming deadlines for various scholarships, and the majority of eligible students probably apply for a government-funded scholarship at one time or another. There is very little information, however, about the availability of funding for entrepreneurial activities; and the process of securing such funding is certainly far more opaque and mysterious to the typical PhD student than the process of securing a scholarship. If the government was to establish, in addition to the ~500 Vanier scholarships funded at any one time, a program of 100 or so \$50,000 grants for initial testing of the commercial application of PhD projects, we might see a sharp rise in the number of students considering entrepreneurship. These grants would not seek to cover the founding and development of a company – that would be far too expensive – but rather would allow a student to spend six months to a year on investigating the possible practical applications of their research; developing an understanding of the potential market, the cost involved with competing in it, and possibly developing a prototype product and doing some preliminary customer research. Of course, many, perhaps 99%, of these ventures would fail – either the \$50,000 would be spent and would demonstrate that a project does not have realistic commercial potential, or a company would be founded but would ultimately falter – but for that small percentage that do ultimately succeed the rewards could be exceptional, and the government, or any private funders, could likely make a significant portion of their money back through tax revenues and by retaining some equity stake in any companies to come out of such a venture.

On the third point the student remarked that he has often seen it said that people who really want to be entrepreneurs will ‘just do it’, or something to that effect. There seems to be a perception amongst many people that those with the skill to found and run a business are born with the magical combination of risk tolerance and business acumen necessary to succeed. Although there are many high profile examples of people just going for it and succeeding, there are many more examples of people becoming successful entrepreneurs after a lengthy and rigorous business education and career in industry, and many failed ventures. If we do truly want to encourage graduate students to consider entrepreneurship as a career path we need to make it a fundamental part of their curriculum, and something which is encouraged and nurtured throughout their degree, rather than just being an afterthought to be dealt with once the science is in place. In the University of Toronto chemistry department, graduate students choose a stream to enter; inorganic, organic, physical, polymers, materials, theoretical etc and this selection partially determines the courses that they must take and seminars that they must attend. Perhaps another stream to be added might be ‘commercialization’ or ‘entrepreneurship’ in which students would be required to take classes on these subjects, and to

present seminars including a (realistic) assessment of the commercial potential of their work.

The other three points above require a significant change across many people to accomplish but this final point is something that professors can choose to achieve as individuals. Even without the previous experience of founding a successful company, many professors have contacts, connections and strong reputations which could be leveraged in order to encourage students to succeed in commercializing their work.

I also spoke with a freshly minted Canadian materials science and engineering graduate with an admirable entrepreneurial spirit raised some interesting points based on his first hand experiences at trying to establish a start-up. This young scientist emphasized a number of interesting points beginning with the dire need for more small pots of money to be available for start-ups, having experienced firsthand a really hard time trying to get any small amounts of money. This student felt that although there are lots of small grants available for 'innovation' based research and development these are only available to tenured faculty, which almost defeats the purpose. Commenting further, what incentive is there for a professor to use this money for real innovation when at the end of the day they will still be a professor? Perhaps it is not more grants that are needed but a shift to innovation grants that can be held by recent graduates or post graduates. This student is ghost writing an innovation award proposal for his ex-supervisor based on the students work seen by the student as ridiculous who would like to be able to apply for the funding them-self. Another problem this student sees is that the bigger start-up grants already require too onerous requirements for a start-up and therefore often get awarded to established companies that are branching out into new markets. The student also argues that the problem with professors is not that they don't provide leadership in regards to innovation and entrepreneurship, it's that with the freedom that an academic position gives, their research often becomes too detached from what industry really needs, for example while it may be good for publications to develop new (nano)materials for solar cells, oleds, fuel cells, batteries and so forth these applications are not necessarily what the market needs or wants. The student remarks, if nanotechnology is so multidisciplinary then one should easily be able to find industrial relevant applications, even within the resource based Canadian economy. Isn't cosmetics one of the biggest market for nanomaterials anyway, how many professors in science and engineering work on cosmetics, and why not more? Perhaps it's the funding model that's broken. Food for thought!

A top rank Chinese graduate in materials research from University of Toronto who is continuing his post-graduate studies at Harvard had an interesting view of the Ivory Tower. The student said that after reading this editorial he began to think about the personal motivation of academics. Curiosity is traditionally the main drive for academic research, which do not seek return-on-investment at

all. Along this line, making money is not the motivation for academics, which had been taken to the opposite extreme that it is not 'scholarly'. This type of thinking may work well on an individual level, provided that there are people who are willing to fund ones' curiosity. But taking the academic research enterprise as a whole, the entire community bears a social responsibility to give back to the people who provided the community with resources. In today's world, tax-payers are the people who fund the research; the government and funding agencies are redistribution channels. This social responsibility of academic community is usually discussed in such forms as the science education, communicating one's research through public outreach; but building a business is the ultimate form of giving back. In this sense, building a business is not about making money, but a way to give back to the society what academics owe them. Not only academics need to be aware of such a responsibility, but also the people who are designing institutional infrastructures at the city level, the regional level, and the national level need to be aware of that as well. People are driven both by individual ambition and by a higher calling for making a contribution to the collective whole. These two are not against each other; they can blend with each other. Likewise, the drive of curiosity and the drive that comes from the awareness of a social responsibility can be blended as well.

I find it interesting that this student comments on the important of giving back, when another tenured colleague with whom I spoke rejected this idea and stated that it is not an academic's place to try to create companies 'for their own personal gain'. It seems that this student takes a far less cynical view of the purpose of entrepreneurship.

Entrepreneurs' Perspectives

An entrepreneurial Canadian who following his post-doctoral studies co-founded and became CTO of a bionanotechnology diagnostics company offered the following insightful thoughts: It is true that in the biotech world, small and medium size companies play a major role in the industrialization because 1) they have a prototype product that they have developed and that gets accepted by a regulatory body, like the FDA, 2) large medical companies tend to acquire such companies after they have been de-risked after a few rounds of investments. This is the way a lot of big players in the biotech industry innovate through mergers and acquisitions instead of spending lots of dollars on internal research and development. Nanotechnology companies are a bit different as they tend to be based on materials solutions and tools that could be used for various applications analogous to microelectronics firms. They face multiple challenges including which application to start focusing on first; some don't focus at all and die while others focus on the wrong application because of a lack of market analysis and face the same outcome. Because the investor community tends to be industry-focused (for example clean-tech or biotech or IT) it is not always easy for a startup to focus on one application if one wants to get a deck in front of VCs in Canada. The VC market is small and if you don't

focus your application on the specific market they invest in, they will not look at it because they don't understand its particular risk. So in order to access various VC markets, nanotech startups will try to focus on several products that could attract each market. While presenting different decks to different investors is important each one should stay focused on one market because starting with the development of multiple products is certain death.

That young Canadian CTO that believes that despite some professors who being able to excel at both basic and applied research, a majority of them would love to either focus on the fundamental research and the academic side and others would love to focus more on the applied side and the commercialization of technologies. Allowing both to strive in their journey is a key to their success. Having better courses in place for academic and entrepreneurship paths will also not put undue pressure on professors more inclined to fundamental research when one of their students wants to become more entrepreneurial as they could find support/mentorship within these courses.

I received some very insightful remarks on from a young German colleague who made the transition from PhD graduate research to a successful German nanotechnology spin-off. A strong point voiced was that a professor cannot be in any important operational position of a spin-off without stopping working as a professor. Therefore, the professor can only be a mentor for scientific tasks of the nanotechnology company. However, the scientific tasks are the easiest to handle for the start-up. Therefore, in the end, he doesn't see the professor as a direct factor for the success of the company, beyond just helping to get it started. The professor can do a lot before spinning off a company: the professor can create a innovative atmosphere, the professor can be very important if the company sits on campus, the professor can be helpful if he has a good reputation and good contacts, the professor can back up entrepreneurial students that use their time not only for science but also for assistance with technology transfer.

In the business of creating a nanotools startup company a German graduate student, who took the plunge as co-founder and CEO, had this fascinating perspective on the ingredients for success in this market sector: In our case, like in many of the examples you mentioned, the market is complex and the consumer market was not within sight at all. But we knew the research market or at least how researchers think. And serving people with the same thinking is much easier than making the big step from science to serving industry. That is a far distance away and it still will take us a few more years until we are there. However, in our case we had experienced believers from industry and we of course also believed and got the gut feeling and feedback from various professors and our professor himself backed up by thorough investigations, statistical developments and market and technology research. Especially working with our corporate partner was a main factor for success, who besides

investing in our company knew the technology, market, manufacturing, potential and risk. Additionally, we got strong support from the university and the department for technology transfer. Our professor paved the way and gave us the chance and time to found a company. But we enjoyed complete freedom from the very beginning but nevertheless could count on support if needed and asked for. From day one you need to be aware that you are now the manager of an own team, not the professor's student any more. If you are still dependent and guided by the professor, then you will never learn to think and act as a leader of a company, you will always act as an employee and will not take responsibility. The benefit of young and inexperienced start-up entrepreneurs is that they are risk-takers who have little to lose and typically do not yet have family at that time. Once you have obligations you will always try to keep the door open to move back to a safer place. It then is a half-hearted effort. If a start-up gets good business mentors who bring them down to earth and who enable them to ask themselves the right questions, then it may turn into a successful endeavor.

Being open for new ideas, reading books on management and success stories etc. is of highest importance in addition to personal experience provided by discussions and mentoring. I fully agree the professor cannot be in any important operational position and it also is not his duty to have the know-how on all the points that you listed. But the professor nevertheless should be aware that there is a world behind science and that even basic research and applied research might have industrial applications and that one needs to keep eyes open and discuss with industry. And it needs a change in the thinking of some professors: business is not boring. Maybe the science behind is simpler than in the lab, but the impact may be high. I know from experience that the most talented PhD scientists are often enticed by the professors to stay in science since they consider going to industry or founding a business is a waste of their talents. My feeling also is that professors favor those students more who stepped into the shoes of their professors and did not go to industry. Being successful in industry still is the enemy of science, isn't it?

I believe that German high-tech success stories in nanotechnology are more likely to happen because of the dense network of university and government research laboratories well integrated with a large industrial complex. But success of a startup needs universities who promote their success stories, it needs highlighted idols. I also am of the opinion that it needs a paradigm shift when it comes to collaborative projects with industry, who asks very pragmatic and critical questions and are therefore perceived as conservative. It needs both sides - the keen and sometimes playful thinking of science as well as those who ask what is it good for, what is the market size, which technologies do we need to compete with, can this ever turn into products, if not, does it nevertheless serve society since it gives insights into new phenomena?

Industry Perspective

You've covered a lot of ground. While your specific focus is nanotechnology, you raise more generic issues related to transformational business development and entrepreneurship in Canadian society and universities in a larger sense. All are valid points, so I'll add a few comments;

All major chemical/ polymeric materials companies have struggled to understand how nanotechnology will have an impact in their technologies and marketplaces. There is a belief that it should and will, but to date it has not. By the way, I think industrial biotechnology is still under-delivering also. Part of its problem is a marketplace badly skewed by government subsidies.

When companies analyze failure/ success of a new product/ process, it almost always comes back to inadequate development and understanding of the business case. I put most of the blame on business/ marketing organizations which do not invest the time to understand the new technology, or to really put an effort into understanding how it could transform their marketplace. They are all too often fully occupied selling current products to make this quarter's revenue targets.

However, I also believe our best scientists don't get out into the real world as much as they should. The best developments I have seen involved scientists and market development personnel getting intimately connected with the potential marketplace and key first adopter companies.

I believe university tech transfer arms should provide technology developers (Professors and their students) in the university with the market understanding/ business evaluation expertise needed to make go/ no go choices based on solid business plans. I've never been impressed with the output of the university tech transfer arms I run into in Canada; I believe they need to be radically overhauled to provide the above service. Their focus today seems to be taking science out to the world (a technology driven model); marketing licenses based on (generally weak) patents just does not work. You mention PARTEQ, but in 20+ yrs of operation, on a rate of return basis, it should not be in business.

I'd like to see universities and industry learn how to work together more effectively. Industry has the routes to market and a lot more business experience and appreciation of risks and uncertainties. I have seen and use the term 'Collaborative Research Agreement' as a tool to underpin more effective relationships. This is not sponsored-research nor is it a grant. It basically means industry scientists and academics contributing ideas together and working together under a disciplined management process to advance some science to a point where its value to society can be determined by something like a net present value.

Market dynamics and commercialization processes, led by industry, can take over from there. Up front specification of realistic distribution of rights/ ownership in the CRA is important. Early, collaborative relationship with industry increases the likelihood that the science/ technology which emerges will actually bring societal benefit as evidenced by industry having the desire to commercialize. Canada has an opportunity here, as industry/ university collaboration is viewed as being more flexible in terms of overheads, government support and IP rights as compared to the USA.

The Economist had a focus article on innovation a month or so ago; one of the items they focused on related to entrepreneurship, was consequence of failure. Where the impact is high (France, where personal bankruptcy can follow someone for up to 9 years in the courts), the level is low. In the USA, personal bankruptcy can be cleared in 1-2 years.

We in Canada need to learn how to make the border invisible again. This is a real issue; our largest market for goods and ideas will always be in the USA. Unfortunately for us, well-intentioned laws have been enacted in the last 10 yrs in the USA that has had the un-intended effect of making it a nuisance to work across the border. Working or selling across the border is critical to us, but not to the US; it therefore becomes our responsibility to manage that nuisance factor so that US colleagues or businesses are not discouraged and focus solely on the many options they have in their own country.

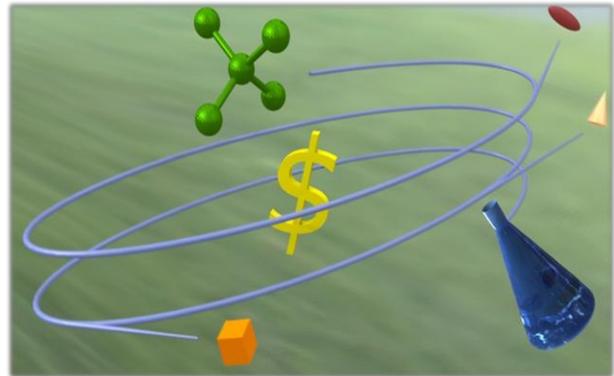
Conclusions

In the context of the five techno-economic revolutions since the eighteenth century defined by Carlota Perez in her classic 2002 paper 'Technological Revolutions and Financial Capital' nanotechnology seems to be following a similar pattern as delineated below:

1. *Installation point* - eureka phase introduces a new innovation threatening existing technologies
2. *Capitalization phase* - private and public investment of the technology
3. *Speculation mania* - financial collapse and recession induced regulatory changes to enable development of the technology
4. *Exploitation period* - favorable conditions facilitate blossoming of the technology
5. *Maturation stage* - diminishing public and private investment opportunities and stagnation

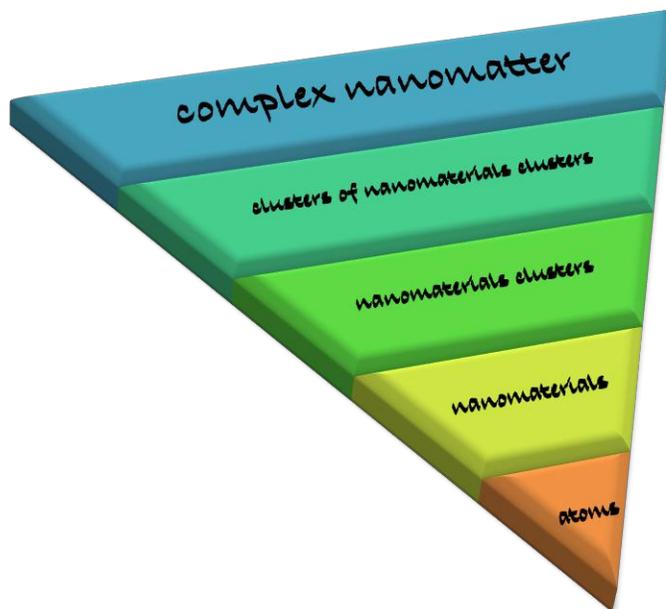
The evolutionary steps of the techno-economic model are clearly not set in stone for nanotechnology as there are so many potential generic radical materials manifestations of the revolution across multiple market sectors. Nevertheless as we transition between the five stages of the nanotechnology revolution delineated above, at the present state of development two directions

for nano-enabled products and processes are becoming apparent in biomedical and advanced materials technologies and these will likely persist long into the 21st century with no end in sight. I believe that with the emerging nanotechnology revolution upon us, we have to make professors more aware of, and receptive to, entrepreneurial opportunities for themselves and their students. To achieve this, it is necessary but not necessarily sufficient to focus entirely on the professors. We also need universities to change their incentive systems; we need granting agencies to increase funding for commercialization activities by students; we need to create innovation clusters of small and medium size companies anchored by large receptor firms; we need measures to increase the supply of venture capital to Canadian companies. In the process Canada can be recognized as a place able to take their great ideas to great innovations in one of the most exciting industrial revolutions of our time: nanotechnology. This is not just a Canadian problem it is a challenge facing all industrial nations!



Spin-of a nanotech spin-off: transferring an idea to innovation – graphic illustration courtesy Dr. Wendong Wang.

23. Evolutionary Nanochemistry



Evolutionary nanochemistry paradigm depicting tiers of increasing complexity of nanomaterials from atoms at the lowest level rising to nanomaterials to nanomaterials clusters to clusters of nanomaterials clusters to complex nanomatter at the highest level of the hierarchy.

organization of these elementary particles came atoms and through making and breaking chemical bonds between these atoms came molecules and their chemistry, and through dynamic self-assembly and evolutionary principles of these molecules involving genetic variation and natural selection came biology and life, complex matter comprising all living organisms, each variety of which learned through Darwinian betterment how to thrive and survive in their particular environmental setting.

Using biological design and a combinatorial library of molecules, Lehn went on to describe how an amalgamation of artificial selection through lock-and-key-based molecular recognition, self-organizing principles, and programmed chemical informatics, can be used to develop a sort of 'evolutionary chemistry' analogous in many ways to an evolutionary biology paradigm, where the possibilities for discovery in polymer, pharmaceutical, and medicinal chemistry can lead to a myriad of applications in polymer materials and medical technologies.

At the 2011 Lindau Nobel meeting, during the International Year of Chemistry, Jean-Marie Lehn, who received the 1987 Nobel Prize for Supramolecular Chemistry with Donald J. Cram and Charles J. Pedersen, posed at the commencement of his lecture the interesting question "how does matter become complex?"

In his presentation, Lehn sees chemistry as a bridge between the universe and its laws, and life and its rules. Beginning with the Big Bang and the birth of the universe came elementary particles and their physics, through self-

Lehn's lecture on the creation of complex matter through evolutionary chemistry got me thinking about whether an 'evolutionary nanochemistry' could be envisioned as a paradigm for making complex nanomatter, by hierarchical assembly of nanomaterial building blocks, and whether its properties would provide unique functionality that transcends that of its parts.

In Lehn's supramolecular chemistry the construction units are a library of molecules with endless compositions whose structures and properties are pre-determined by primary forces between the constituent atoms (i.e., covalent, ionic and coordination bonding) and secondary forces between the molecules themselves (i.e., hydrogen and non-covalent bonding), which through self-assembly create molecule-based clusters, polymers, and networks with increasing tiers of chemical complexity.

What about nanochemistry? Can this be an exemplar for thinking about complex nanomatter built from bricks-and-mortar where the bricks are nanoscale forms of metal, semiconductor or insulator materials with pre-determined sizes and shapes (crystals, wires, tubes or sheets) and the mortar is their surface (naked or capped), which through colloidal forces directs and assembles the bricks into aggregates traversing multiple length scales to create increasing degrees of nanomatter complexity at rising levels of the assembly.

In this model of generating nanomatter complexity, the key components of the colloidal growth process ideally make use of monodispersed charge and sterically stabilized nanometer scale building blocks, between which operate colloidal repulsive, attractive and compaction forces for stabilization and entropic forces, capillary interactions, electric and magnetic fields for assembly.

In this hierarchical-assembly scheme one visualizes tiers of increasing complexity of nanomaterials, beginning with the smallest atomic constituents of the nanomaterials to the form of the nanomaterials and the nature of their surfaces to the incorporation of the nanomaterials into nanomaterials clusters and ultimately to assimilation of these into clusters of nanomaterials clusters residing at the top tier in the ladder of complex nanomatter. The possibilities are endless for innovative research in what I perceive as a nanochemistry playground, a 'multidimensional periodic table of nanomaterials' based upon infinite variations and combinations of nanomaterials compositions, sizes, shapes and surfaces that form the substance of complex nanomatter.

There are so many extraordinarily impressive case histories in the recent literature that re-enforces this pattern of 'evolutionary nanochemistry' depicted in the graphical illustration of 'tiers of complexity of nanomaterials'. Some excellent examples of constructing a cornucopia of complex nanomatter forms from simple nanomaterial building blocks include the following:

 Self-assembly of nanocrystal mixed-ligand shell morphologies

- ✚ Galvanic etch driven nanocrystal porosity
- ✚ Kirkendall diffusion driven nanocrystal porosity
- ✚ Environment responsive anisotropic nanocrystal motion
- ✚ Multi-shell nanocrystals by successive ion-layer absorption reaction
- ✚ Nanorod tip selective growth of heteronanostructures
- ✚ Ion-exchange induced formation of barcode nanorods
- ✚ Ligand-exchange tunable charge-transport nanocrystal superlattices
- ✚ Oriented assembly of nanocrystal clusters and nanocrystal crystals
- ✚ Colloidal supercrystals from nanorod assembly
- ✚ Nanotetrapod networks and lattices
- ✚ Environment responsive assembly and disassembly of nanocrystals crystals
- ✚ Nanorod chain growth by step-growth polymerization
- ✚ Ultrathin nanowires that look, grow and behave like organic polymers
- ✚ Ultrathin nanoplatelet heteroepitaxy
- ✚ Unary and binary nanocrystal superlattice films
- ✚ DNA programmable assembly of nanocrystal clusters, crystals and films
- ✚ Magnetic cluster nanocrystal cluster photonic crystal
- ✚ Semiconductor nanocrystal opal
- ✚ Nanocrystal Bragg mirror

Evolutionary nanochemistry that captures nanomaterials assembly as well as disassembly principles embraces in an appealing form the creation of complex nanomatter from simple nanomaterial constituents and through judicious design and creative experimentation portends a profusion of nanotechnology application opportunities.

The dynamics of nanomaterials exemplified by dissociative-associative exchange of nanocrystal surface ligands and reversible construction-deconstruction of nanocrystal clusters in response to changes in their environment raises the possibility of a combinatoric nanochemistry optimization strategy. This approach uses a dynamic library of reversibly exchanging nanocrystals evolving to an adaptive nanochemistry through dynamical nanocrystal variation and selection, a 'Darwinian nanochemistry' for self-sorting and self-discovery of the best performing complex nanomatter for a targeted nanotechnology.

A 'problem' with taking nanochemistry to this high level of structural sophistication is the challenge of achieving the control and uniformity that biology makes good use of. For example sp^3 carbon reliably has four neighbors, not three or five, at the corners of a tetrahedron because of quantum mechanical rules. And all those biological macromolecules, whose wonderful asymmetry enables all sorts of lock and key interactions, cranked out from the same gene (before post-translational modification) are identical in primary structure. These atomic-level controls are used far up the hierarchical ladder in biology.

In this vein, the concept of valency in chemistry, that is the number of bonds an atom can form with the same or other atoms, is difficult to realize with nanomaterials assembly. Advances in the gallant pursuit of 'nanomaterials molecules' with pre-determined geometry are slowly being realized with spatially-controlled and surface-functionalized (hybridized) nanomaterials, where chemical 'patches' direct the assembly of the nanomaterials amongst themselves or with other molecules and nanomaterials. Another step forward involves the chemical-coupling of end-functionalized nanorods to form cis- and trans-linked nanorod configurations.

Another issue is that in biology and chemistry, new forms of complex matter have new functions. An example of this is the allosteric enzyme with two or more binding sites, where a binding event at one cooperatively influences the other. The central dogma of nanochemistry is that size, shape and surface matters, but it is not clear that building more complex nanomatter will lead to new properties and new functionality. To do this, one must understand how to put things together in a meaningful way so that cooperative functionality will be achieved. In this regards, the concept of the 'nanomatter enzyme' is perhaps something to think about, where tweaking one site of a cluster of nanomaterials clusters causes a cooperative effect at another site, such as lost or exchange of a capping ligand or building block or more dramatically induces the cluster assembly to reconstruct or deconstruct.

We have a long way to go to develop this structural richness and fidelity in nanochemistry before we even get to the problem of mimicking the central

dogma of biology. But we can start with building less than perfect hierarchical structures made of nanomaterials with properties and functionality that do not demand such a high degree of structural perfection and still get a long way towards reaching certain goals. Indeed that is what most practitioners of the field of nanochemistry currently do all the time.

The ability to exploit variations in the state and extent of aggregation, nature of the hierarchical architecture and degree of perfection of nanomaterials generates complex nanomatter portends cross-disciplinary potential to improve the performance of a myriad of advanced materials technologies that utilize passive and active electronic, optical, photonic, magnetic and mechanical components. The approach also provides opportunities for enabling radically new solutions for a sustainable future in energy, climate, environment and human health.

Now that's one Big Bang for your buck!

24. Tribute to Richard Barrer

Inspiration



When I reflect on a long, exhilarating and expanding career in materials chemistry and nanochemistry there are a number of scientists whose work has inspired and excited me at different stages of the evolution of my research and Richard Maling Barrer (1910-1996) features prominently amongst them. A New Zealander by birth with a long and illustrious career as Chemistry Professor at Imperial College University of London, he is regarded by many as the father of zeolite chemistry. His inventive contributions to this field are remarkable and the technological innovations that emerged from his many discoveries have brought true

benefit and well being to humankind.

The enormity of Barrer's fundamental research contributions to the field of zeolite science can be appreciated from the synopsis of his most notable works listed below:

- Zeolite adsorbents
- Zeolite membranes
- Zeolite catalysts
- Zeolite synthesis
- Zeolite templating
- Zeolite ion exchange
- Zeolite solid acid catalysts
- Zeolite shape selective catalysts

Basic research of this genre spawned many large scale technologies the most prominent of which are exemplified in the following:

- Zeolite applications driven by environmental concerns have reduced toxic waste and enabled energy conservation
- Zeolite conversion of crude oil to high octane fuels and feed-stocks for the chemical industry
- Zeolite enabled separation and purification of O₂ and N₂ from air as well as a host of other gas and liquid mixtures

- Zeolite enabled replacement of phosphate in detergents world-wide
- Zeolite alkylammonium templating expanded the structure-composition field from aluminum and silicon to include the periodic table of elements such as, phosphorus, the main group and transition metals
- Zeolite dealumination or retro-synthesis has provided a major source of commercial catalysts and hydrophobic sorbents
- Zeolite ZSM-5 natural gas to petroleum process provides ~30% of the fuel needs of Barrer's homeland New Zealand

It is a great honor to receive the Royal Society of Chemistry Richard Barrer award that recognizes meritorious recent pure or applied research in the field of porous inorganic materials. In my lecture on this special occasion I will present personal recollections of my groups explorations of the basic science associated with the development of a wide range of 'materials filled with holes', the compositions of which reach many corners of the periodic table, the dimensions of which traverse multiple length scales from nanometers to microns, the scale of molecules to the light scale, a 'panoscopic' vision of this class of solid. As part of this journey I will recollect the technological opportunities that became apparent along this scientific highway and how they led to the manufacture and commercialization of products the utility of which was founded on the special features of 'holey materials'.

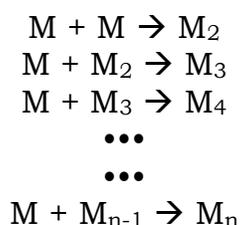
Where Did It Begin?

Let me reminisce briefly how I stumbled into this field as a newly arrived immigrant from the UK to Canada in 1969, in my first position as Assistant Professor in the Chemistry Department of the University of Toronto. As I sat in my empty laboratory space contemplating future research directions I remember being inspired by the 'Plenty of Room at the Bottom' speech of Richard Feynman in 1958 at Caltech and the idea of being able to reduce to practice atom-by-atom self-assembly of materials with nanoscale dimensions. The big question I was confronted with at the time as a synthetic chemist and that was unanswered, was how could one use chemistry to prepare nanoscale forms of well-known metals, semiconductors and insulators with physical dimensions in the quantum size regime of around 1-100 nm and study their purported size tunable behavior with an eye to utility .

Coincidentally around this time of pondering which way to go in my research the first experiments with 'naked' metal atoms were appearing in the literature and the one that caught my attention the most was that of Peter Timms at Bristol University who showed that by vaporizing Cr metal and depositing it with benzene at liquid nitrogen temperatures it was possible to synthesize in one step pure dibenzene chromium ($\eta^6\text{-C}_6\text{H}_6$)₂Cr , which normally took multiple steps and purifications using the Fischer-Hafner reductive Friedel-Crafts

organometallic synthesis involving the reaction of CrCl₃, Al and C₆H₆ in the presence of AlCl₃.

The idea of performing chemistry with ‘naked’ metal atoms under cryogenic conditions in this way opened my mind to the tantalizing possibility that one could control their nucleation and growth to well-defined metal nanoclusters by allowing them to self-assemble in low temperature solid matrices [1]. To control the embryonic stages of metal atom aggregation reactions required cryogenic temperatures of 10-20 K and these experiments were conducted by co-condensing metal atom vapors with the noble gases Ar, Kr or Xe. In this way metal atom nucleation and growth reactions of the following were observed to occur in noble gas solids, and their kinetics were monitored for the first time:



were observed to occur in noble gas solids and their kinetics monitored for the first time. Furthermore, in the presence of small molecules like L = CO, N₂, O₂, C₂H₄, C₂H₂ it was possible to observe never before seen organometallic compounds of the kind M_nL_m where n, m = 1, 2, 3, 4...[2]. One of my favorites in this context was an experimental and theoretical study of Ni_n(C₂H₄)_m with William Goddard and coworkers Tom Upton and William Power undertaken while I was working as a Fairchild Fellow at Caltech in 1977 that described for the first time ‘naked’ nickel atom and nickel cluster chemistry with ethylene including a localized bonding model for ethylene chemisorbed on bulk nickel [2].

What was significant about these 1970’s experiments was the unveiling of an unprecedented view of ligand-free and ligand-bound low nuclearity metal nanoclusters, the synthesis of which enabled the first explorations of the transition from molecular to quantum confined to bulk forms of metals, which provided a unique platform for investigating cluster-surface relations, [1,2].

Zeeing Zeolite

I expect the reader may now be wondering what all of this has got to do with the field of zeolite science. The connection emerged from my desire to take the insights gained from my work on metal atom cryochemistry and these classes of newfound nanomaterials out of the cold and into the real world of ambient temperatures where detailed studies of their structure, property, function, utility, and the relations between them could be undertaken [3]. In this context it occurred to me that because these low nuclearity M_n and M_nL_m

nanomaterials were inherently metastable with respect to further undesired agglomeration reactions leading towards thermodynamically stable bulk materials they had to be stabilized by some kind of surface protecting sheath and one way to accomplish this was to perform the nucleation and growth reactions within the voids of zeolites. This was the commencement of my early career relationship with zeolites as porous hosts for synthesizing and characterizing a variety of metal, semiconductor and insulator-based nanomaterials [3,4].

While this was a prolific and exciting phase of my materials chemistry and nanochemistry research there were aspects of the work that I found frustrating. One related to the scientific philosophy of the zeolite community whose conferences I would attend and discover to my dismay the narrow focus of their interests on the properties and applications of zeolites in catalysis, gas separation.



Being trained as a materials chemist I preferred to look at zeolites as solids filled with nanometer dimension voids and wondered how they could perform and compete in the advanced materials research space that was concerned more with their electrical, optical and magnetic properties and potential utility in areas such as electronic, optoelectronic, optical and photonic devices, information processing and storage media, photovoltaic, battery and fuel cells, photocatalysis, electrocatalysis and photoelectrochemistry, chemical sensors,

chemical and pharmaceutical storage and delivery systems.

I worked with Edith Flanigen and Robert Bedard at Union Carbide in Tarrytown New York for five years to reduce some of these new ideas to practice and our vision of the future direction of the field was expounded in a 1989 Advanced Materials paper in *Angewandte Chemie* written with co-authors Andreas Stein and Alex Kuperman entitled 'Advanced Zeolite Materials Science', [4]. Today this is a vibrant field of basic research with a global reach, which has led to many examples of new technologies and it is satisfying to see that zeolite journals and conferences now include sessions on advanced zeolite materials science as well as their staple diet of zeolite catalysis, gas separation and ion-exchange applications.

Around this time Edith Flanigen's Union Carbide team made the extraordinary discovery that microporous materials could be templated from many elements of the periodic table thereby greatly expanding the composition field of zeolites

way beyond that of aluminosilicates and silicas. I was fortunate enough to join their research and development effort that focused attention on advanced materials applications of microporous metal chalcogenides, working on the novel idea of semiconductors filled with nanometer holes; these can be viewed as anti-dot superlattices to be compared with superlattices of semiconductor dots and were investigated for use in molecular size and shape specific chemical sensing, providing an early proof-of-concept of a electronic nose [5].

Escape from the 10 Å Prison



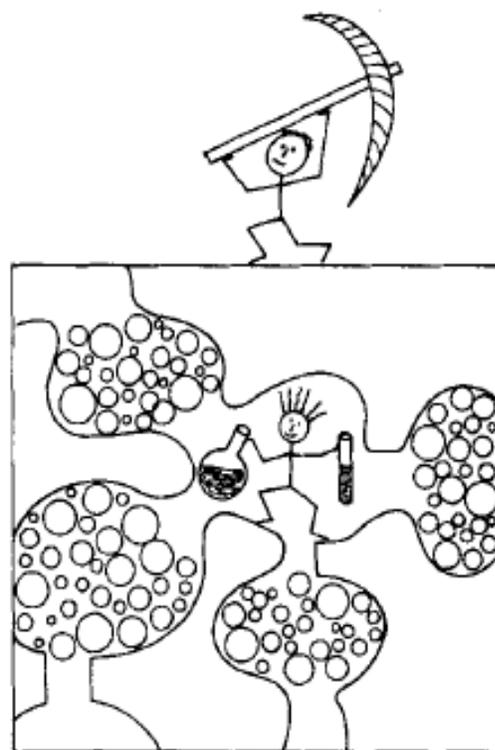
Another frustration of mine was related to what I called the 10 Å prison that zeolite hosts imposed on their imbibed guests, troublesome not only for large molecule researchers but also an impediment to my quest to nucleate, grow, and stabilize quantum confined nanomaterials that needed physical dimensions in the 1-100 nm range defined by quantum physics, which necessitated much larger voids than those offered by zeolites.

It was my collaboration with Charles Kresge at Mobil New Jersey whose team

discovered a way to synthesize silica materials containing periodic arrays of 2-100 nm diameter mesopores using supramolecular templating based on surfactant micelle assemblies that enabled my group to break free from the 1 nm prison of zeolites into this more spacious world of periodic mesoporous materials. The news of this new class of porous materials spread like wildfire around the world and the revolutionary effect of the Mobil breakthrough can be seen today in the >16,000 citations of their 1992 Nature and JACS papers that described their work and inspired a movement in mesochemistry; materials synthesis at intermediate length scales.

Birth of Nanochemistry

It was this phase of research that led me to a vision of a futuristic field that I dubbed 'Nanochemistry', which laid out the essence of a chemical approach to nanomaterials, published

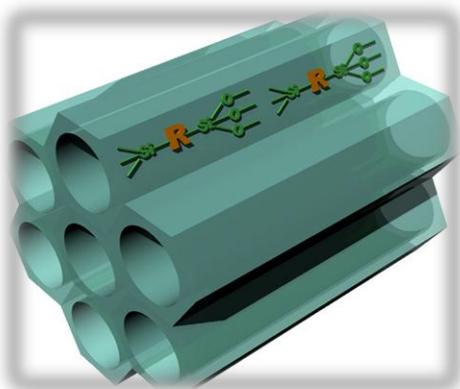


in *Advanced Materials* in 1992 and that set the scene for a new materials revolution that continues unabated today [6]. In this paper I envisioned the novel world of nanochemistry with its 0-D dots, 1-D wires, 2-D layers, and 3-D open frames, configurations that surprised, shape- and size-dependent behaviors that startled. Here were the conceptual foundations, the description of a bottom-up paradigm for synthesizing nanoscale materials with nanometer-level command over size, shape, surface and porosity, and their self-assembly. The potential I saw was breathtaking. It would be possible to produce materials perfect in size and shape down to the last atom from organic, inorganic and organometallic components, with structure-property relationships specifically designed to yield new materials characterized by an array of novel behaviors and these materials would have real-world applications. If one Google's 'nanochemistry' today one obtains more than 300,000 hits!

Micropores to Mesopores to Macropores

This work set the foundation for much of my group's research work on mesoporous and macroporous solids, a selection of which will be described in synopsis form below:

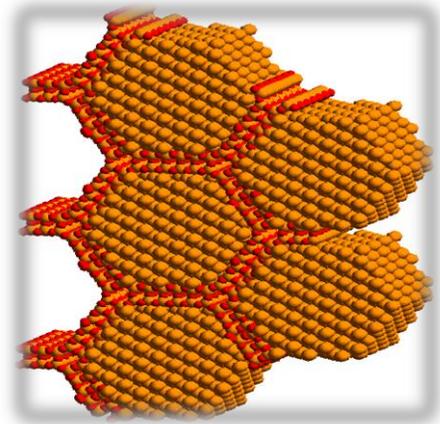
1. Biomimetic materials chemistry – transfer of Nature's best materials ideas into the advanced materials and nanomaterials chemistry laboratory – founded the field of morphosynthesis that focuses on growth and form of organic template co-assembled inorganic materials with “natural form” exemplified by faux diatoms and radiolarian, [7].



2. Hybrid nanomaterials chemistry –invention of a new class of organic-inorganic nanocomposite materials called periodic mesoporous organosilicas (PMOs), with bridge-bonded groups integrated into the pore walls including organic aliphatics and aromatics, dendrimers, fullerenes, and silicon-based polyhedral oligomeric silsesquioxanes and nanocrystals, delivering properties that transcend the sum of their inorganic and organic components, and currently finding widespread interest in

microelectronic packaging, chromatography stationary phases, catalysis, dental implants and drug delivery, [8].

3. Host-guest inclusion chemistry –synthesis of size-, shape- and surface-controlled quantum confined semiconductor and metallic nanomaterials nucleated, grown and stabilized within the spatial confines of nanoporous hosts, which inspired subsequent research on surface-stabilized colloidal nanocrystals, [9].

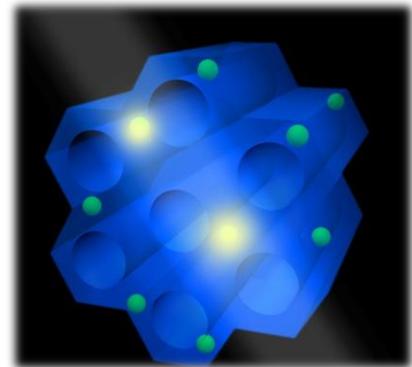


4. Mesoscopic materials chemistry – new insights

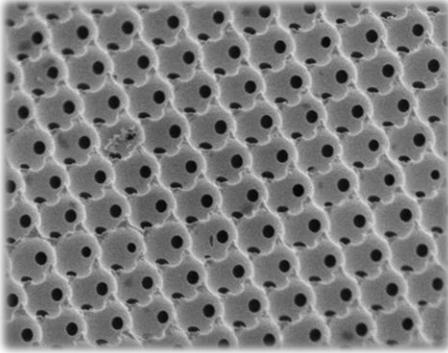
into the growth, form and mode of formation of a wide composition field of organic template-directed self-assembled materials with structural features between nanoscopic and macroscopic scales, with a range of curved morphologies exemplified by spheres, wires, rods, helices as well as surface templated films

and soft lithographic patterns, displaying diverse and unique materials properties that enabled many new nanotechnologies, [10].

5. Nanocrystal mesochemistry – discovery of periodic mesoporous hydridosilica, meso- $\text{HSiO}_{1.5}$ that theoretically should not exist because every $\text{HSiO}_{3/2}$ tetrahedral building block in the material is three-coordinate, namely an ‘impossible’ fully disrupted thermodynamically unstable open-framework silica-based material. The unexpected ‘metastability’ of meso- $\text{HSiO}_{1.5}$ originates from pore wall $\text{SiOH}\dots\text{HSi}$ hydrogen-bonding. Interestingly, the pore walls of this meso- $\text{HSiO}_{1.5}$ were found to undergo a thermally induced disproportionation to ncSi and SiO_2 without collapsing of the pores to form meso-ncSi- SiO_2 in which brightly photoluminescent ncSi was embedded within the SiO_2 pore walls, promising new opportunities in the development of optoelectronic and biomedical devices, [11].



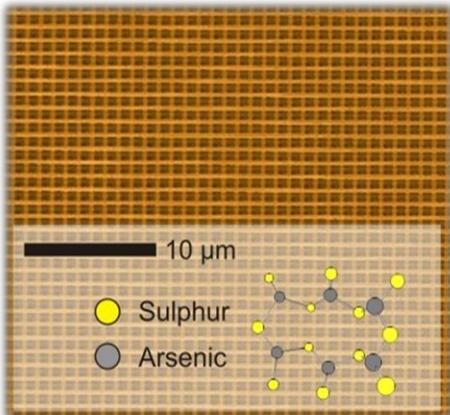
6. Photonic crystal materials – a bottom-up chemical approach to the world’s first 3D silicon photonic crystal with a complete photonic bandgap operating at optical telecom wavelengths – this research enabled the full gamut structural color and slow light amplified absorption and emission attributes of nanomaterials fashioned as 3D photonic crystals, some incorporating designer defects, to be usefully employed to enhance the performance of photovoltaics



and photocatalysts, and develop a new class of chemical and biological colour sensors, [12].

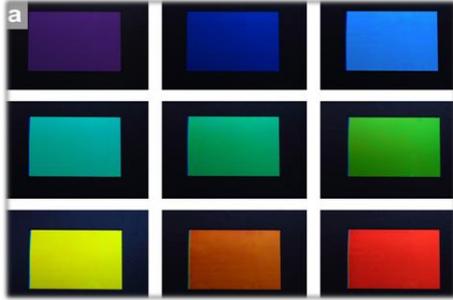
7. Smart Bragg mirrors - comprised of alternating composition multi-layers made from a wide range of nanomaterials comprised of main group and transition metal oxides, zeolites, mesoporous materials and clays, providing high porosity and surface area, ion-exchange and molecule size discriminating

properties to the constituent layers, enabled dynamic tunability of the structural colour reflected or transmitted by the Bragg mirrors through chemically and physically induced changes in the thicknesses and/or refractive indices of the constituent layers that led to the development of a new class of colourimetric sensors and antibacterials with controlled release and detection capabilities – with multi-layer constituents made from transparent and conducting metal oxides such as antimony and indium tin oxides, this new class of Bragg mirrors enabled the development improved performance organic light emitting diodes and a new genre of solid state dye and polymer lasers, [13].



8. Multiphoton direct laser written (DLW) silicon photonic crystals that have a full photonic bandgap around 1.5 microns – this top-down nanofabrication methodology involves a first inversion of a DLW polymer template in silica by atomic layer deposition (ALD) which enables a second inversion in silicon by disilane chemical vapor deposition (CVD), leading thereby to a silicon replica of the original polymer template - silicon photonic crystals created by this ‘double inversion’ method may enable the development of silicon-based all-

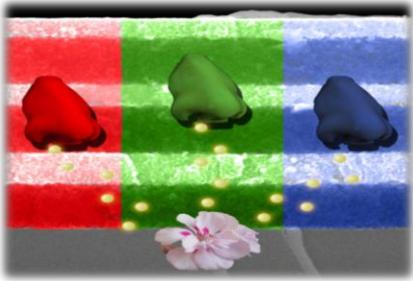
optical devices, circuits and chips with utility in optical telecommunication and computer systems – a creative extension of this work involved DLW in a high refractive index inorganic photoresist, exemplified by arsenic sesquisulphide, As_2S_3 , an advance which opens the door to a large variety of new photonic bandgap materials and architectures that can be made by DLW without inversion of a sacrificial polymer template, [14].



8. Photonic crystal technology – research on different kinds of photonic crystals led to the invention of actively tuned photonic color systems that include full colour displays, authentication devices for anti-counterfeiting, and colour sensors for food and water quality control and pathogen detection all being commercialized by a spin-off company that I co-founded in 2006, [12].

Seeing the Light

A hallmark of my group’s research over the years has been the creative exploitation of the properties of regular arrangements of pores in solids whose dimensions traverse length scales from nanometers to microns, which in the language of the International Union of Pure and Applied Chemistry, IUPAC, defines micro- to meso- to macroporous materials.



To expand a bit upon our research on periodic macroporous materials, which I aptly call light-scale materials, a focus of our recent work has been to exploit their ability to electrically, thermally, mechanically, and chemically tune colour from structure. This revolutionary concept forms the basis of photonic colour technology, a breakthrough currently finding significant application and impact in a range of devices. In

this context Opalux Inc. was founded to develop, manufacture, and commercialize photonic color technology, and has readied three unique manifestations of the technology for the market mentioned below.

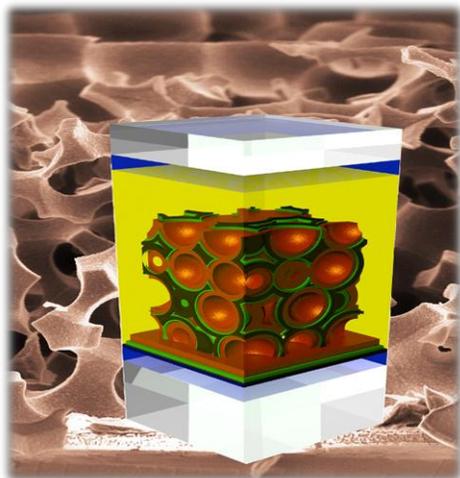
P-Ink is a flexible, electronic paper-like material offering a full spectrum of electrically-tunable, reflective colors - extremely power-efficient it is one of three competitive technologies vying to add color to black-and-white electronic book readers such as Kindle and Kobo.

P-Nose is an artificial nose comprised of a simple, cost-effective pixilated array of surface-functionalized nanoporous materials that enable discrimination of different analytes, such as molecules comprising the unique identifiers of different bacteria. Think of the possibilities for medical diagnostics, and food and water quality-control.

Elast-Ink is a touch-sensitive material that responds to mechanical pressure while offering exceptional resolution and customizability. It is poised to answer

global demand for effective authentication-technology – serving, for example, the pharmaceutical and banknote-printing industries.

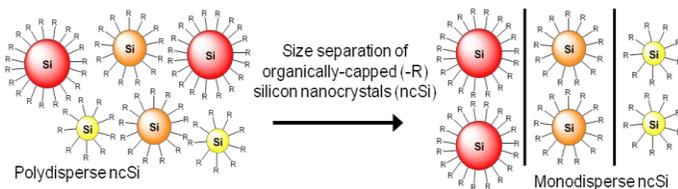
What Is Next?



This requires pores for thought, which I chose as the title of my lecture and after much deliberation I have decided to embark on a multidisciplinary collaborative program of research that focuses attention on expanding and enriching three recent nanochemistry breakthroughs with nanomaterials in our laboratory that provide a springboard for innovative fundamental nanomaterials research that crisscrosses the borders of nanoscience, nanoengineering and nanomedicine and which could ultimately lead to novel nanotechnologies:

1. Enhanced efficiency light harvesting solar cells – investigations of improved performance solar cells using photonic crystal, plasmonic and up-converting, advanced light trapping – clean, safe and cost-effective sustainable energy for the human race [15].

2. Artificial photosynthesis - carbon dioxide recycling to solar fuels such as methanol or methane – research into the science of solar fuel materials to enhance the efficiency of the transformation of carbon dioxide and water to methane and methanol using nanocrystal based photocatalytic solar converters – a brand new and natural solution to the greenhouse gas problem facing humankind – this work is the only magic bullet for simultaneously resolving, at globally significant scales, the interrelated energy, greenhouse gas and population problems that humanity faces today, [16].



3. Green nanochemistry – research designed to expand and enrich the basic chemistry and physics of our recently reported size-separated

quantum confined silicon nanocrystals, expressly to explore the materials science, engineering and medical aspects of implementing nontoxic, colloidally stable silicon nanocrystals in a range of nanodevices – these include full colour light-emitting diodes, printed high efficiency size separated silicon nanocrystal solar cells, and size separated silicon nanocrystal medical diagnostics and theranostics, a potentially revolutionary new approach to detect, visualize and target cancer without the fear of heavy metal cytotoxicity side effects that pervade commonly used heavy metal chalcogenide based nanomaterials, [17].

Pause for Thought

On a final note, none of my discoveries in the field of Nanochemistry and the sub-field of Nanoporous Materials would have been possible without the incredible support and encouragement from University of Toronto colleagues, coworkers, provincial and federal funding agencies, national and international collaborators, industrial partners and of course my wife and best friend, Linda Ozin. I am also deeply indebted to the RSC for recognizing my pioneering contributions to the field of porous materials with the Barrer award and I am most gratified by the benefits that my research has brought to humankind.

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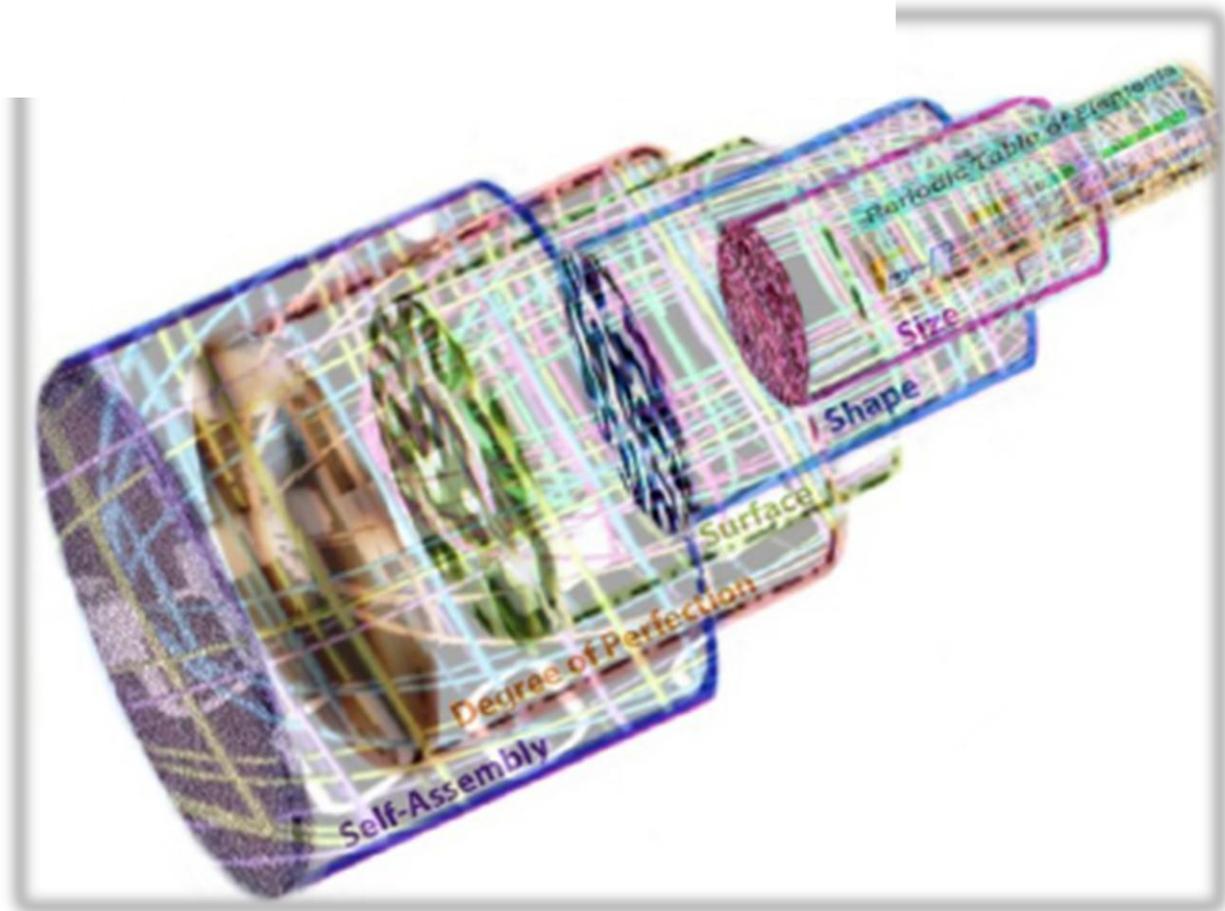
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25. Nanomaterials Kaleidoscope – Building a Nanochemistry Periodic Table



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Nanomaterials Kaleidoscope- Building a Nanochemistry Periodic Table

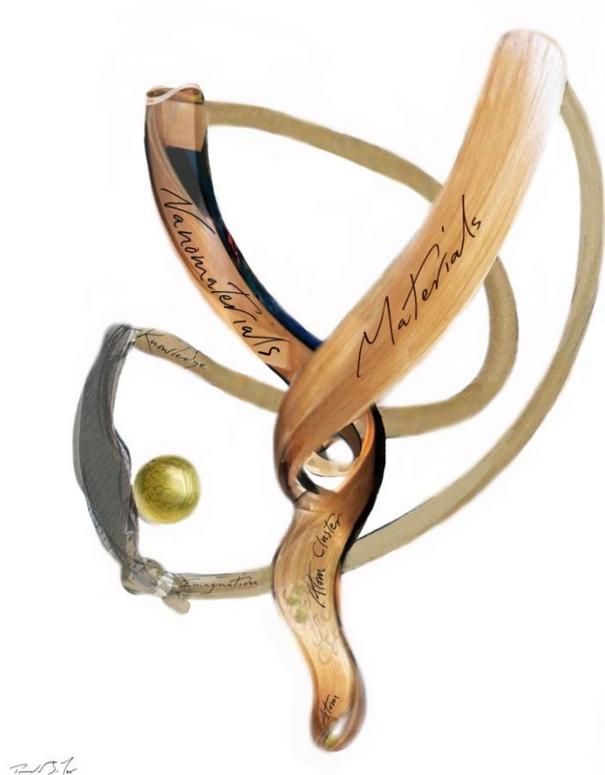


Figure 1 Thought-sketch of conceptual steps that interconnect atoms at the lowest tier to bulk forms of materials at the highest tier of a hierarchical assembly passing through intermediate levels of complexity comprised of atom clusters to quantum confined nanoscale materials – graphic illustration copyright Todd Siler ArtNano Innovations©

I have been cogitating about the idea of a nanomaterials kaleidoscope, a type of combinatorial strategy for the design and synthesis of complex nanomatter from nanomaterials building blocks, a vision of a DNA of nanochemistry, which essentially mirrors the reality but not the details of the information content, complexity, growth, development and natural beauty underpinning basic and applied genomic research.

My thinking about a nanomaterials kaleidoscope was inspired by work on the human genome project, which began in 1989 (<http://www.genome.gov/>) and the recent emergence of research on a materials genome project in 2011 (<http://www.whitehouse.gov/blog/2011/06/24/materials-genome-initiative-renaissance-american-manufacturing>) the former intended to create information databases to hasten the pace of discovery in biomedical research by mapping the human genome for the benefit of humanity and the latter to facilitate the more rapid transformation of innovative materials ideas into new products and processes in the marketplace.

Thinking about the biological world, a gene denotes a specific sequence of nucleotide bases in a strand of DNA that encode proteins and define function in an organism. The gene is the biomolecular carrier of heredity, the biochemical control system of life. In this context, it is worth mentioning that the DNA genome project was only possible after DNA was recognized as being the central molecule that leads to protein generation and cell/life function. It is a way of working back from molecularly complex to molecularly simple, call it 'simplicity'. In a similar vein, I envision the development of a nanomaterials genome, namely the inherited behavior of complex nanomatter from its constituent nanomaterials building blocks, has the potential to serve the nanoscience community with a similar opportunity to speed up the development continuum of nanomaterials through the steps of discovery, structure determination and property optimization, functionality elucidation,

system design and integration, certification, manufacturing to deployment of nanomaterials enabled technologies.

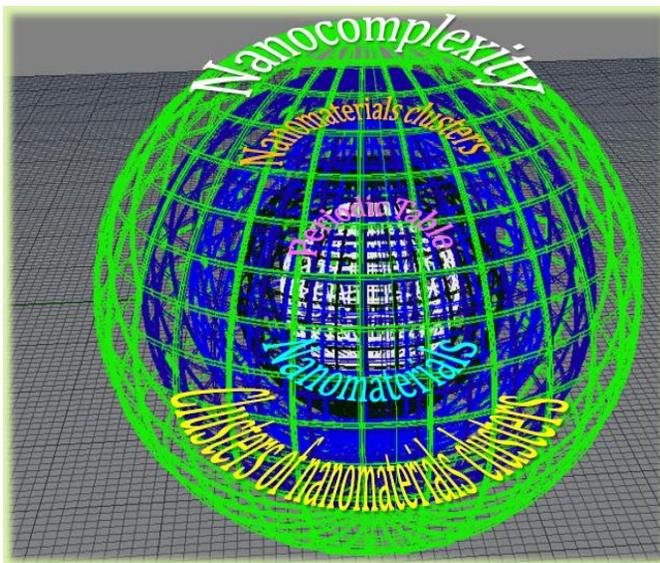
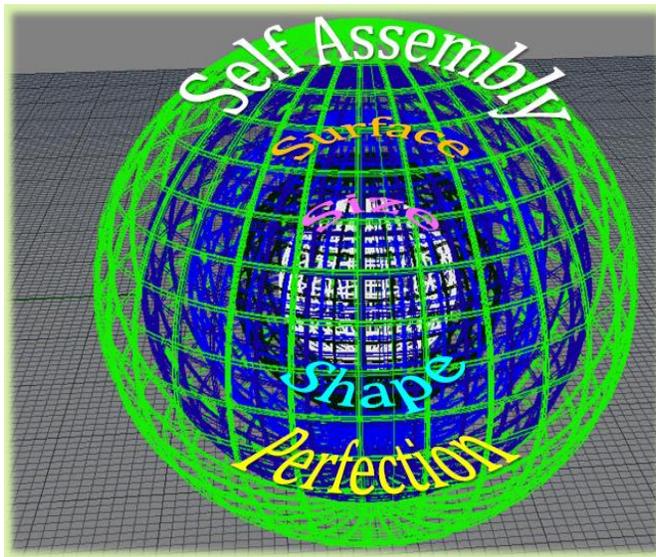


Figure 2 Nested sphere illustrations that portray the connection between the basic concepts of nanochemistry, size, shape, surface, perfection (top) and how nanocomplexity emerges from the hierarchical assembly of nanomaterials building blocks (bottom) leading at the topmost tier of the assembly to the far-reaching notion of a nanomaterials genome – graphic illustrations courtesy Dr. Wendong Wang.

By a nanomaterials kaleidoscope I imply the formation of complex nanomatter that evolves from the pre-programmed assembly of nanoscale pieces of inorganic matter that in their bulk form behave for example as metals, semiconductors or insulators and when reduced to the nanometer scale adopt distinctive properties that follow the scaling rules of quantum confinement.

My thinking begins with Mendeleev who organized the elements that were known in his time in the form of a two-dimensional periodic table that provided a palette of atomic building blocks for making materials. In this same vein I foresee a multidimensional periodic table of nanomaterials construction units organized in terms of composition, size, shape, surface and degree of perfection from which evolves complex nanomatter with information encoded in a genomic format.

In this perspective, I see the conceptual steps that interconnect materials to nanomaterials to atom clusters and atoms not just spiraling upwards and downwards implicit in the curious 'nexus' that appears in the middle of the general thought-sketch displayed in Figure 1 but pictured as intertwined by nature, like the two helical ladders that are integrated by the four nucleotides that make up DNA. In this picture, the analogue of the four basic construction units that encode information into DNA (adenine, guanine, cytosine, thymine, AGCT) are the building blocks of size,

shape, surface and perfection of nanomaterials, which through long range colloidal forces between building blocks are driven to assemble into multidimensional complex pre-programmed forms of nanomaterials clusters and clusters of nanomaterials clusters, with

embedded information rich in content, portending and enabling advanced materials and biomedical technologies. There is of course a problem with this picture related to the fact that the key of the genome and of chemical function displayed by proteins and living organisms is the fact that the morphology is encoded with information and this information is written, to an extent, in the morphology. What we are currently capable of doing with nanomaterials is to make periodic patterns in superlattice films and supercrystals made of nanomaterials, which only contain the structure and property information of the unit cell or amorphous assemblies of nanomaterials, which contain less usable information as it is not non-predictable and/or non-deterministic.

What do I mean by the information encoded in complex nanomatter? It is the chemical, and physical properties contained within and imprinted upon the surface of the nanomaterial building blocks that are integrated hierarchically, tier by tier, to higher and higher levels of complexity in an assembly to create new properties, new functions, new identities and new uses, which transcend those of the individual construction modules, Figure 2. The challenge of course is how to gain access to the 'information encoded in complex nanomatter' and how to utilize this information in a purposeful way to facilitate the long and arduous road from nanomaterials discovery to nanotechnology. This will necessitate adopting a 'reverse engineering' experimental approach complemented by a computational materials modeling strategy to elucidate how each particular choice and arrangement of constituent nanomaterials building blocks cooperate to provide the emergent properties, form, function and utility of a nanomaterials assembly.

The size (1-100 nm), shape (e.g., sphere, cube, octahedron, prism, tetrapod, rod, tube, sheet), surface (e.g., structure, charge, ligand) and degree of perfection (e.g., intrinsic variations in size, shape and surface, and intentional or unintentional presence of dopants, defects and impurities) of these modules carry embedded information on functionality, such as their optical, electrical, magnetic, mechanical and chemical behavior. It is the particular geometrical and spatial arrangement of these construction units driven by the forces of self-assembly that access increasing levels of nanomatter complexity, which we see through a 'nanomaterials kaleidoscope' and imagine as a 'nanomaterials gene' with materials character traits, inherited from its nanomaterials building-block code, an instruction blueprint that ultimately affords it with utility in advanced materials and biomedical technologies. Thinking about nanochemistry in this way, through a type of combinatorial nanochemistry, does add a number of variables to our nanomaterials design portfolio and those variables can be entangled in nontrivial ways to build a library of nanomaterials where changing each of the parameters allows one to be able to predict the output property. This is an important capability but the analogy with DNA is limited and should be treated with care. Information is useful when it is processed in a complex way through an algorithm which is what the DNA represents and we have a long way to go before we can do this with nanomaterials.

I wonder if a nanomaterials kaleidoscope can be an exemplar for thinking about complex nanomatter built from bricks-and-mortar where the bricks are nanoscale forms of metal, semiconductor or insulator materials with pre-determined sizes and shapes, and the mortar is afforded by their surfaces, which through colloidal interactions directs and

assembles the bricks into aggregates traversing multiple length scales to create increasing degrees of nanomatter complexity at rising levels of the assembly.

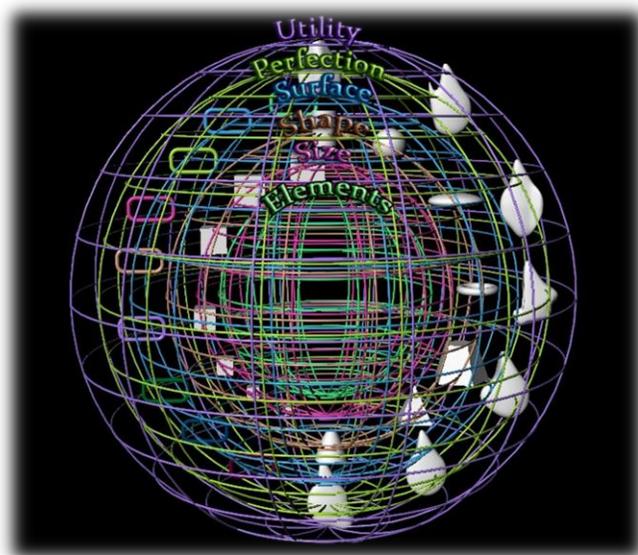


Figure 3 Graphical representation of a nested-sphere concept of a multi-dimensional periodic table of nanomaterials depicting some of the infinite number of possible combinations and permutations of nanomaterials elemental compositions, sizes, shapes, surfaces and degree of perfection arranged on the points where longitude and latitude lines cross on the exterior surface of different spherical shells starting from the inside shell and moving outwards - graphic illustrations courtesy Dr. Wendong Wang.

In this model of generating nanomatter complexity, the key components of the growth process make use of charge and sterically stabilized nanometer scale building blocks, between which operate colloidal repulsive, attractive and compaction forces for stabilization and entropic forces, capillary interactions, electric and magnetic fields for assembly into different forms of complex nanomatter.

The possibilities here are endless for innovative research in what we perceive as a nanochemistry playground, founded upon a periodic table of nanomaterials a tabulation based upon infinite variations and combinations of nanomaterials compositions, sizes, shapes, surfaces, perfection that form the ingredients of self-assembled complex nanomatter with functionality and utility programmed into the assembly by the information content endowed by its component building blocks.

What do I mean by a 'periodic table of nanomaterials'? While Mendeleev's periodic table is a two-dimensional planar arrangement that organizes the chemical elements according to increasing atomic numbers, electronic configurations and trends in chemical behavior, I imagine a 'periodic table of nanomaterials' to be a multidimensional organizational scheme. One way I visualize this scheme is in the format of nested spheres, where the grid points defined by the intersections of adjacent longitudinal and latitudinal lines on every shell, from the center-out, depict the infinite number of possibilities (i.e., encoded information content) that can be amassed through combinations and permutations of composition, size, shape, surface, perfection and self-assembly to provide complex nanomatter with functionality and utility, Figure 3.

To amplify upon this idea, let the innermost sphere represent the elements ordered by atomic weight at grid points with a format that maintains the familiar periodic table structure of blocks, rows and columns. This sphere-shaped periodic table of the elements is surrounded by a sphere that represents all possible nanomaterials size variations for different compositions. Running north to south on a particular longitudinal line one

tabulates at each grid point nanomaterials with monotonically diminishing size with a specific elemental composition. Each longitudinal line on this sphere depicts a nanomaterials element composition. The same model applies to the surrounding spheres which consecutively represent variations of nanomaterials shape, surface and perfection, thereby graphically depicting the infinite number of possible combinations of nanomaterials compositions, sizes, shapes, surfaces and perfection starting from the inside shell and moving outwards in the spherical nest, Figure 3.

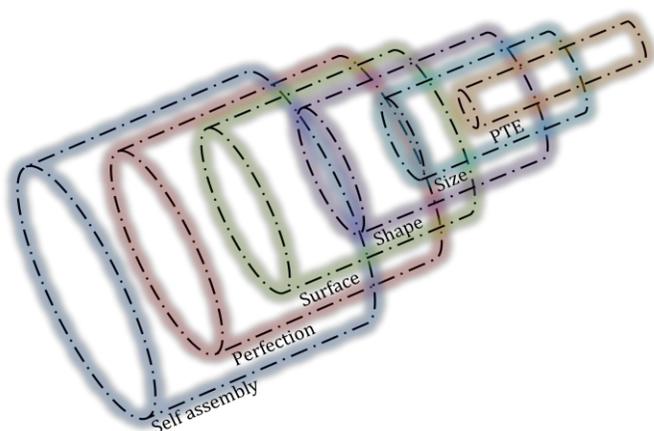


Figure 4 Telescope representation of a multi-dimensional periodic table of nanomaterials where each cylindrical component of the telescope, from smallest to largest, when rotated with respect to one another can depict a kaleidoscope of combinations of nanomaterials composition, size, shape, surface, degree of perfection and self-assembly and hence the infinite number of nanotechnology opportunities.

Taken together, these possibilities can be seen to embrace concepts of nanochemistry for the synthesis of nanomaterials and express the idea of nanocomplexity through hierarchical assembly of nanomaterials to nanomaterials clusters, clusters of nanomaterials clusters, ultimately to provide complex nanomatter and its application opportunities in advanced materials and biomedical technologies. Nested shells of exemplary nanomaterials sizes, shapes, surfaces and perfection are illustrated in Figure 3 to bring out the essence of the graphical rendering of nets of nanocomplexity.

Another way of representing this same concept is to deconstruct the nested spheres into their constituent smaller spherical forms, in order to more clearly reveal the interior architecture and design of each, inspired by the **Russian Matryoshka nested doll**. Perhaps the separated spherical shells are not necessarily identical in size, shape and surface but rather vary slightly to highlight the possibility that they may be subtly asymmetrical and irregular, meaning, they're not perfect in all aspects of the nano concepts and design principles rendered.

Yet another way to visualize a multidimensional periodic table of nanomaterials is in the form of a telescopic arrangement of concentric coaxial cylinders intended to provide a kaleidoscope of nanomaterials compositions, sizes, shapes and surfaces with varying degrees of perfection that can be hierarchically assembled into nanomaterials clusters and clusters of nanomaterials clusters at increasing tiers of nanocomplexity, as sketched in Figure 4. In the tradition of Sir David Brewster, the Scottish inventor of the kaleidoscope in 1817, named from the Ancient Greek (*kalos*: beautiful, *eidōs*: form, *skopeō*: to look) I would argue that this representation of a multidimensional periodic table of nanomaterials in the configuration of a 'nano kaleidoscope' makes it the 'observer of beautiful forms' through its multiple dimensions, its boundless shapes and its cornucopia of opportunities for

facilitating the transformation of creative ideas to innovative nanotechnologies.

Some examples of different kinds of complex nanomatter assembled from simple nanomaterial building blocks, that can be considered to take us closer to the recognition of nanocomplexity and a nanomaterials kaleidoscopic way of thinking, include the following:

-  Nanocrystal clusters and nanocrystal crystals
-  Nanorod supercrystals
-  Nanotetrapod networks and superlattices
-  Stimulus responsive assembly and disassembly of nanocrystal crystals
-  Step-growth polymerization of nanorod chains
-  Nanocrystal Langmuir Blodgett film
-  Binary nanocrystal superlattice films
-  DNA programmable assembly of nanocrystal clusters, crystals and films
-  Bio-hybrid crystals of nanoparticles and protein cages
-  Nanocrystal nanorods and nanocrystal opals
-  Nanocrystal electrochromic Bragg mirror
-  Nanocrystal metamaterials

Take the case of end-functionalized gold nanorod chains where the component gold nanorod building blocks in the chain are pretty monodisperse and regular in shape. Here I contend the encoded information is encapsulated in the nanorod size and shape, nanorod chain aggregation number and nanorod chain conformation, which can be either cis- or trans- because of the faceted structure of the tips of the nanorods. These gold nanorod chains therefore contain an immense package of encoded information manifest not just in their overall structure but also in their plasmonic properties. I think this example and the others referenced above in my list of complex nanomatter are similarly crammed with vast amounts of encoded information beyond just the collection of nanomaterials building blocks but together with the properties of the whole, a kind of self programmed complex nanomatter.

On a point of clarification, mapping the information content of the genetic code of biological organisms involves DNA sequencing of the chromosomes *via* a deconstruction analytical protocol. By contrast the nanomaterials kaleidoscope I have in mind is intended as a blueprint to guide the formation of complex nanomatter by design rather than chance. In

this framework, colloidal forces between nanoscale building blocks that are pre-programmed with size, shape and surface information, drive them into higher level architectures, such as nanocrystal chains, crystals, superlattices, photonic crystals and metamaterials as mentioned above. Here it is interesting to draw an analogy between DNA Origami and nanomaterials engineering, where I see the pre-programmed nucleotide sequences encoded in the linear strands of DNA and their sticky ends designed to enable the assembly of targeted complex DNA topologies, as mirroring the action of the size, shape and surface functional group information built into nanomaterials with respect to their ability to direct their assembly via a map of forces operating over multiple length scales into more complex forms of nanomatter.

A nanomaterials kaleidoscope that captures nanomaterials assembly principles and maps the information encoded in the above mentioned assemblies can serve to embrace in an appealing form the creation of complex nanomatter from simple nanomaterial constituents with property-function relations that portend a profusion of nanotechnology applications.

As a case in point consider how the dynamics of nanomaterials exemplified by dissociative-associative exchange of nanocrystal surface ligands and reversible construction-deconstruction of nanocrystal clusters in response to changes in their environment raises the possibility of a combinatoric nanochemistry optimization strategy. This approach uses a dynamic library of reversibly exchanging nanocrystals evolving to an adaptive nanochemistry through dynamical nanocrystal variation and selection, a 'Darwinian nanochemistry' for self-sorting and self-discovery of the best performing complex nanomatter for a targeted purpose.

In practice, a problem with taking nanochemistry to this high level of structural sophistication is the challenge of achieving the control and uniformity of which biology makes good use. For example sp^3 carbon reliably has four neighbors, not three or five, at the corners of a tetrahedron because of quantum mechanical rules. And all those biological macromolecules, whose wonderful asymmetry enables all sorts of lock and key interactions, cranked out from the same gene are identical in primary structure. These atomic-level controls are used far up the hierarchical ladder in biology. Can we ever mirror this level of sophistication through nanochemistry knowing a population of nanomaterials is usually a poly-dispersion, albeit with a narrow polydispersity index even after the application of size separation methods like size exclusion chromatography, density gradient ultracentrifugation or size selective precipitation?

In this same vein, the concept of valence in chemistry, that is the number of bonds an atom can form with the same or other atoms, is difficult to realize with nanomaterials assembly. Advances in the gallant pursuit of 'nanomaterials molecules' with pre-determined geometry are slowly being realized with spatially-controlled and surface-functionalized (i.e., hybridized) nanomaterials, where chemical 'patches' on the surface of the nanomaterials direct the assembly of the nanomaterials amongst themselves or with other molecules and nanomaterials. Actually the lack of deterministic valence can be considered both a problem and a blessing, as one can construct many more complex clusters based on nanoclusters with different exposed facets. For example, an icosahedral nanocluster would

have a valence of twenty, an octahedral nanocluster eight and a tetrahedral nanocluster just four although the material these clusters are made out of can be the same.

Another issue is that in biology and chemistry, new forms of complex matter often exhibit new functions. An example of this is the allosteric enzyme with two or more binding sites, where a binding event at one cooperatively influences the other. The central dogma of nanochemistry is that size, shape and surface matters, but it is not yet clear that building more complex nanomatter will lead to new properties and new functionality. To do this, one must understand how to put nanomaterial building blocks together in a meaningful way so that cooperative functionality will be achieved in the assembled nanomaterial. Here the concept of the 'nanomatter enzyme' is perhaps something to think about, where tweaking one site of a cluster of nanomaterials clusters causes a response at another site, such as loss or exchange of a capping ligand or building block or more dramatically induces the cluster assembly to reconstruct or deconstruct.

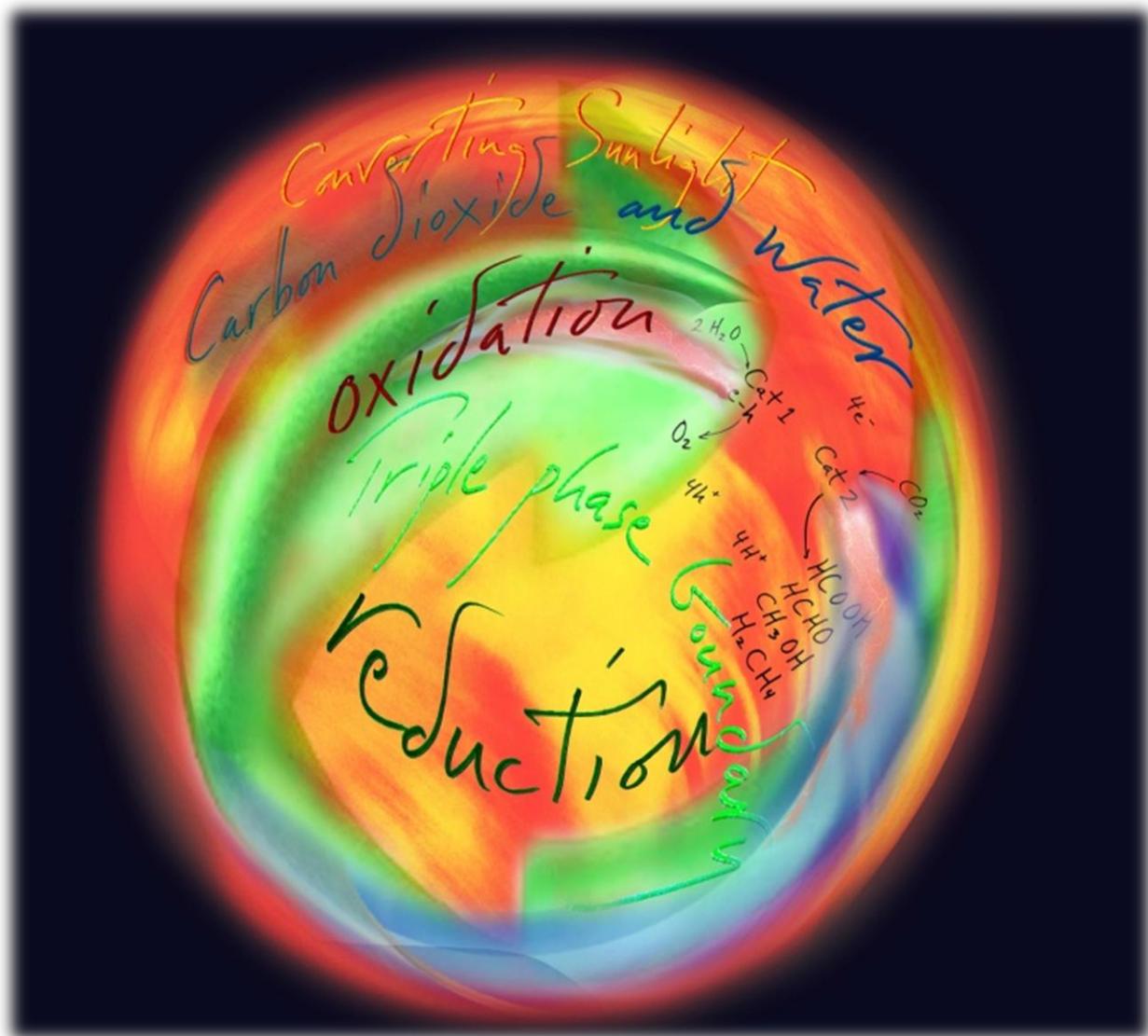
We have a long way to go to develop this structural richness and fidelity in nanochemistry before we even get close to the problem of mimicking the central dogma of biology and achieving the complexity and degree of perfection of the genes of living organisms. But we can start with building less than perfect hierarchical structures made of nanomaterials with properties and functionality that do not demand such a high degree of structural perfection and still get us a long way towards reaching certain goals. Indeed making such defect tolerant complex nanomatter is what most practitioners of the field of nanochemistry currently do all the time.

The ability to exploit variations in the nature and degree of perfection of a hierarchical architecture to generate complex nanomatter portends cross-disciplinary potential to improve the performance of a myriad of advanced materials technologies that utilize passive and active electronic, optical, photonic, magnetic, mechanical and chemical components. The approach also provides opportunities for enabling radically new solutions for a sustainable future in energy, climate, environment and human health.

There are so many extraordinarily impressive case histories in the recent literature that reinforces this nanochemistry paradigm of nanocomplexity, which strengthens our notion of a kaleidoscopic way of thinking about the rapidly emerging nanomaterials world. While still in a nascent state-of-development, we look forward with anticipation to nanochemistry research that targets a universal scheme for organizing the information content of nanomaterials into a multidimensional compartmentalized form that brings forth periodic trends of the chemical, physical and biological properties of nanomaterials and complex nanomatter made of nanomaterials assemblies. This scheme and these properties are imagined to be akin to Mendeleev's periodic table of the elements that provides a rationalization of elemental properties such as electronic configurations, atomic radii, ionization potentials, electron affinities, electronegativities and cohesive energies. Armed with a multidimensional tabulation of nanomaterials and their assemblies, the ideas presented herein of mapping the myriad forms of complex nanomatter could become a reality.

In closing it is worth noting the idea of "messages encoded in complex nanomatter" is akin to Jean Marie Lehn's "messages in supramolecular materials" - the challenge of any attempts to develop a genomic rather than a kaleidoscopic approach to nanochemistry as well as supramolecular chemistry is how to get access to that information and how to use it in a purposeful manner to achieve a useful objective. A reverse engineering approach of deconstructing complex nanomatter into its information (property) carrying nanomaterials building units is perhaps the best way forward to make the nanomaterials kaleidoscope project scientifically and technologically worthwhile.

26. Fuel from the Sun



Fuel from the Sun

Why Do We Care? Nature is the archetype chemist having synthesized everything 'under the sun'. Nowhere is this more apparent than in photosynthesis practiced by plants, algae and bacteria that convert sunlight, carbon dioxide and water into stored chemical energy and oxygen and maintains life on earth. Moreover, the chemical capacity of photosynthetic organisms to convert carbon dioxide to organic compounds is around 100 G Tons annually making it the 'largest chemical factory on earth'.

For a billion years since the emergence of oxygenic photosynthesis on earth the symbiotic cycle of carbon capture, carbon fixation and carbon utilization has remained in balance but in recent times with population growth and increasing demands for food, clean water, air and energy the concentration of carbon dioxide in the troposphere from the combustion of fossil fuels is gradually increasing by about 2 ppm annually, has attained record highs and is continuing to increase. As global consumption increases especially in the developing world, carbon dioxide emissions are expected to keep on rising to levels that potentially threaten life on earth.

Whether one is a believer or a disbeliever in the greenhouse gas effect, a controversial and divisive issue scientifically, socially, economically and politically, decisive preventative action needs to be taken now in order to stabilize the concentration of carbon dioxide in earth's atmosphere to minimize the risks of the doomsday scenario resulting from global warming, ice-cap and glacier melting and ocean acidification.

In the words of Nobel Laureate Jahn Marie Lehn, "if it exists it can be synthesized" implying the ability of chemists to make materials that mimic the redox chemistry of photosystem II and photosystem I in photosynthetic plants, algae and bacteria to produce fuel from the sun, carbon dioxide and water is within our grasp.



Nanosolution - Clean Fuel from the Sun -Todd Siler and Geoffrey Ozin - ArtNanoInnovations©

Imagine life in a 'clean house gas rather than a green house gas world'.

If this utopian vision of solar fuels from carbon dioxide capture and recycling could be reduced to practice to make greenhouse gas an enabling chemical resource rather than a waste stream and if the process could be conducted at a technologically significant efficiency, at a globally relevant scale and at a cost competitive with fossil fuels, then the development of a sustainable future for following generations becomes an attainable goal.

Solar Fuels Materials Dilemma The challenge in designing and making materials that can transform carbon dioxide, water and sunlight to an energy rich fuel akin to Nature's photosynthesis, is the one often faced by scientists and engineers working in the field of advanced materials technology, namely one of providing processes and devices that either perform at high efficiency but utilize critical materials that are in short supply and too pricey or rather work at low efficiency but use materials that are earth abundant and accessible at a competitive cost. So the difficult choice one has to make in today's solar fuels research is whether or not to focus ones efforts on reducing the cost of a high efficiency process based on rare expensive materials or improving a low efficiency process founded on common cheap materials.

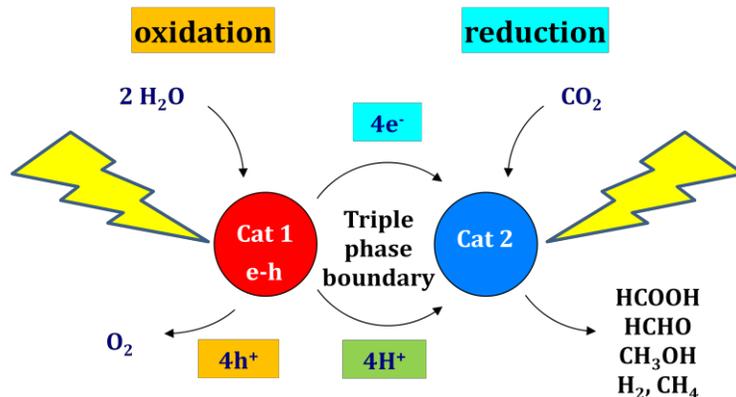
An added requirement for a viable artificial photosynthesis process, which is able to handle the rising concentration of greenhouse gas in the troposphere at a level that can rival natural photosynthesis, necessitates searching for a material that can transform carbon dioxide, water and sunlight to an energy rich fuel with economy of scale and cost of manufacturing. From a practicality standpoint this will likely favor a gas phase light driven heterogeneous process rather than a photoelectrochemical process in aqueous solution with control over pH and ionic strength and an applied voltage bias to overcome the extra potential required to drive an energetically uphill solar fuel reaction.

Hence one is forced to direct research efforts on a gas phase photoprocess using what tantamount to be 'zero cost' photoactive materials with elemental compositions in abundance, exemplified by metal oxides, carbon and silicon. These will require shrewd size, shape and surface materials engineering, judicious incorporation of additives and control of defects, and thoughtful design of the way these materials are integrated to an architecture that optimizes the optical, electrical and chemical requirements of the system.

All of these considerations are important to avoid future production issues associated with materials scarcity and economy of scale, commonplace requirements for the successful operation of large volume production chemical manufacturing industries.

Can we Match Nature? Establishing photosynthetic efficiency of plants, algae and bacteria for converting sunlight, carbon dioxide and water to chemical energy is a complex issue that depends on the type of organism and environmental conditions and whether the efficiency is averaged over an annual cycle estimated at 1-3% or growing season at 3-7% (Science, 2011, 332, 805-811). These natural photosynthesis efficiencies are to be compared with the best laboratory mimics researched over the past thirty years which currently are roughly three orders of magnitude less.

The challenge therefore is to discover materials that are able to more efficiently harvest and utilize sunlight, and catalyze the photo-oxidation of water and photo-reduction of carbon dioxide to energy rich fuels such as methane or methanol, illustrated in the scheme. The goal is to synthesize photoactive materials able to chemically couple these light driven redox reactions together and achieve conversion rates and efficiencies of carbon dioxide and water into energy rich fuels at a level that begins to match nature's photosynthesis.



About 85% of the world's energy supply is transported in the form of gaseous and liquid, carbon containing fuels!

Why Has Progress Been So Slow? While water oxidation and carbon dioxide reactions that generate solar fuels look simple on paper in practice they are exceptionally demanding to implement in practice as they involve thermodynamically uphill, multi-electron, multi-hole and multi-proton processes occurring on a multi-component photo-catalyst as envisioned in the scheme. The photo-catalysts needed to facilitate these processes, besides having to be made of earth abundant, non-toxic, light-stable, scalable and low cost materials also have to satisfy additional requirements that include, high surface area and porosity to maximize the adsorption, transport and desorption of reactants, intermediates and products as well as strong visible light absorption to enable the efficient generation, transport and utilization of electrons, holes and protons at water oxidation and carbon dioxide reduction centers.

In the context of light absorption, a number of optical techniques are potentially useful for boosting the effectiveness by which light is harvested in the photo-active material including *structuring*: (i) to increase the effective optical path length by multiple light scattering or photonic crystal slow photon amplification; *surface plasmon resonance* (ii) to enhance local electric fields and optical absorption strength; *up-conversion* (iii) to transform non-absorbed infrared to absorbed visible light; ; *multiple carrier generation* (iv) to achieve quantum yields greater than 100%.

One paradigm in the field of solar fuels is that a single nanostructured material can provide electronic band energies and band gaps that under solar insolation facilitate both water oxidation and carbon dioxide reduction. Another is that these requirements are best achieved in a multi-component heteronanostructure in which electronic band energies and gaps of the constituent materials are matched to the solar spectrum and oxidation and reduction potentials for water and carbon dioxide. The interface between the components

of the hetero-nanostructure ideally should be lattice matched in order to optimize the photo-generation and separation of electron-hole pairs and be competitive with their recombination. In addition their electrical conductivity and diffusion length should be as high as possible to minimize recombination of these electrons and holes and facilitate their transport to surface reaction sites to do productive chemistry.

Equally important is that co-generated protons from water need to be able to rapidly diffuse from the surface of the oxidizing component of the hetero-nanostructure to the reducing one and react with carbon dioxide and electrons to form the carbon-hydrogen bonds of the organic product. This may need the assistance of an organic or inorganic or organic-inorganic hybrid proton conducting membrane to assist simultaneous proton and electron transport between the oxidizing and reducing components.

Additional considerations involve complications arising from carbon residues formed on the surface of the hetero-nanostructures during their synthesis originating from organics in precursors, ligands and solvents. Adventitious carbon on the surface of the hetero-nanostructure could be hydrophobic and would have the effect of reducing the adsorption of water and carbon dioxide and the absorption of light thereby reducing the efficiency of producing solar fuels.

Other difficulties concern competing photo-oxidation reactions of methane or methanol by co-generated oxygen and formation of hydrogen from recombination of photogenerated protons and electrons from the photo-oxidation of water, both of which can reduce the efficiency of converting carbon dioxide and water to solar fuels.

If a photosynthetic mimic is to really produce solar fuels on a globally significant scale it will have to efficiently and economically capture and cleanup carbon dioxide from thin air and in a chemically and optically engineered gas phase photocatalytic process convert it and water into methane or methanol and separate these organic products from co-generated oxygen, at a cost that is competitive with their production from fossil fuels.

What Have We Learnt? In all studies reported to date, conversion rates and efficiencies are about three orders of magnitude too low to be of practical significance and the challenge has been to try to understand the reasons for the poor performance and to find materials, chemical and optical engineering remedies for its improvement.

A major impediment in earlier work has been finding reliable means to sort out fact from fiction in the production of solar fuels. The literature since the beginning of the field has been replete with reports that as-synthesized and post-treated materials produce organics at significant rates but only very recently have $^{13}\text{CO}_2$ isotope tracer methods been employed to decide unequivocally whether they originate from carbon dioxide or carbon residues on the surface of the photo-catalysts or both. After much study the consensus is that one of the best ways to reduce adventitious carbon to manageable levels is through ultraviolet light post-treatment of photo-catalysts in humid air or in pH and ionic strength controlled aqueous solution.

Designing and making well-defined nanostructures with all the necessary features mentioned above, to reduce to practice an efficient solar fuels photocatalyst, has proven to be much more challenging than originally anticipated by research scientists and initially expected by government, industrial and private sponsors of this research.

At this point in time a number of key questions still remain to be answered to realize the dream of fuel from the sun at a technologically significant rate and efficiency. These include: (i) how to choose a solar fuels nanomaterial, (ii) how to integrate them into a higher level architecture, (iii) how to harvest and amplify sunlight to generate, separate and transport multiple electrons, holes and protons and (iv) how to utilize these photo-generated charge carriers to oxidize water and reduce carbon dioxide to store solar energy in the form of energy rich chemical bonds, at a rate and efficiency that matches photosynthesis.

The 'super-leaf' challenge is x1000!

Steps Toward, a Sustainable Future

Approximately 75% of the current 48 Gt CO₂ equivalents per year of anthropogenic emissions of greenhouse gases are due to combustion of fossil fuels and until these emissions are reduced to zero, human interference with the climate and its associated social, economic and political uncertainties will continue.

Solar fuels research aimed at the sunlight powered conversion of carbon dioxide and water vapor to methane holds out the promise of large-scale electrical generation fueled entirely by the energy of the sun. One could envision a photo-reactor system would be employed as a 'bolt on' technology used in conjunction with existing, well-established energy systems and combustion technologies, minimizing the capital and infrastructure cost of effecting the transition to sun-powered electricity. The result would be to wean electrical generation off fossil fuels and to reduce to zero the CO₂ emissions of existing gas-fired electrical generating plants – an enormous step toward creating a sustainable energy future.

Alternatively, the photo-reactor system might be configured to generate methanol – a clean-burning liquid fuel that can readily be stored and transported. This methanol could be used in a wide variety of applications ranging from the very large (e.g. production of



Recreating Nature Inventing a Sustainable Future:
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industrial chemicals) to the very small (e.g. power generation in homes and businesses). It could also be used in internal combustion engines with minimal modifications to energy infrastructure and engine design, enormously reducing reliance on fossil fuels and reducing the contribution of vehicles to global CO₂ emissions.

What is needed now are rudimentary materials, chemical and optical engineering analyses of various options imagined for these kinds of solar fuels technologies in order to gain a preliminary understanding of the scientific, technical, economic, and commercialization challenges that different approaches to carbon capture and solar recycling will inevitably face with respect to competing renewable and non-renewable energy sources.

While the 'super-leaf' concept is elegant in its simplicity and powerful in terms of its promises for a sustainable future, it will only transition from laboratory curiosity to technological reality if the materials and engineering costs are understood and proven to be competitive with alternative approaches for making methane and methanol.

27. Climate Conundrum

Why Worry? Being British by birth I was brought up in a climate where the main topic of conversation was the weather and so I became acclimatized to it raining most of the time. Now a naturalized Canadian, I have learned to live with and enjoy the extremes of hot and cold weather. As a scientist working in the field of artificial photosynthesis, where worrying about the effect of carbon dioxide on the weather usually motivates funding, I am becoming increasingly concerned and frustrated about the dissent that currently permeates the debate on the evidence for anthropogenic causes of weather change, even amongst climate scientists. This uncertainty is exacerbated by self-interest lobby groups, the press and media who benefit from climate confusion. The difficulty of unequivocally separating fact from fiction is disquieting for scientists who are incessantly searching for support from funding bodies, peer reviewers, media outlets and the public to further their thesis that artificial photosynthesis could provide a long-term solution to the intertwined climate change and sustainable energy problems facing society today. Climate confusion is also a conundrum for government, industry, institutional investors who are contemplating support of artificial photosynthesis research and anyone interested in following scientific advances. Suffice to state, the only 'truth' we know fairly certainly is that there is 'evidence' of anthropogenic climate change and due to the nature of the problem and the nature of science this 'evidence' will always remain what it is, 'evidence not certainty'.

Why Do We Care? The climate change debate continues to generate discussion amongst scientists, economists, sociologists, legal scholars and policy makers attempting to analyze the risks and costs posed by over-reacting or under-reacting to the potentially serious and adverse consequences that could flow from a scenario of increasing global warming from escalating greenhouse gas emissions. Scientists can estimate the risk associated with not doing anything as well as doing something and with this knowledge, political, social and economical decisions can be formulated and implemented.

With all this uncertainty, one thing is indisputable to chemists, materials scientists and engineers working on different forms of renewable energy, such as solar cells, wind mills and tidal mills that produce electricity. They all suffer from the intermittency and variability of solar irradiance, air stream and tidal power as well as the difficulty of storing large amounts of electricity, as it has to be used essentially as it is produced. Hence there exists an urgent need to find a green way of producing energy in a form that can be transported and stored for use on demand. A long-term solution to this important problem is to discover materials and processes that can make fuel from sunlight akin to the way the leaf utilizes sunlight to transform carbon dioxide and water to carbohydrates in a process called photosynthesis.

In this context, solar fuels research is aimed at harnessing solar energy *via* the paradigm of artificial photosynthesis to make an energy rich portable fuel. It is inspired by the belief

that the long term use of fossil fuels is not sustainable and not practical and the rush to develop bio-fuels is short-sighted as evidence grows that its production, by any means, has a poor energy balance and does not lead to any appreciable reduction of carbon dioxide emissions that could be better achieved by modest energy conservation. Moreover, with a population increase of about 75 million per year, bio-fuels are considered a regrettable misuse of land and water resources sorely needed to maintain the earth's growing population.

There is also a debate whether carbon capture and storage (CCS) should be implemented to achieve climate change targets. Arguments against CCS is that it is a largely untested technology with health and safety concerns, it is energy intensive to apply and it will raise the cost of electricity, so much so that a renewable energy infrastructure could be developed quicker and cheaper.

The longer term investment in artificial photosynthesis research and development, rather than the shorter term focus on bio-fuels and carbon capture and storage, presents a more practical and appealing solution to the intertwined climate change and sustainable energy challenges faced by our society today. Whilst the scientific and technical hurdles of artificial photosynthesis are in the process of being understood and surmounted, through strong and sustained solar fuels basic directed research over the next 10-20 years, a global artificial photosynthesis strategic plan, akin to the human genome project of the 1990's, can be formulated and implemented to provide a lower cost and more sustainable green fuel, offering genuine rather than misplaced benefits promised by bio-fuels and carbon capture and storage.

Artificial Photosynthesis Goes Global

Artificial photosynthesis has gone global. The objective is to discover innovative uses for greenhouse gas emissions, namely turning a waste product into fuels or value-added chemicals. In the context of artificial photosynthesis, the top twelve performing solar fuels nations can be identified in the histogram of publications (Figure 1) since the inception of the field around three decades ago

(<http://statnano.com/index.php?ctrl=index&lang=2>). In the last decade there has been an explosive increase in artificial photosynthesis research, which coincides with global concerns over anthropogenic climate change. Governments in the United States, Europe and Asia have realized the social, political, economic and strategic ramifications of a breakthrough in artificial photosynthesis and have

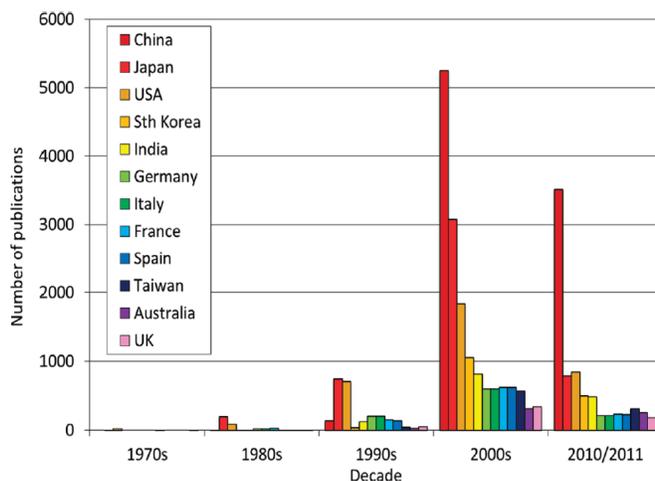


Figure 1: Top 12 solar fuels nations, ISI 2012.

invested hundreds of millions of dollars in basic research to discover if materials and processes can be found that match or exceed the efficiency of nature's photosynthesis in the laboratory.

Inspired by the words of Thomas Founce, *Energy & Environmental Science*, 2013, 6, 695, there are a number of ways to rationalize a global initiative in artificial photosynthesis, even as the climate change debate intensifies:

- (i) *Biological photosynthesis is complex and its understanding requires cross-disciplinary expertise and collaboration between teams of scientists*
- (ii) *Discovering materials that can mimic photosynthesis is a grand challenge.*
- (iii) *Increasing the public visibility of fuel from the sun by artificial photosynthesis would encourage government, industry and institutional stakeholders to invest in the rapid deployment of solar fuels technology.*
- (iv) *Artificial photosynthesis research and development should be allowed to grow naturally and rationally and not motivated by a crisis that destabilizes societies.*

Unfortunately the low cost of and easy access to fossil fuels have meant that funding for artificial photosynthesis has remained small compared to carbon capture and storage technologies. Nevertheless, activity in the field of artificial photosynthesis is exponentially increasing and new materials ideas, innovative photocatalytic reactors, techno-economic analyses for scaling materials and processes and manufacturing solar fuels, are appearing daily in the literature.

By coordinating the research efforts and knowhow of scientists around the world, progress will accelerate towards the practical realization of fuel from the sun, providing thereby a secure and long-term solution to a carbon neutral secure energy supply, to ensure the health and well being of future generations.

x1000 – The discovery of the sunlight powered photocatalytic reaction: $\text{CO}_2 + \text{H}_2\text{O} + h\nu \rightarrow \text{CH}_4$ or CH_3OH ignited the idea that anthropogenic greenhouse gas could be recycled from a waste product to a value-added fuel or chemical feedstock. This breakthrough inspired scientists around the world to search for materials and processes that could match or exceed natural photosynthesis. Three decades later, after exploring essentially every corner of structure- composition space in the periodic table of the elements, the rates and efficiencies of gas and aqueous phase $\text{CO}_2 + \text{H}_2\text{O} + h\nu \rightarrow \text{CH}_4$ or CH_3OH photocatalysis have improved very little over the initial report and researchers in the field of artificial photosynthesis continue to scramble for the magic bullet material that will provide the x1000 enhancement to make the process techno-economically competitive with alternative sources of methane or methanol.

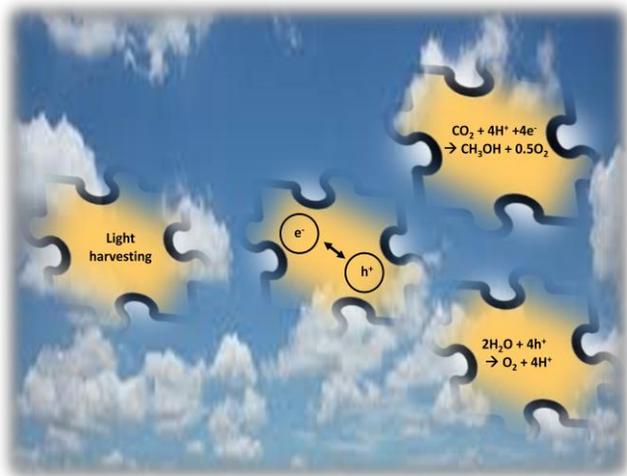


Figure 2 Assembling the right pieces of the solar fuels materials puzzle to find x1000 efficiency gains

So what is the origin of the x1000 problem? It is a kinetics conundrum where the challenge is to discover chemistry approaches to reduce the rate of recombination of photo-generated electron-hole pairs in the picosecond to nanosecond range to the millisecond to second time regime so that the much slower chemically and electronically coupled water oxidation and carbon dioxide reduction reactions with the electrons and holes and protons can compete. It is a matter of selectivity, namely how to tailor materials to gain control over the ratio of the rate of productive e-h reaction chemistry to unproductive e-h recombination, which

currently stands at around x1000. This concept, simple in theory, is proving to be exceptionally difficult to implement in practice.

Assembling the right pieces of the puzzle in order to prolong the lifetime of photo-generated electron-hole pairs in photocatalysts, illustrated in **Figure 2**, are well documented and include structuring and doping of materials at the nanoscale, junctions between semiconductors and liquids, semiconductors and metals, semiconductors and semiconductors, co-catalysts, blocking layers, hole scavengers, redox-shuttles, electron transport cascades, conducting substrates, and bias potentials.

Thirty four years since the pioneering 1974 artificial photosynthesis work of Honda and co-workers, researchers in the field of solar fuels are still searching for at least three-orders of magnitude enhancement in the conversion rate and efficiency, to endow it with the technological significance and commercial potential it promises. If this was an easy task it would have been done by now. In some ways the long arduous adventure to discover a solar fuels material that can compete and beat nature's leaf reminds me of Michael Gratzel's 1991 landmark discovery of the dye sensitized solar cell with a reported efficiency 9% and the following twenty two years it took to achieve 15% making it a low-cost contender for the silicon Samurai!

CO₂ Industry Road Map

Experts in the chemical industry have recently evaluated the science and technology time line for the cost-effective transformation of renewable energy to chemical energy in the form of organic molecules that can be easily stored, transported and integrated as a raw material and source of power and fuel into the chemical production food chain.

Because the chemical industry is one of the largest consumers of energy from fossil fuels, it is in their self-interest to learn how to manage carbon dioxide as a chemical resource rather than a waste product and strive to develop a carbon dioxide based resource-efficient

economy for powering their industrial processes and providing green fuels and energy for a sustainable society. The energy intensive chemical industry sees the introduction of carbon dioxide into the petrochemical value chain as a source of raw materials, power and fuels, using known catalytic processes working towards a viable and cost-competitive solar fuels technology.

By inspecting the timeline that the chemical industry proposes, to increase the use of renewable energy, one can see the short term perspective (2020) involves the utilization of excess electricity from wind and solar for electrolyzing water to hydrogen, which can be used in known industrial catalytic processes to reduce carbon dioxide to chemical vectors such as syngas, methanol, formic acid, alkanes, olefins and dimethylether. For these processes to be cost effective the price of electricity has to be around \$0.05/kWh.

The medium term view of the chemical industry (2030) is that hydrogen production technology from the photo-electrochemical splitting of water, will improve in efficiency and cost competitiveness compared to other sources of hydrogen and will be used to catalyze the reduction of carbon dioxide to organics providing the over-potential problem can be overcome. This technology becomes interesting from a commercial standpoint when the cost of producing hydrogen falls in the range \$2-3/kg.

In the long term view of the chemical industry (2030-) it is highly likely that materials for an artificial leaf technology will eventually be developed which are able to efficiently capture and convert carbon dioxide, water and sunlight directly to specific chemicals and fuels in a distributed production system. Industry experts acknowledge huge challenges have to be overcome with regards to the discovery of photocatalysts that can mimic and even surpass the photosynthetic performance of the biological leaf.

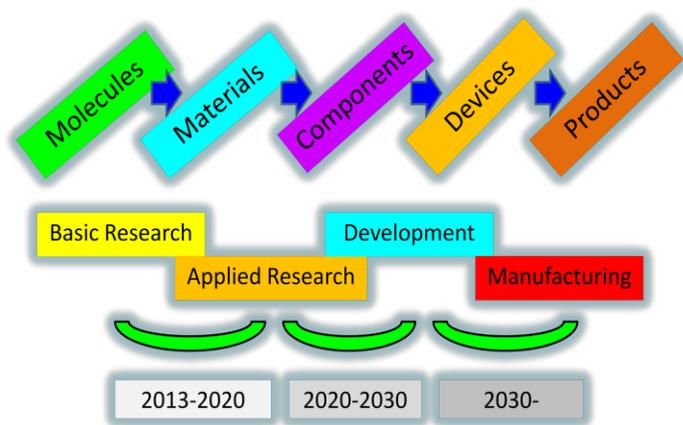


Figure 3: Carbon dioxide to solar fuels time line.

to be able to deliver the fundamental knowledge that will enable the subsequent steps from basic to applied research to development and manufacturing, envisioned in the carbon dioxide to solar fuels time line, **Figure 3**.

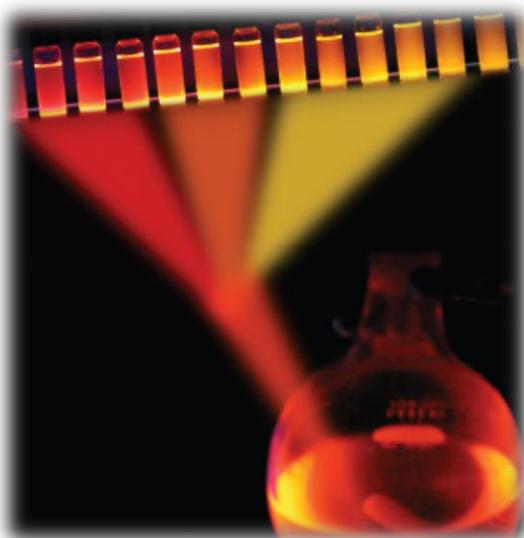
Success in this endeavor when achieved will be celebrated as a massive breakthrough and will set the field of solar fuels alight thereby setting the scene for the development of global artificial photosynthesis renewable energy technologies and policies!

an artificial leaf technology will eventually be developed which are able to efficiently capture and convert carbon dioxide, water and sunlight directly to specific chemicals and fuels in a distributed production system. Industry experts acknowledge huge challenges have to be overcome with regards to the discovery of photocatalysts that can mimic and even surpass the photosynthetic performance of the biological leaf.

Strong and sustained long-term basic research on solar fuels is envisioned

28. Nanochemistry Reproducibility

Why Worry? The six concepts of nanochemistry that constitute the foundation of a chemical approach to nanomaterials are size and shape, surface and defects, self-assembly and utility in advanced materials and biomedical applications. In this bottom-up paradigm for making nanomaterials, synthetic methods for controlling the degree of perfection of nanomaterials have improved enormously compared to the early days of colloid chemistry that more recently underwent metamorphosis to nanochemistry but how well has the field progressed since then with respect to the reproducibility of a synthesis and why do we care?



Size-separated, color-tunable, colloidally-stable and allylbenzene-capped silicon nanocrystals by Melanie Mastronardi, Advanced Materials.

Nano Reproducibility The scientific method is founded upon the principle of reproducibility. It has been claimed that the reproducibility of research published in scientific journals is as low as 10-30% a worrying assertion for the long-term credibility of scientific results. In the context of a nanochemistry approach to nanomaterials, a fair question to ask is what do we actually mean by reproducibility and how reproducible is your nanomaterial synthesis? The degree of agreement between replicate syntheses, by the same or different persons under identical experimental conditions, is a measure of the reproducibility of the synthetic method described in the open literature or patent

sources. In academic and industrial research, synthetic protocols reported in a paper or patent should enable replication of the work as a platform for new discoveries, as validation of a claim and as an enabler for commercialization opportunities. So what is the best measure of reproducibility for the synthesis of a nanomaterial, a unique state of matter having properties intermediate between molecules and materials but without the benefits of their atomic perfection and purity? And how reproducible does a nanomaterials synthesis method have to be in order to be useful?



Ultrathin inorganic nanowires that look, grow, and behave like polymers, Ludovico Cademartiri, Advanced Materials.

Size and Shape

The problem with nanomaterials is that the product of a synthesis is invariably a poly-dispersion, namely an ensemble of nanoparticles with a distribution of sizes and shapes rather than a collection of identical nanoparticles. Only recently have size separation and analytical techniques been applied to poly-dispersions of nanoparticles to narrow the size distribution in order to better define structure-property relations. So reproducibility in this context perhaps can be best measured and reported in terms of the ability to replicate the distribution of

nanoparticle sizes and shapes in a given sample, defined by a poly-dispersity index, $PDI = [\sigma/d]^2 + 1$ where d and σ are the mean size and the estimated standard deviation of the nanoparticle size distribution. The trouble here is the precision with which one can measure the size and shape of a statistically meaningful population of nanoparticles in distribution. Because many properties of nanoparticles are described by quantum mechanical scaling laws that result from spatial confinement effects of electrons and holes, ideally the size and shape of nanoparticles could be defined with atomic exactitude but in practice this is not possible. Even for the best mono-dispersions typically with PDI of 1.05 the standard deviation of the measurement of nanoparticle size and shape within a distribution in atom equivalents may be tens to hundreds to thousands. Variability of this order of magnitude from nanoparticle synthesis to synthesis can manifest, for example, as inconsistent chemical, electrochemical and photochemical behavior; discrepant optical, electrical, optoelectronic, thermoelectric and piezoelectric properties; and variable activity in biomedical diagnostics and therapeutics.

Surface, Defects, Self-Assembly

External surfaces of nanomaterials present even more serious challenges with respect to reproducibility. The surface is perhaps the most poorly defined, difficult to control and hard to understand property of nanomaterials. Here one has to be cognizant of the surface structure and composition, charge, different kinds of defects (e.g., point, line, plane and cluster) and bonded and adsorbed impurities as well as the number and distribution of organic and/or inorganic capping groups bonded to these surfaces. These features are exceptionally hard to quantify and are never exactly the same from nanoparticle to nanoparticle and between repeat syntheses. Further, because of the high surface to volume ratio inherent to

nanoparticles, a large fraction of coordinately unsaturated atoms exist on the surface that can cause the composition to be inherently non-stoichiometric, a property that is exceedingly difficult to quantify analytically. The outcome of non-stoichiometry in nanoparticles can be manifest as doping, mixed valence and trap states. In addition, the forces that control the self-assembly of nanomaterials into functional architectures are varied and complex and the nature of the surface plays a dominant role in determining the structure and properties of the resulting nanoscale constructs. So the ability to control and quantify the reproducibility of nanoparticle surfaces and defects and their self-assembly is nearly impossible. This presents a serious challenge for many advanced materials and biomedical applications with their associated health and safety related issues that rely on command and control of the chemical and physical properties of nanoparticle surfaces.

Yield For molecules and materials that can be purified as single product and single phase, their yield is a quantity that in principle can be precisely defined but what do we mean by yield of a nanomaterial that is presented as an ensemble of nanoparticles with variable sizes, shapes, surfaces and defects? Is measured mass yield of the entire distribution with its estimated standard deviation the meaningful measure of yield and does it adequately define the reproducibility of the synthetic method or does one need to examine each component nanoparticle in the histograms of size, shape and surface?

Nano Care Because of these synthetic uncertainties, experiments conducted on nanomaterials emerging from different preparations are reporting results for an ensemble average, which for some applications might be quite acceptable but for others could prove to be problematical. Each situation has to be carefully scrutinized with respect to its tolerance to the variations in heterogeneity inherent in the reproducibility of all synthetic nanomaterials.

Towards Reproducibility Standards The misery about reproducibility of nanomaterials presented in the literature is a worrisome situation for the academic and government research community, and industries that manufacture nanomaterials and develop products and processes thereof. The crux of the problem is a lack of standards and procedures for quantifying reproducibility of known and new nanomaterials. Surely it is the responsibility of the authors of papers and inventors on patents as well as peer reviewers, examiners and publishers of these papers and patents to diligently attend to this aspect of the research, which is blatantly missing from most reports of nanomaterials syntheses.

One could resolve this problem by requiring evidence of the degree of reproducibility to be a prerequisite for publication of papers containing a nanomaterials synthesis. It is true that many analytical methods for defining reproducibility approach their limit of resolution for nanoscale materials therefore it is even more important to provide a sufficiently large set of data to inform the reader about the accuracy and reproducibility of the results.

In this regard, transmission electron microscopy TEM should not be regarded as science but art. At least for the purpose of reporting on reproducibility of a nanomaterials synthesis it cannot serve as a defining experimental diagnostic of the entire product but more often than not a biased slice of reality. Angle dependant dynamic light scattering, DLS and small angle X-ray scattering, SAXS could instead become mandatory standard characterization methods because they give meaningful information on the nanoparticle size and shape distribution of an assembly. Whenever quantum size effects come into play, preparative ultra-centrifugation could be practiced whenever possible in order to obtain and report upon narrower size distributions and the power of analytical ultra-centrifugation could be exploited to define the number of molecules on the surface and atoms in the core of nanoparticles in a distribution.

Ultimately a higher standard is expected of researchers and a tougher stance by referees and publishers for evidence of reproducibility of a nanomaterials synthesis as these higher standards of practice would greatly benefit the nanochemistry community as well as facilitate the transformation of nanomaterials ideas in the laboratory to innovative products and processes in the market place.

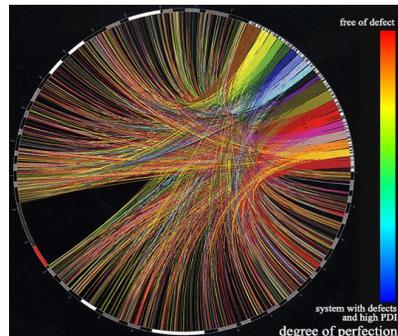
I am well aware of the problem to introduce these standards into every day practice and the additional time and effort required to implement them but all one can do is appeal to the scientific conscience of nanochemistry researchers to investigate and report on the extent of reproducibility of their synthetic nanomaterials work.

Nano Food for Thought

On a final note in the context of nano reproducibility, how does the nano community judge scientific quality? Some might say that the work with amazing images and routine science is looked upon more favorably than the work with amazing science and routine images. High quality images cannot be a substitute for high quality science. It should be science first and photography second! The question is, how representative are these art nano images of your pet nanomaterial and the reproducibility of the synthesis. The dilemma the nano community faces is that the literature is replete with the litter of irreproducible nanomaterials syntheses, which undermines progress in the field, diminishes its credibility scientifically and jeopardizes its commercial potential.

29 Exploring the Possibilities and Limitations of a Nanomaterials Genome

What are we going to do with the cornucopia of nanomaterials appearing in the open and patent literature, every day? Imagine the benefits of an intelligent and convenient means of categorizing, organizing, sifting, sorting, connecting and utilizing this information in scientifically and technologically innovative ways by building a Nanomaterials Genome



founded upon an all-purpose Periodic Table of Nanomaterials. In this Concept article, inspired by work on the Human Genome project, which began in 1989 (<http://www.genome.gov/>) together with the recent emergence of the Materials Genome project initiated in 2011 (<http://www.whitehouse.gov/blog/2011/06/24/materials-genome-initiative-renaissance-american-manufacturing>) and the Nanoinformatics Roadmap 2020 instigated in 2010 (http://nanoinformatics.org/nanoinformatics/index.php/Main_Page, accessed: Dec, 2013), we envision a Nanomaterials Genome (NMG) smart database with the most advanced data-mining tools that leverage inference engines to help connect and interpret patterns of nanomaterials information. We foresee it will be equipped with state-of-the-art visualization techniques that rapidly organize and picture, categorize and interrelate, the inherited behavior of complex nanomatter from the information programmed in its constituent nanomaterials building blocks. A Nanomaterials Genome Initiative (NMGI) of the type imagined herein if reduced to practice has the potential to serve the global nanoscience community with an opportunity to speed up the development continuum of nanomaterials through the innovation process steps of discovery, structure determination and property optimization, functionality elucidation, system design and integration, certification, manufacturing to deployment in technologies that apply these versatile nanomaterials in environmentally responsible ways. The possibilities and limitations of this concept are critically discussed and evaluated in this article.

1. Pre-amble

What do we mean by genome? The term genome was originally coined by the botanist Hans Winkler in 1920. He combined the words gene and chromosome to describe the origin of a species in terms of its constituent set of chromosomes and protoplasm. These days it is an informatics descriptor used in molecular biology and genetics to describe how the heredity of an organism is encoded in its DNA. In the context of informatics, while it is true that the elements of Mendeleev's periodic table of the elements are not the same as the nucleotide base code-carriers of DNA, they do carry all the information required to enable the design and discovery of molecules and materials with specific functionality and purposeful utility through chemical control of composition, structure, bonding, property relations. Although the number of permutations and combinations of more than a hundred elemental building blocks provides infinite molecules and materials synthetic possibilities, it is only through the rational and systematic understanding and manipulation of the chemical and physical properties of the elemental building blocks that the molecules and materials discovery process becomes tractable.

On this basis and in the context of chemistry, one could argue that Mendeleev's periodic table is the most fundamental of all genomes, the 'element genome' although in the framework of physics, all matter ultimately evolves from a 'sub-atomic particle genome'. In a chemical sense, the 'element genome' is the basic building code for all matter, biological or abiological, inorganic or organic, soft or hard, including matter intermediate between molecules and materials, namely nanomaterials. In the language of chemical informatics, the element genome stores all the information required to form chemical bonds and make molecules and materials of any kind by design and the human genome and materials genome build on this platform to categorize and store patterns of structure and properties in biological and abiological matter that expose function and manifest utility.

By analogy, the nanomaterials genome can be contemplated to emerge naturally into the genomic paradigm through the information content programmed into a periodic table of nanomaterials ^[1] coupled with the coded interactions/forces that direct nanomaterials to assemble into functional and useful structures. On this basis, maybe it is time to expand and transform the term genome to include the information content embedded in all forms of matter, the 'omninome', the all-purpose genome. By expanding the informatics descriptors for the term genome we can encompass a broader spectrum of examples of animate and inanimate matter, from the atom-up over all-scales, broadly and deeply applied from idea to innovation, research to development, industry to business.

This raises a fundamental question: how are two seemingly different physical and biological systems similar to one another? That question stands at the crux of the scientific challenge to connect various forms of matter, and to understand the creative potential of these connections.

Our Concept article addresses this important question and many others, while presenting the essence of a strategy with examples for showing how emerging nano intelligence can be built into nano data-mining, in order to give it real value and significant impact. To be clear, the computational details of the advanced search engines needed to support the NMGI are not heralded here as revolutionary science or big innovation. We regard these technological developments as incremental innovation, which is, nonetheless, essential to the advancement of science and human knowledge. Our hope is that the NMGI will free our minds and creativity to be as imaginative as we were born to be, rather than corner us into becoming a society of automatons managing and amassing our knowledge of the infinite details of Nature while overlooking the whole integrated system of matter that we're still groping to understand in-depth.

2. Introduction

One breakthrough insight into the relationship between genes and the Human Genome project is that the amount of protein produced for a given amount of mRNA not only depends on the gene it is transcribed from but also on the biological environment in which it exists. Researchers now understand that the protein is not correlated with the gene as closely and exclusively as once assumed. From this deep insight emerged the field of proteomics, which manages a large-scale study of the structures and functions of proteins. The proteome refers to an entire set of proteins, produced or modified by a definite system, such as an organism.

Both genomics and proteomics are based on massive studies of the biological interactions between genes and proteins. These studies are becoming increasingly more extensive and systematized. Recently the Human Proteome Organization has launched an international collaborative Human Proteome Project, which aims to experimentally observe all of the proteins produced by the sequences translated from the Human Genome.

As the global activity in nanomaterials research and development continues to grow in intensity and its practical implementation becomes more pronounced, the use of new nanomaterials and new methods for making and examining them and exploring their potential uses are becoming more systematized and layered with complexity. Despite the huge diversity and complexity we have reached, simple rules that regulate the

development and evolution of nanomaterials need to be re-addressed and understood better. This will help to further codify, characterize, categorize and utilize nanomaterials in a safety conscious way.

We endeavor to systematically build on this natural pattern that has been revealed, aiming to empirically confirm and reproduce them in a predictable, and reliable manner with the aid of the proposed Nanomaterials Genome and its building block representations in the form of an envisioned periodic table of nanomaterials.^[2,3] In this context, the National Nanomanufacturing Network in the U.S. in 2010 started a community-owned program called “Nanoinformatics” and announced the “Nanoinformatics 2020 Roadmap”. The goal of this initiative is to identify, collect, validate, store, share, analyze, model and apply nanoinformation that is deemed pertinent to the science, engineering and medical community, to enable and enhance connections between researchers in academia, industry and government agencies. It shows a community-wide resolution in building up a shared network and a tool that fosters efficient scientific discoveries and regulates health and safety in the work place and population.^[4]

It is worth mentioning here that the groups of Mirkin and Tomalia ^[5,6] have introduced the concept of a Periodic Table of Nanomaterials previously but point out the difficulty of calling it a “Periodic Table” as long as intrinsic imperfections of the nanomaterials building blocks with respect to their variations in their size, shape and surface exist. Whilst this is currently the situation, with continuing improvements in nanochemistry synthetic methods and broader implementation of nanomaterials separation and purification techniques the ubiquitous problem of nanomaterials polydispersity could eventually be resolved and the use of the term periodic would become more apt. Such a Periodic Table of Nanomaterials with improvements in building block perfection could ultimately prove to be a convenient instrument to help organize ones thoughts and provide a guide to what is possible.

Herein, we aim to provide an overview and general description of an atlas of nanomaterials, created and categorized by means of the Nanomaterials Genome. By naming it as the Nanomaterials Genome, we believe it is more than just a tool in the mode “nanoinformatics” will function. It urges one to understand the inner nature of nanomaterials, to sort out the connections of their chemical and physical parameters, and how this relates to function and how recognition of that function enables the development of value in advanced materials and biomedical applications.

3. The Nanomaterials Genome: Concept, Realization and Visualization

3.1. The Concept

The Federal Government of the US first used the term materials genome in its report “Materials Genome Initiative for Global Competitiveness”. [7] The objective of the MGI is that to achieve global competitiveness in the 21st century it is crucial to reduce the time that it takes to transition a materials discovery to the market place from 20 years or more to a much smaller time frame, at least by half, through the development of a materials innovation infrastructure that integrates computational and experimental tools with digital data and collaborative networks. To enable MGI to realize its full potential, we propose a comprehensive complementary “Nanomaterials Genome Initiative (NMGI),” which operates with an equally important, urgent and tandem mission: namely, studying the inherited behavior of complex nanometer scale matter from its constituent nanomaterials building blocks that consist of nanocrystals, nanowires, nanotubes and nanosheets to synthesize a world of materials targeted for advanced materials and biomedical technologies. [8]

To amplify, there are no new materials in the known universe that are not explicitly represented in the Periodic Table of Elements. These materials include an infinite number of nanomaterials that can be created and in principle represented in a Periodic Table of Nanomaterials. [5] Our primary goal aims to both sort out and build upon the interconnections between materials and nanomaterials. These interconnections underscore the creative act of making nanomaterials themselves, as well as overseeing their self-assembly into higher order advanced structural materials. By comparing and connecting (gene and genome) to nanomaterials, we mean to highlight these two important pieces of nano-information: (1) the order and hierarchy within the system from the building blocks to higher order structures, and (2) the representations and connections between the elements (or descriptors) that define the identification of each type of nanomaterial.

In the context of biology, a gene denotes a molecular unit of heredity of a living organism, or, described in modern terms, “a locatable region of genomic sequence, corresponding to a unit of inheritance, which is associated with regulatory regions, transcribed regions, and or other functional sequence regions”. [9,10] The term nanomaterials genome is used here in a non-biological context.

In terms of the unit itself, a gene is defined by four basic construction subunits that encode information into DNA (adenine, guanine, cytosine, thymine, AGCT), while a nanomaterials gene is identified by the descriptors elemental composition, structure, size, shape, surface, degree of imperfection, self-assembly, and how these are connected function and utility.

Notice that in the Nanomaterials Genome we are mixing together structure and function. Also, note that we list self-assembly as a descriptor. We think of it as a descriptor in so far as it describes the differences in the way a particular 'nanomaterials gene' self-assembles. And, nanomaterials don't self-assemble in one-and-the-same way. They all have different rates and characteristics in the process of self-assembly and there are five major classes of self-assembly with overlap between them: static self-assembly, dynamic self-assembly, co-assembly, hierarchical self-assembly, and directed self-assembly.^[11]

In addition, by comparing materials with living organisms, we imply the formation of complex nanoscale matter that evolves from the pre-programmed assembly of nanoscale building blocks. Their functional architecture and actions behave, more or less, in a naturalistic or organic way that resembles the process in which a living organism grows and evolves. The change of a given phenotypic trait observed for an organism owes its origin to the change of the nucleic acid sequence. Similarly, the inherited characteristics and behaviors of complex nanomatter vary as the information encoded in a genomic format varies. This information flow starts from the combination and sequence of all key construction units – namely the element composition, size, shape, surface, self-assembly, function and utility with due cognizance of the effect that nanomaterials imperfections will have on these property carriers.

In other words, similar to the central principles of molecular biology, a given combination and sequence of those key construction units, regulates the formation of a corresponding form of complex nanomatter with pre-programmed relations between its structure and properties, desired function and ultimate use.

Like all analogies regardless of how they seem to possess a “ring of truth” ^[12], we must rely on our skepticism and critical thinking as we move through the door of this conceptual connection. It is a truism that molecules are, for a large majority, in thermodynamic equilibrium. They are stable. In a good solvent, they do not dissociate, re-associate. If they do, we know exactly how much, and how they do it. With nanomaterials, their state is dependent on their environment. The surface ligand concentration will depend on the concentration of ligands in the solvent around them. Are you going to standardize that as well? In high purity conditions, on top of the problem of polydispersity, many nanoparticle systems will ripen and change size, shape, concentration, and so forth. Now that the information you need to fully characterize one nanomaterial is beyond the means of most laboratories, how is it that anyone will be able to associate their nanomaterial to an entry in the database? Do you account for incomplete and incorrect entries? How do you do so when any of the missing characteristic can be a determinant of the property you are looking to optimize? These are all good points especially the reality that nanomaterials do

not have the perfection of molecules, that should be posed and explored in-depth. They're seminal questions beckoning insightful responses by the nanoscience community.

We plan to use the Nanomaterials Genome as a generative tool for controlling the combinatorial creations of nanomaterials in a reliable and predictable manner. This tool enables us to see the order and hierarchy contained within complex nanomatter. Meaning, it helps see through the apparent complexities of nanomatter, spotting the "simplicity within the complexity" of the Nanomaterials Genome. This approach is similar to molecular biologists and geneticists using their tools to see the simple basic building blocks in the complex biological matter manifested in the Human Genome.

Expressed another way, we can glean some simple organizing principles nested within the complexity of nanomatter. It fosters an explicit and intuitive way of designing, engineering and deploying nanomaterials, without losing its scientific precision and elegance to observe a particular group of nanomaterials and its inner nature as a whole.

3.2. The Beginning of Realization: Building a Central Database of Nanomaterials

In order to bring the idea to reality, academia and industry need to work collaboratively to build a central database of nanomaterials. This database might bear a resemblance to an encyclopedia or atlas, where each particular type of nanomaterial is assigned one entry, which is written according to a common standard. Each entry should be utility-directed, since the ultimate function of any material is to serve humankind. For every particular type of nanomaterial with single or multiple utility, we link with it a unique Reference Number as an identifier after we register that nanomaterial in this universal database. "Universal" means more than "central", which implies, in the foreseeable future when this database is brought to reality, we can use the Reference Number of the nanomaterials to do any cross-database search. This Number can be used by international organizations, national institutions and governmental departments such as WHO, UNESCO, NIST, NIH, FDA, DOE, DOF, DARPA, etc.

For example, an entry of titania nanoparticles would look like the following but might be more detailed than the following lines of descriptors:

- I. {Reference Number}: BRP100XXXXXXXXXX
- II. {Elemental Composition}: TiO₂
- III. {Structural Information}: Anatase
- IV. {Size (min, max /nm)}: 20, 35
- V. {Shape}: Elongated Rhombic (specific geometrical parameters, face index, etc.)

VI. {Surface}: OA capped

VII. {Degree of Imperfection}: (Polydispersity Index, crystallinity, defects, etc.)

VIII. {Utility and Function}

Other descriptors can be added, as well, for purposes of clarity and innovation. Note that this information can be presented as a matrix in which all the key descriptors are named and described for easy identification, like a pharmacy codifies prescribed medications. To standardize every descriptor or term and to avoid scientific mistakes and unnecessary contradictions, introducing a systematic nomenclature might be helpful as well.^[13] How to implement this is still under discussion and development and already the International Standards Organization has been working on the creation of a useful nomenclature system.^[14,15]

The initiation of this database would require considerable effort since every research group in academia, government and industry would have to help edit the entries of nanomaterials reported from their previous work (from publications, patents, etc.). It could be an open-source, operating system like Linux.^[16] Once this first step is done, the rest will be a standard procedure whereby getting a Reference Number of the newly-reported nanomaterials is required for publication purpose, just like crystallographers will have to get a CCDC (Cambridge Crystallographic Data Centre) number before their crystal structure get published.

It's important to mention here every effort will be made to ensure that the NMG Database will not be used as a governance system that determines the publication of one's research. More to the point: many research scientists share a growing concern that Big Data may inadvertently create masses of useless bureaucratic workload that can hinder human creativity rather than foster it. Already in academia there is an assessment and evaluation process in place that requires researchers to simulate every trace of one's experimental idea. If the simulations don't support one's idea, then the researchers are not funded.

This Database, when reduced to practice, would be not only the central connector of all research databases and patents libraries, it would act as the center of the Nanomaterials Genome Initiative. The peripherals of the system, would take the advantage of the central database, serving all the researchers, companies and institutions, facilitating their research and production (see sections 3 & 4 below). However, the building of such a database will not be easy and short-term work – it took hundreds of researcher's years to analyze a few percent of the Human Genome – we believe the start of a Nanomaterials Genome would take longer but in view of the burgeoning activity in the field it should be initiated in haste. Though the discussions in this Concept article are based on a proposed central database, a network of de-centralized databases may also be of great help for materials scientists to

share their data, as long as every node supports open-access and shares the same standards for exchanging data.^[17] Those with knowledge and expertise in computer science would be needed to build such a network.

3.3. A Note of Nano Caution

As mentioned earlier nanomaterials are not molecules and materials and they are not perfect. The inherent imperfections of nanomaterials originate from variations in the size, shape and surface of the building blocks, which will complicate the exactitude of the NMG data base and limit its usefulness until synthetic methods have improved to the point that the perfection of nanomaterials begins to approach that of molecules and materials. Is this a realistic expectation in the foreseeable future?

Currently, the heterogeneity of a nanomaterial currently makes it virtually impossible to define a precise code or even an accurate building block entry in a NMG so it is not yet productive to make gross generalizations with so many variables contributing to nanomaterials properties, which will ultimately influence functionality and utility. And policing the suitability of an entry will be challenging in order to avoid the generation of misinformation and prevent incorrect predictions. This situation is however expected to improve with advances in the quest to “perfect the imperfection” of nanomaterials building blocks. Here it is worth noting that there is an analogous problem of imperfection with the biological genome which influences and impacts the behavior of genes, so in that regard nanomaterials are really no exception

3.4. Towards Visualization: A First Step

Circos is a data visualizing tool, widely used in various fields, especially the field of bioinformatics by cell biologists. In scientific journals, it's the standard of genome plotting.^[18] That said, there are plenty of other available and proven tools for plotting multi-variant data, which may also be very useful. To be clear, the Nanomaterials Genome is totally different from the Human Genome both by definition and by nature. How do we represent the Nanomaterials Genome with the Circos diagram? How do we present the qualitative or quantitative descriptions of each determinant (composition, structure, size, shape, surface, degree of imperfection, function, utility) and their interconnections? Different from plotting the Human Genome, Nanomaterials Genome plotting is multi-dimensional rather than just two-dimensional. So the challenge appears to be, how to display this multi-dimensional space in a plain, comprehensible and user-friendly way to researchers, to governments and to the public? In recent years, other related models with similar geometries have been proposed, exploring new tools for mapping the "genometries" of nanomaterials. The multi-dimensional Periodic Table of Nanomaterials

and Nanomaterials Genome are aimed to visualize, describe, and demonstrate the interconnectivity of these determinants.^[3, 19] These alternative models and approaches provide valuable insights into the nature of nanomaterials, and their creation involving morphogenesis and morphosynthesis.^[19]

One possible layout of the Circos diagram presenting the Nanomaterials Genome is designed as shown. Use the *link* (as seen in the Human Genome diagram) to connect the composition-structure pair and size-shape pair. For example, the composition-structure pairs of a group of nanoparticles can be presented as Figure 1.

As shown in Figure 1, points on the circle stand for different elemental compositions or different structure (amorphous or various crystal structures). The colored lines (*links*) connecting composition-structure pairs stand for all nanomaterials featuring the corresponding composition-structure combinations. Similarly, we can plot a Circos diagram for size-shape combinations, as shown by Figure 2.

By assembling those two circles we form a cylinder like that shown in Figure 3. Imagine a 2-dimensional sheet determined by a given composition-structure-size-shape combination. This sheet contains an infinite amount of nanomaterials, which are further described with different surface conditions and different functions – those two variables make these two additional dimensions.

Another variable shown in Figure 3 is the color. It's a scale of degree of imperfection. As we know in the world of nanomaterials, the degree of imperfection is a significant property of almost all kinds of nanomaterials. In a narrow sense, it measures the fine quality of a nanomaterial, providing information about its purity, its compositional precision and structural exactitude. In a broader sense, it stands for a group of other descriptors, e.g. defects (including surface defects), dopants, non-stoichiometry, impurities, poly-dispersity index (PDI), etc. An inclusion of all these determinants depicts a generalized visualization of Nanomaterials Genome for a specific range of nanomaterials (shown in Figure 4).

With an infinite amount of combinations of these determinants, we can pinpoint any specific nanomaterial, e.g., an aggregation of rhombic-shaped titanium dioxide nanocrystals with an anatase structure [Tetragonal (4/m 2/m 2/m)], sized from 20-30 nm with a PDI of 1.15, passivated with oleylamine on the surface. It is presented as a point, located on the corresponding composition-structure-size-shape sheet within the Circos cylinder, with the color of pink.

What we have proposed above is a idea, an example of the visualization of representative data in the Nanomaterials Genome database. Others might think of better ways of

visualization.^[19] With the development of information technology and biotechnology and the promotion of open-access, the Nanomaterials Genome system bodes well for a bright future.

4. Proposed Applications, Benefits and Impact

4.1 Applications

The Nanomaterials Genome has the potential to serve the nanoscience and materials science communities with an opportunity to speed up the development continuum of nanomaterials through the steps of discovery, structure determination and property optimization, functionality elucidation, system design and integration, certification, etc.

When we take its application into consideration, what first comes into our mind is providing platforms for data management, analysis and synthesis – that’s usually the second step after we have a database. The world’s leading sources of intelligent information can provide access portals of the database, data management software, data analysis software to customers, most of who are from academia or businesses.

How does this serve researchers and technology developers? A good example can be given in the field of materials research for sustainable energy. Suppose we have both the Nanomaterials Genome database and the omnipotent platform provided by an intelligent source at hand (by “omnipotent” we mean the platform has integrated functions of database access, data management and data analysis). A user in this field is capable of accessing the database, doing a fast and comprehensive search by filtering selected keywords, and drawing intuitive graphs for analysis and decision-making. These keywords might be, for example, given composition, given size range, given electronic band-gap range (if they are semiconductors for photocatalysis), required minimum quantum efficiency, required maximum cost of materials, and even device parameters like power conversion efficiency, device cost, etc. These essential details would be useful and necessary for scoping out the feasibility of manufacturing the nanomaterials for this energy-related application. They’re also important for securing venture capital funds and financial support from governmental and nongovernmental investment groups that require this information for their stakeholders.

Another benefit is that by filtering data as a keyword we can even see research trends on every aspect of these energy materials, including the development of intellectual property that’s grown along with these innovative materials. It’s true that most of these details are embedded in scientific papers and patents; ferreting them out takes some serious effort.

However, if such a database of nanomaterials and a multifunctional platform are provided to researchers, it will facilitate their research and profoundly enhance their understanding in this field. Users will learn to appreciate its power just as they are grateful for things like reference management software and citation analysis reports. This will inspire researchers to choose the best candidate energy nanomaterials for evaluation and optimization. Equally important, both researchers and developers will be able to leverage the collective wisdom of this collaborative enterprise in interpreting the rich data in such a way that leads to “making uncommon connections, “ a process of inventing and innovating practiced by leading organizations such as The Lemelson-MIT Program.

Unfortunately, the most compelling argument for this NMGI cannot just be the basic pursuit of scientific knowledge. In today's globally market-driven environment - in the life of business - there's an unspoken belief that knowledge is worthless unless it is somehow productized and monetized. This leads us to consider the commercial use of the NMG in everyday life. There are many applications for this new knowledge if we take advantage of the Nanomaterials Genome. One example is the employment of the QR code scanner and reader for identifying a commercial product. This QR code is a unique identifier linked with the Reference Number of the corresponding nanomaterial in the Nanomaterials Genome Database. It works as a technological brand, as important as (if not more than) the commercially registered brand. Customers with portable devices such as smart phones can access the technological background of the nanomaterial used in the product in seconds. The day when shoemakers print patent numbers on their shoes has passed with the QR code reader linking to the central database of the nanomaterials world. A buyer of water-proof shoes can easily be informed with all the knowledge he needs, e.g., technological principles, working conditions, preserving conditions, etc. Advertisements from the media can thus provide more information to interested readers by simply placing a small QR code, without taking too much costly space.

Noting the practical commercialization of this new knowledge in no way is meant to imply that we've run out of solid scientific ideas on how to make our materials better. If anything, the above earmarked example serves merely to invite the communities of potential users to weigh in on the most important products to highlight. Clearly, there are a handful of significant and urgent products to consider, such as nano-related energy products for artificial photosynthesis devices applied to climate control or health-related examples, such as nanomaterials designed for treating neurodegenerative diseases, or improving oncological treatments for cancers.

No doubt, the number of nanomaterials that will be permitted to enter the marketplace at the level we envision will be relatively small, because each material and preparation will be subjected to FDA/EPA approval; this carefully controlled process can still be made more

effective and efficient. Needless to say, this approval system is essential, since it guarantees there will be strict criteria for maintaining the high quality of nanomaterials.

Simply put: It's neither necessary nor advantageous to produce a million different types of non steroidal, anti-inflammatory drugs such as Motrin and Advil. The same may hold true for a million different types of nanomaterials. No one really knows, any more than the specialists managing the MGI know what they're going to do with the massive data they're aiming to collect and analytically mine. However, this current reality shouldn't exclude the fact that there may well be many compelling examples proposed, as our international community of scientists, begin to earnestly percolate on determining and prioritizing the best examples. Here and now, we openly invite our readers to suggest their outstanding examples. We welcome individuals or teams of researchers showing-and-telling us why their examples are important. Perhaps, there are specific problems or challenges that they see a way of solving by accessing the Nanomaterials Genome Database.

One particularly useful application for industry is the employment of the NMG Database in market intelligence. In the area of nanomaterials and nanotechnology, data and citing from this database can enrich the background of a market intelligence report, making it more convincing for the purpose of guiding accurate and confident decision-making in determining market opportunity, market penetration strategy, and market development metrics. It saves consulting groups huge amount of money and saves producers huge amount of time and opportunity costs as well.

We are confident that smart businessmen will come up with elegant and responsible ways of utilizing the Nanomaterials Genome Database. Once the human ecosystem is built and the dating-mining tools are working synchronously, researchers, industries and service providers bound to it will be all in a virtuous circle.

4.2 From Materials to Nanomaterials: The Impact

The significance of materials chemistry and materials science, materials engineering and materials technology in both our daily life and throughout the human history is self-evident – every industrial revolution in history is preceded with, or accompanied by advances in materials science. That's why the US government proposed the Materials Genome Initiative (MGI). Our proposed Nanomaterials Genome Initiative (NMGI) starts where the other stops so to speak. It builds on the work and results of the MGI, rather than being built into it as a subdivision, which is also a possibility. The point is we aim to go beyond that point.

We have passed the era when humankind depends only on natural materials and metallurgy. Apart from further advancement and improvement of the study of traditional

materials and metallurgy, materials scientists today also deal with advanced materials, paying close attention to the morphology, surface chemistry, doping, defects, and self-assembly on a micro-scale.

We have entered the era of solid-state chemistry and physics where there is increasing demands for structured nanophase materials with stringent requirements of size, shape and dimensionality, as well as the type and concentration of dopants, defects and impurities.^[20] In a broader sense, a modern view of materials should encompass nanoscale or mesoscale building blocks which self-assemble at different length scales to form hierarchical structures, and finally, to perform its functions as an integration. It's a general preconception but should be true from both a materials chemist's and a condensed-matter physicist's point of view. It also makes sense no matter what the approach is used: either bottom-up chemical synthesis or top-down lithography, or a creative integration of both.

Today, thinking small is the new way of thinking big. That's also why the US government in recent years has readdressed the significance of the National Nanotechnology Initiative (NNI) started during the Clinton Administration.^[21,22] Recently there has been some feedback on how the MGI and NNI have been changing the way materials scientists work, which infers that researchers are beginning to adopt data sharing with collaboration between them becoming much closer in the future.^[17] Now that researchers in the US are going through the early stage of the NNI and GMI supported by the US government, we feel it is important to establish an international collaborative cross-disciplinary program, based on our idea of mapping the Nanomaterials Genome as delineated in this concept article.

In April 2013, the Obama administration of the US announced the BRAIN (Brain Research through Advancing Innovative Neurotechnologies) Initiative, which challenges scientists to map the brain to better understand how we think, learn, and remember. It is regarded as the government's latest ambitious Big Science initiative. There have been three of these before the launch of the BRAIN initiative – most notably the Manhattan project, the Apollo program, and the Human Genome program, which changed the course of history. We believe that implementing the Nanomaterials Genome Initiative, as a comparable endeavor, could make a similarly important contribution in the history of innovation. It would benefit humankind and the globally emerging Nanotechnology enterprise by promoting public health, by easing the energy crisis and by contributing to economic growth and the quality of life.

Granted, the Manhattan Project changed the world because it yielded the unique capabilities of Nature by unlocking the potential of energy stored in the atom. Keep in mind that it wasn't clear or certain that nuclear energy would result from that remarkable achievement. Moreover, there were serious concerns about *controlled* nuclear fission (or

fusion energy, for that matter). The commercialized, civilian use of nuclear energy was in many respects an afterthought rather than forethought. In fact, there were plenty of die-hard skeptics who sided with the view of the 1908 Nobel laureate in Chemistry Ernest Rutherford: "The energy produced by the breaking down of the atom is a very poor kind of thing. Anyone who expects a source of power from the transformation of these atoms is talking nonsense." And there were scientists who accepted the view of the 1923 Nobel laureate in Physics, Robert Milliken: "There is no likelihood that man can ever tap the power of the atom."

The Manhattan project suggested the possibility of realizing the Holy Grail of Energy: tapping a limitless energy supply from a completely new source that few experts knew anything about. To this day, we're still groping to figure out that stellar technology especially, controlled nuclear fusion energy systems. These continue to confound plasma physicists and fusion specialists who are building the next generation of magnetic confinement machines, inertial confinement devices, and hybrid fusion-fission reactors with the prospect of producing high-temperature, commercial-grade plasmas in a self-sustaining system. And one day soon, we're counting on them succeeding.

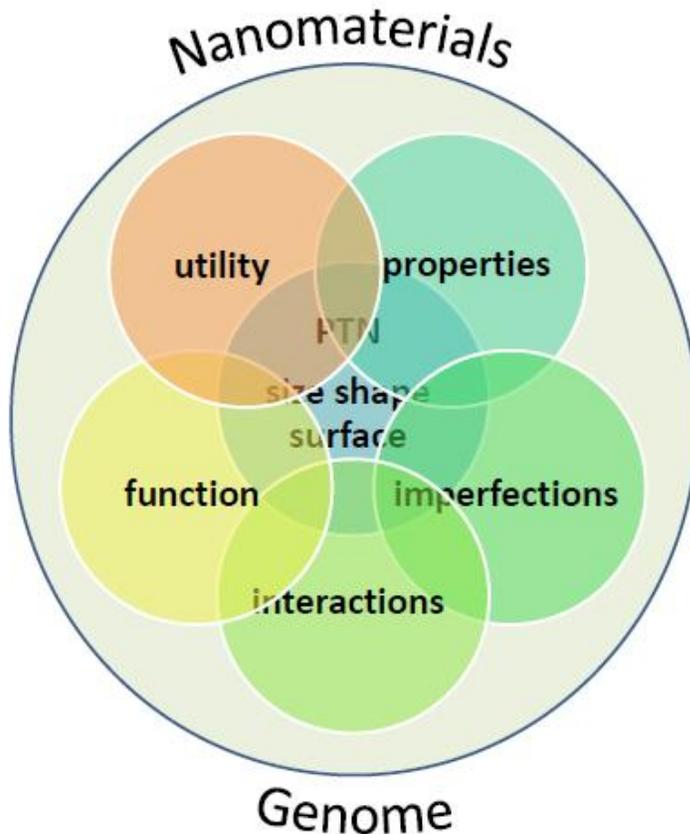
At this nascent or seedling state of development, no one can say with any authority that the NMGI will be able to show-and-tell us exactly what the absolute best nanomaterial for a specific application will be especially, if that material doesn't even exist yet. There simply is no crystal ball or magic crucible that can show conclusively how to best do this and get the desired results in a reliable and efficient manner. To make good on that promise, we'd all have to be living aboard Gene Roddenbury's *Star Trek: Enterprise* controlling a universe of virtual matter composed in the boundless space of the Holodeck!

The Nanomaterials Genome Initiative would also have a great impact on materials research targeting two of the most urgent challenges confronting our world: the search for a sustainable source of carbon neutral renewable energy and the improvement and protection of public health. No matter what NMGI aims to achieve or is tasked to do at any given time (e.g. designing more efficient solar cells and hydrogen fuel cells, or researching cures for common cancers, or devising new medical devices for treating neurodegenerative diseases), university, industry and government scientists around the world will benefit from the existence of a Nanomaterials Genomic Initiative and the scientific and technological platform that support it.

This platform will enable researchers and developers to engage in a more effective and creative collaborations that search, connect, analyze, synthesize, interpret and share information. It will help facilitate the whole process of ideating and innovating, which drives creative and critical thinking from research to development to application. The

Nanomaterials Genome promises a highly integrated form of collaboration, communication and cooperation throughout the global nanoscience community.

4.2 Not Just a Data Base



The working principle of the NMG that endows it with scientific assets beyond a nanomaterials registry can be expressed in a type of Venn scheme. At its center point is featured a periodic table of nanomaterials, which comprises a multi-dimensional searchable library that compiles and organizes all known forms of nano matter in terms of its basic building block, size, shape and surface, descriptors. Each one of these building block descriptors interlaces at the next level of complexity, with all known information concerning their properties (e.g., electronic, optical, magnetic), their

imperfactions (e.g., dopants, non-stoichiometry, defects, impurities, polydispersity, surface irregularity) and their interactions (e.g., self-assembly, co-assembly, directed assembly, hierarchical assembly).

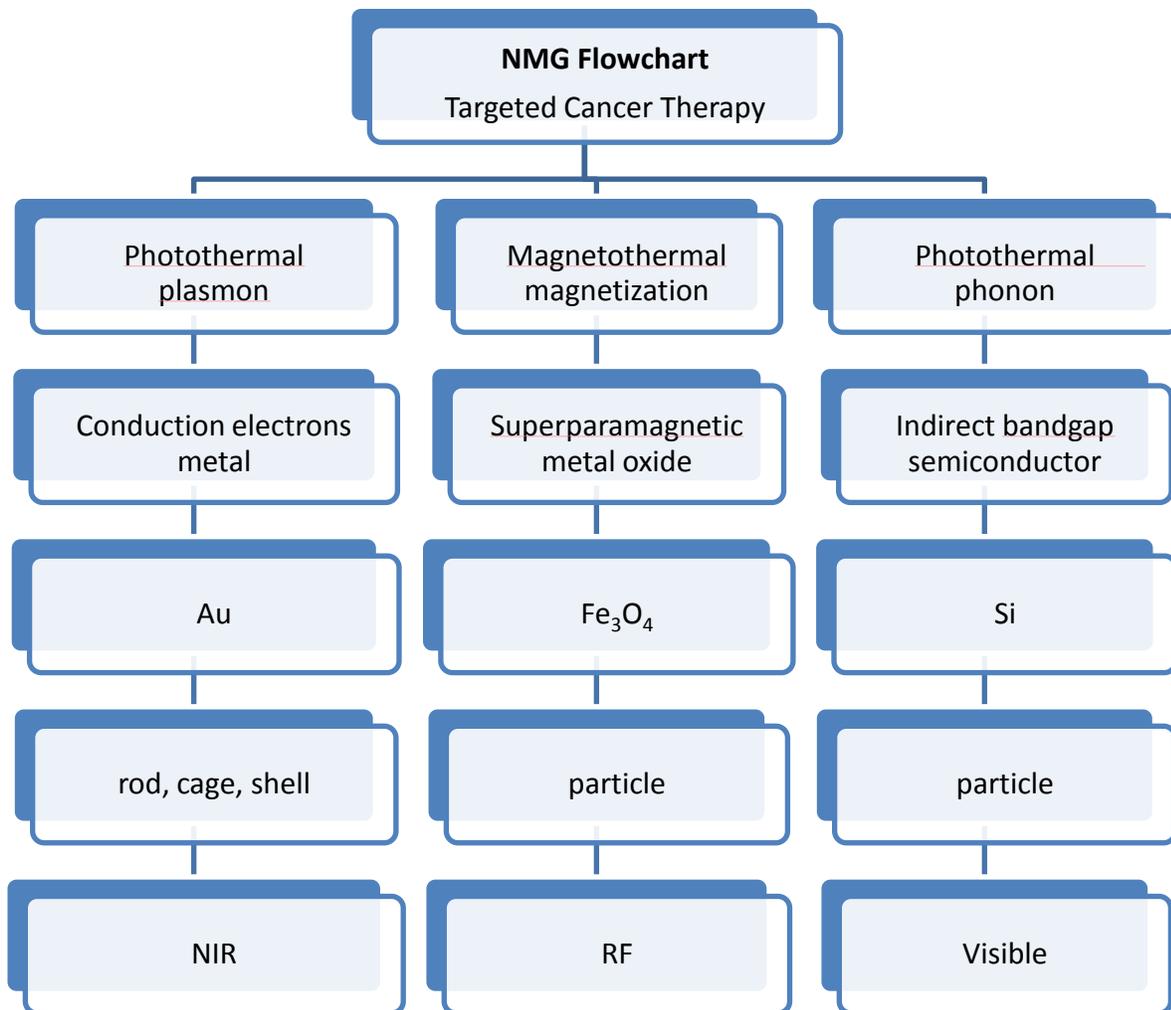
This panoply of integrated nanomaterials information provides a platform to the next level of the decision making process where connections to nanomaterials function are made and deciphered at the highest level in terms of nanomaterials utility in advanced materials and biomedical technologies.

In this way the NMG if programmed judiciously can be seen to be much more than just a data base. It is the way the makers, characterizers, testers and users of nanomaterials working across the borders of the disciplines of chemistry, materials science, engineering, biology and medicine, actually 'think' and 'act' in their quest to solve a nanomaterials based problem.

It is the creative thought process based on connecting an umbrella of nano information that defines the various pathways to achieve an objective and it is this entire way of thinking that can in principle be encapsulated in the concept of the NMG as illustrated in the Venn diagram.

4.3 Invent, Discover, Connect and Apply

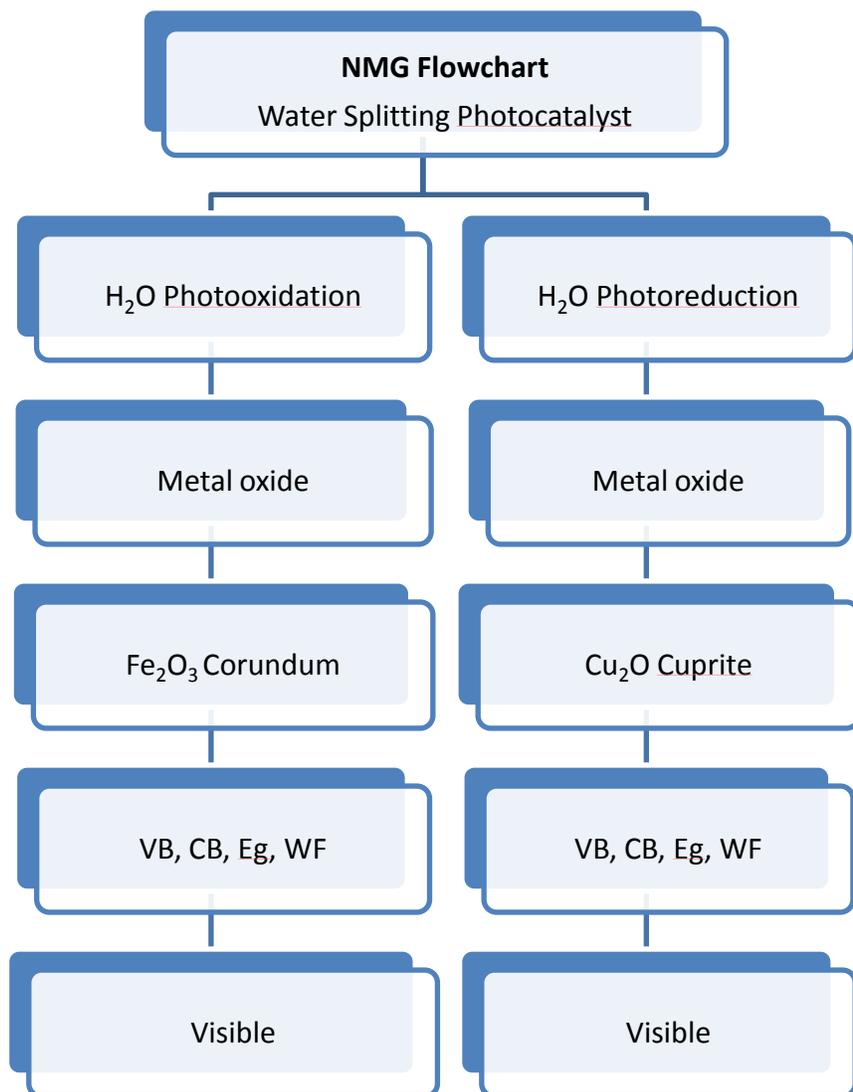
One of the major challenges for practitioners of the art of making nanomaterials with a designated purpose is the stream of consciousness that is required to actually go into the laboratory and literally know where and how to begin. It takes extraordinary background knowledge, experimental and theoretical expertise, within and across the science,



engineering and biomedical disciplines, to be able to intelligently sift through increasingly large mounds of chemical, physical and biological information on masses of nanomaterials

and connect and envision how to discover the best nanomaterial targeted for a specific task. It is not just a matter of classifying nanomaterials with a particular composition, size, shape and surface to know what it is good for, it also entails understanding how this particular combination of nanomaterials parameters work synergistically to create the properties required to provide the desired function and use of the nanomaterial.

A rudimentary attempt to express this way of thinking in the form of a NMG flow diagram, for two classes of nanomaterials, one for a targeted cancer therapy and another for a water splitting photocatalyst, is illustrated in the following schemes. The



information included in these schemes would represent the first elementary steps on a staircase of increasing complexity that would include synthesis and characterization details with associated information on chemical, physical, biological properties. The key to success

of the NMG will be to elevate its capability beyond that of just a searchable data-base of codified nanomaterials but instead one that has the capacity to stimulate integrative thinking that connect, relate, explore, analyze and transform diverse information, knowledge, ideas and experiences and make and discover connections between them into new meaning and uses in advanced materials and biomedical science and technology. It is foreseen that the NMG will eventually be able to generate blueprints for making and assembling nanometer scale advanced materials and biomedical systems.

5. What Is Next – Think Small to Think Big

Mapping the Nanomaterials Genome and responsibly exploiting its attributes are core processes of building a “human ecosystem”, one that respects “The Human Element,” as one popular Dow Chemical advertisement wisely heralds. In this human ecosystem, researchers, product and service providers, universities and governments are all playing an important role, forming a complex web of information with a flexible knowledge-creation and sharing system of communication. The entire nanoscience community is obliged to add to its diversity, growing this communication system while maintaining its stability and viability. By “diversity” we mean the construction of more and more applicable peripherals of the Nanomaterials Genome, along with the products and services those peripherals provided. Once started, this human ecosystem will be able to produce a massive output in terms of scientific, technological and socioeconomic benefits.

The Nanomaterials Genome provides a new window through which researchers, governments and the public can better observe, understand, and utilize the nano world. The immediate task and responsibilities of its builders entail first figuring out how to make this window on the nano world transparent, accessible and meaningful for the public so they are informed about this work and learn to embrace it, rather than fear it. That is one critical reason why optimization of this system is so important and must include some educational outreach programs that engage the public in the whole discovery process.

We hope the Nanomaterials Genome imagined in this Concept article, even in its embryonic form with its existing imperfections and limitations, will be enhanced and enriched by future generations of innovators whose mission will be to make the Nanomaterials Genome as useful and versatile a tool as the Human Genome, which is proving to be an indispensable tool for enhancing the health and well being of the human race.

In our view, this Big Data work is not revolutionary science. But it certainly helps accelerate and facilitate an abundance of scientific discoveries leading to a wealth of technological innovations. It's worth noting that early visionaries in computer sciences

assumed that building computers would free our minds from the burden of doing mindlessly repetitive work, and that they would enable everyone to concentrate on what the brain does best and enjoys most: imaginative work that works our imagination. Ironically, the opposite seems to be happening, as some pioneer scientists have pointed out not as a caveat but as a cautionary measure. So we need to be cognizant of this fact and factor it into the creation of a new innovative system that cultivates human creativity and fosters wonderment - one that safeguards our sense of humanity by avoiding accidentally turning this Database into little more than another ambitious information-collecting platform for serving a world of consumer automatons.

Acknowledgements

GAO is Government of Canada Tier 1 Canada Research Chair in Materials Chemistry. The strong and sustained financial support of his research by the Natural Science and Engineering Research Council of Canada (NSERC) is deeply appreciated. Todd Siler profusely thanks the World Cultural Council for connecting him and GAO during their remarkable award ceremony at the University of Tartu in Estonia, which hosted the 2011 Leonardo da Vinci World Award of Arts and the Albert Einstein World Award of Science. Chenxi Qian is deeply grateful to the Connaught Foundation for the award of a graduate scholarship.

This Concept article has been read and critically appraised by Chad Mirkin, Warren Chan, Younan Xia, Greg Scholes, Dwight Seferos, Markus Antonietti, Rafael Levy and Ludovico Cademartiri. Their thought provoking comments and insightful suggestions have proven to be invaluable and allowed us to create a much improved article.

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Figures and Captions

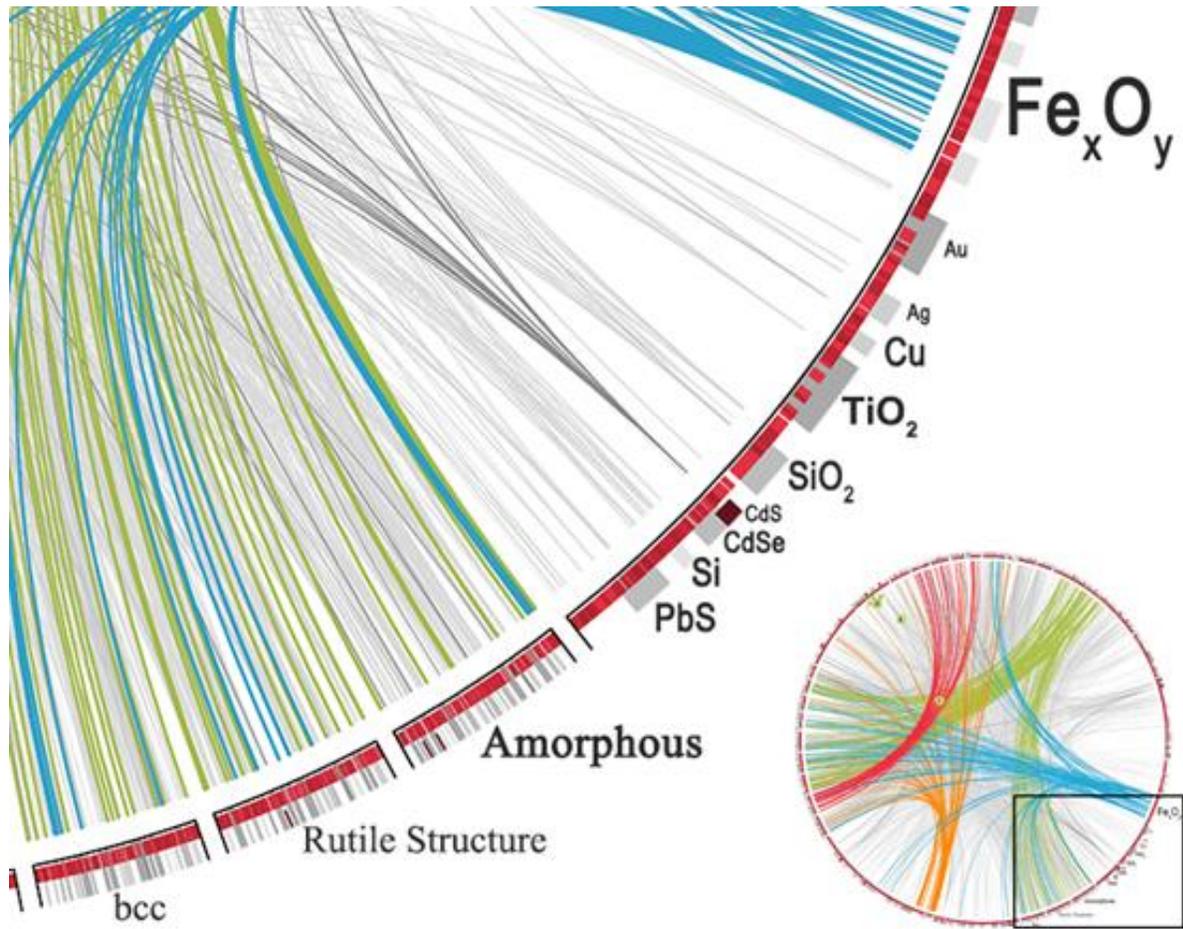


Figure 1. Circos diagram of Nanomaterials Genome composition-structure relations

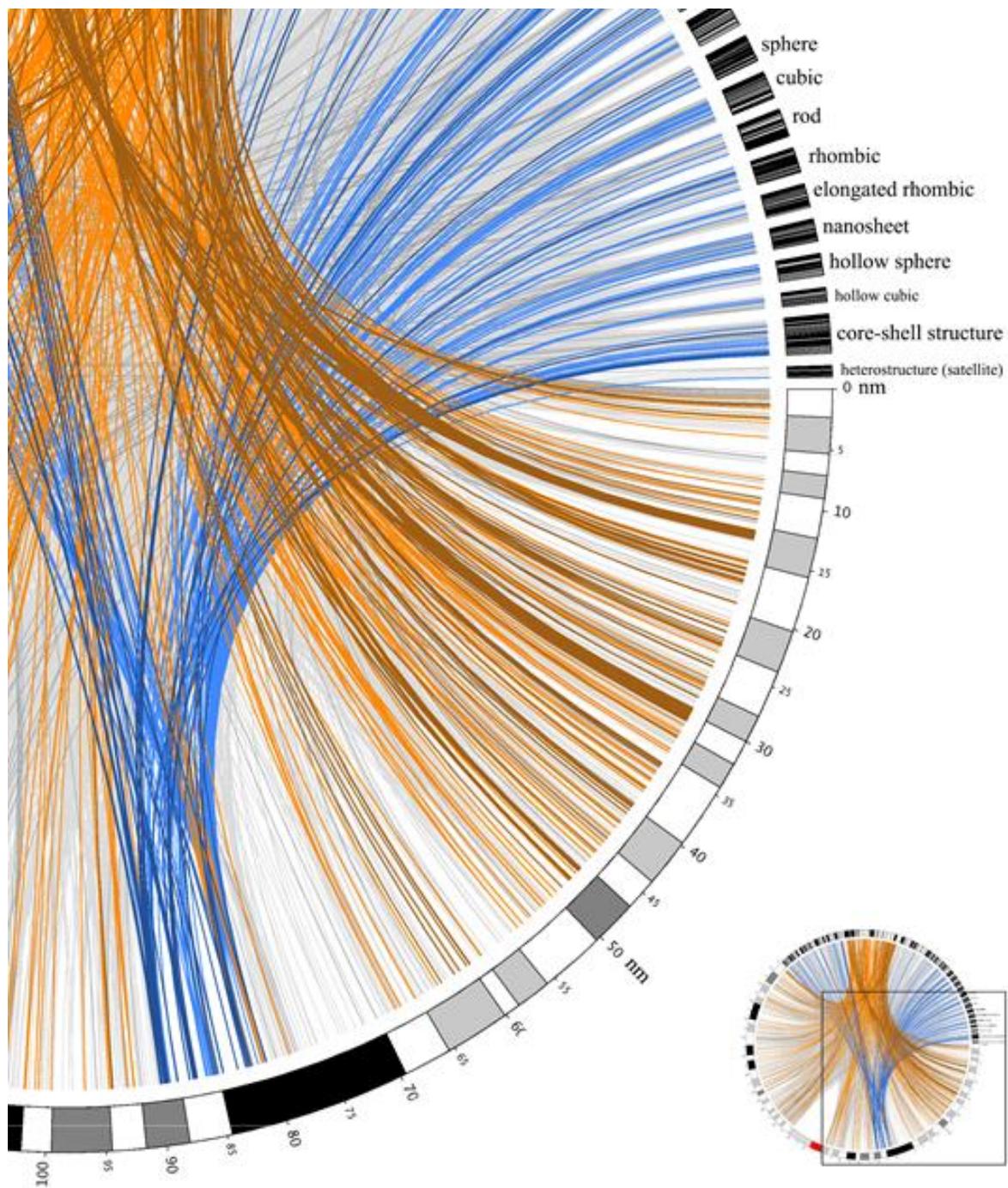


Figure 2. Circos diagram of Nanomaterials Genome size-shape relations

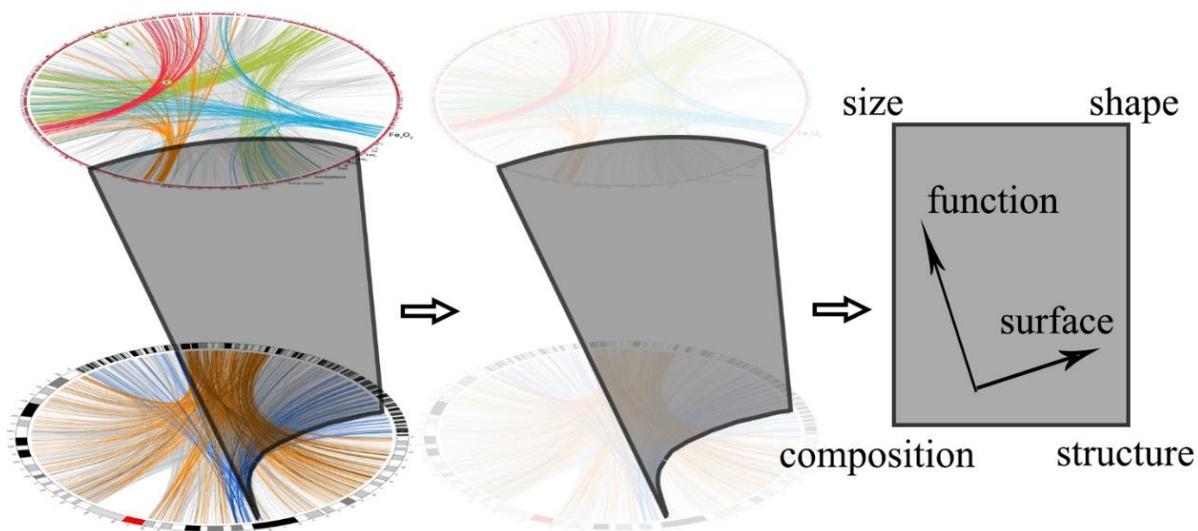
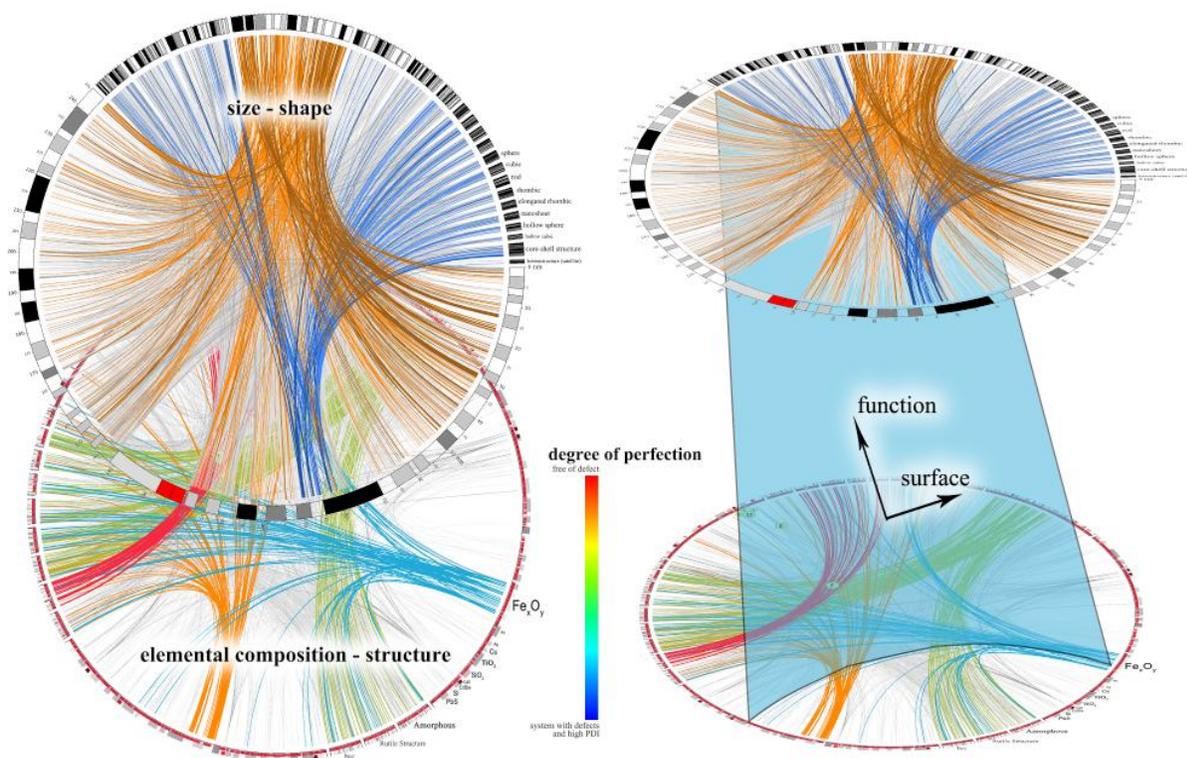


Figure 3. Two additional dimensions within the cylinder: surface and function of the Nanomaterials Genome



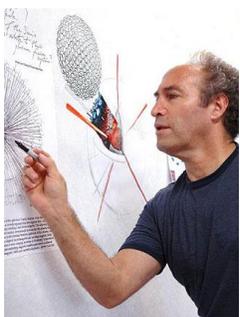
The Nanomaterials Genome - Plotted as a Circos® Kaleidoscope

Figure 4. Visualization of the Nanomaterials Genome: an example by the Circos kaleidoscope

Biographies



Chenxi Qian received a B. S. in chemistry from Department for Intensive Instructions at Nanjing University, China in 2012, with university and departmental honors. In the same year he was named a Connaught Scholar and joined the lab of Prof. Geoffrey A. Ozin at the University of Toronto as a PhD student with a focus on inorganic nanomaterials. He is currently interested in investigating the properties and applications of silicon nanocrystals with novel structures.



Todd Siler is an internationally recognized visual artist, author, inventor and consultant. He received a Ph.D. in Interdisciplinary Studies in Psychology and Art from the Massachusetts Institute of Technology in 1986, becoming the first visual artist to receive this doctoral degree at M.I.T. Siler began advocating the full integration of the arts and sciences in the 1970s and is the founder of the ArtScience Program and movement. The World Cultural Council, who awarded him the 2011 Leonardo DaVinci World Award of Arts, recognized Siler's lifelong practice of applying the "ArtScience" process to envision viable solutions to real-world global challenges.



Geoffrey Ozin studied at King's College London and Oriel College Oxford University, before completing an ICI Postdoctoral Fellowship at Southampton University. Currently he is the Tier 1 Canada Research Chair in Materials Chemistry and Nanochemistry and Distinguished University Professor at the University of Toronto. Internationally he is Distinguished Research Professor at Karlsruhe Institute of Technology (KIT) and Global Chair at the University of Bath. He is renowned for pioneering research and teaching accomplishments in nanochemistry that defined, established and popularized this rapidly expanding trans-disciplinary field, a cornerstone of modern chemistry and a foundation for innovative nanotechnology in materials science, engineering and medicine

30. Todd Siler's Nano World – Think Billionths of a Meter

The inaugural ArtNano works, NanoWorld, www.artnanoinnovations.com, sponsored by Ronald Feldman Fine Arts New York, www.feldmangallery.com, is being held at The Armory Show, Pier 94, New York, on March 6-9th, 2014, www.thearmoryshow.com.



The Trillion Dollar Nano Solution to Artificial Photosynthesis, Todd Siler, 2014, ArtNanoInnovations®

Working with renowned artist Todd Siler, www.toddsilerart.com, I have experienced, more or less every day for the past two years, the emergence of his artistic vision of the Nano World. This happened literally from the bottom-up, where I had the pleasure of observing first-hand the beautiful transformation of my Nano World, www.nanowizardry.info, into Siler's ArtNano works, www.artnanoinnovations.com. Sketch-by-sketch, color-by-color, mold-by-mold, he has transformed images and ideas of the nanomaterials developed in my research lab everyday into thought-provoking paintings and sculptures.

My scientific career began deep down in the nanometer-scale world of materials more than four decades ago. It is a truism that much of my inspiration working in this field has derived from the aesthetics of the shapes and colors that pervade this small world, and their orchestration into purposeful technologies.

Today I am enthralled to see how Todd Siler, in a glorious burst of brilliant hues, daring images and organic forms, has captured the essence of this tiny world in a myriad of stirring and inspiring artistic works. Within each of Todd Siler's abstract impressions of the Nano World, I see the heart, I touch the pulse, and I feel the excitement of Nanotechnology. This is a field I helped mold from the atom up and Todd Siler now challenges us, through his art work, to visualize the Nano World from the top down.

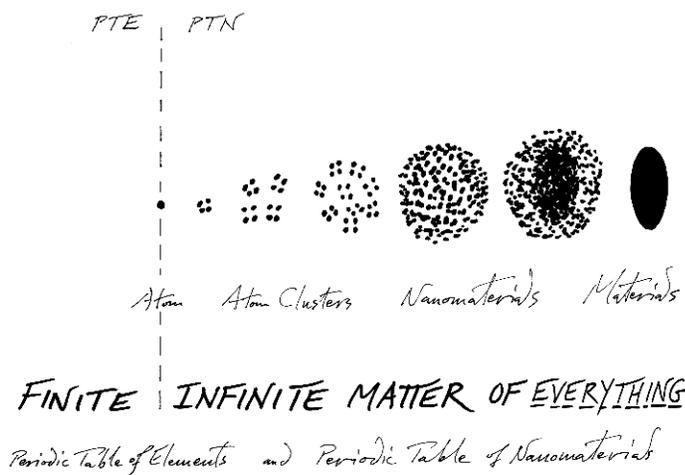
Often, without even knowing, the Nano World is touching the lives of all of humankind, through its global impact as a cornucopia of advanced materials and biomedical



Nano Scale – Think Billionths of a Meter, Todd Siler, 2014, ArtNanoInnovations©

chemistry and made into countless nano systems, built from individual components with nano meter scale dimensions. These versatile nano components can be fashioned in a spectrum of shapes resembling spheres, wires, rods, sheets and tubes. And these shapes, in turn, can be assembled into hierarchical architectures intentionally designed to have form and function frequently akin to those found in the natural world.

In a profusion of colors and forms, Todd Siler’s Nano World ingeniously captures the ‘Nano Advantage’, the distinctive feature of nano scale materials that differentiates them from all other materials at larger scales whereby their behavior changes with size. Amazingly, even the addition or subtraction of a single atom can influences the chemical, physical and



Nature Invents – Humanature Innovates, Todd Siler, 2014, ArtNanoInnovations©

technologies. These are used in numerous practical things many of us take for granted, in large part because we neither see them without the aid of sophisticated microscopy nor are aware of how they work. Consequently, we may not appreciate how they evolved from the bottom to have the transformative effects they have on our day-to-day existence.

At the core of the Nano World is a periodic table of about a hundred elements. They have been combined in innumerable ways through

biological properties of nano scale materials. From this infinity of choices emerges the ‘Nano Advantage’ with its promise of infinite opportunities for the discovery of new nano science and a springboard for the development of a wealth of new nano technologies.

Todd Siler has ‘metaphormed’ (connected and transformed) the panoscopic vision of the world of integrated nano systems into his symbolization of the Nano World. Moreover, these works of art help us

creatively see, think, discover, and learn about how the human mind and nature connect diverse information and ideas, transforming them into new meanings that can spark innovative thinking in all of us.

Todd Siler's passion to engage our imagination, to spark curiosity, and inspire wonder by illuminating the hidden Nano World in new ways through his metaphorical art work marks an extraordinary contribution to both art and science. It is a joy for me to have facilitated and experienced the creative way he has portrayed my Nano World of Science in his Nano World of Art.

31 A Fossil Fuel Free World

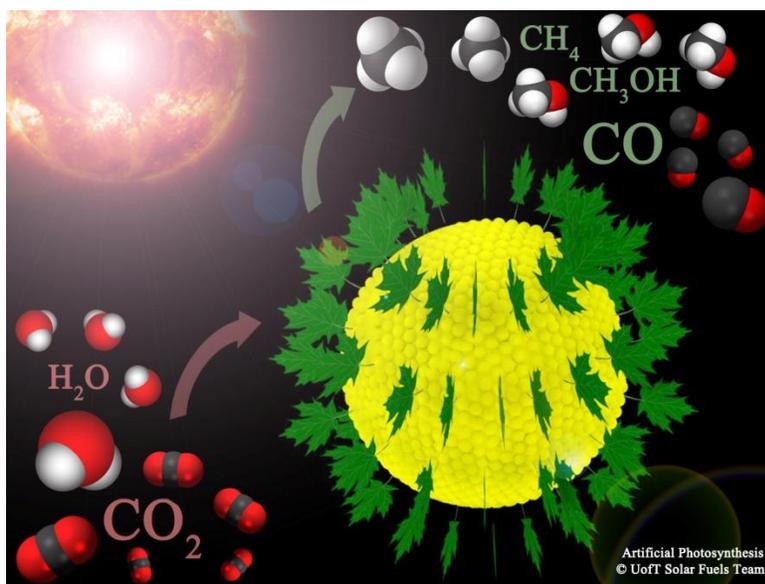


Illustration depicting how the leaf's photosynthetic machinery for processing carbon dioxide, water and sunlight to solar fuels such as carbon monoxide, methane and methanol, is integrated into the nanoworld - graphical illustration courtesy of Chexi Qian.

Carbon Dioxide

Economy Imagine a time in the not-too-distant future when all our legacy fossil fuels have been depleted because of our incessant demand for energy and chemicals, obsession with consumerism and never ending drive for economic growth. Ignoring for a moment that a global catastrophe will almost certainly ensue, what will be left for our newly fossil fuel free society but carbon dioxide, the combustion product of our long-time addiction? And there will be plenty!

In a fossil fuel-free world it is unlikely that our global hunger for energy, chemicals, consumerism and growth will be satisfied by renewable sources of energy. So what choice will we have? I would suggest that we need to learn how to run the world in reverse: we need to make our carbon dioxide-rich atmosphere our source of fuels and chemicals. The sun then becomes our fusion reactor, the engine to sustain life.

In order to rise to the challenge of developing a global economy founded on carbon dioxide it is vital to get government, investment, and university and industry leaders, together with the public, to understand that carbon dioxide is not a waste product to dread. Instead carbon dioxide should be showcased as a feedstock for making fuels and chemicals, a bountiful resource of latent carbon spread uniformly around the globe. With the right chemistry it can be transformed into a boundless supply of carbon neutral renewable energy and chemicals to sustain and support a high quality of life for eternity.

This vision of carbon dioxide as the powerhouse that drives a new economy is based on artificial photosynthesis. This is the approach upon which a sustainable future could be founded. The support of the global community must be enlisted to make it happen.

Our journey to mimic nature has just begun. Imagine a carbon dioxide economy inspired by biological photosynthesis, a process honed to perfection over an evolutionary time scale.

Global Challenge Copying the leaf is a most appealing vision, but it is not yet a reality. No material is known today that can use energy from the sun to convert carbon dioxide into a storable and transportable fuel or chemical feedstock at an efficiency that outperforms biological photosynthesis and a scale that can handle hundreds of billions of tons of carbon dioxide a year. This is a challenge for the global community, and it is incomparable in complexity and magnitude to any other faced before. The consequences of 'willful blindness' on climate change, namely ignoring the obvious perils of continuing to increase the concentration of anthropogenic carbon dioxide in our atmosphere, could be more deaths than all those caused by war, terrorism, famine, poverty and disease throughout the history of humankind.

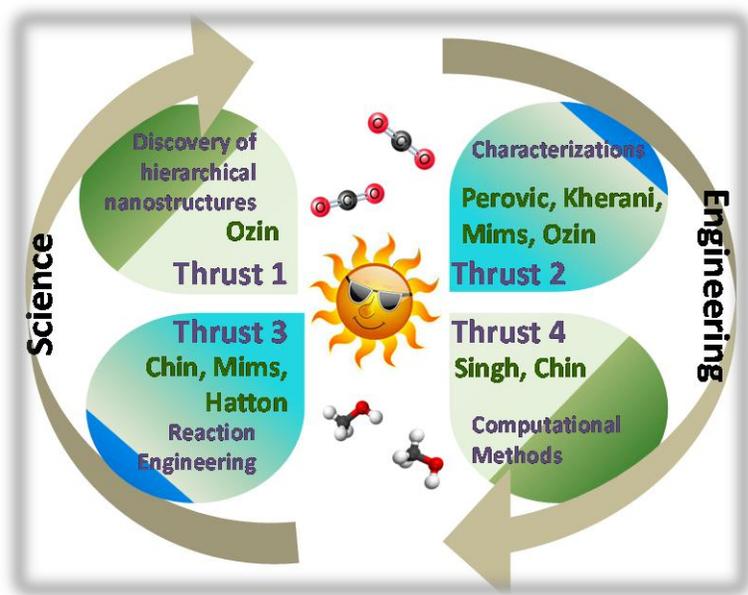
The scientific challenge is to discover a class of materials made of earth-abundant, low cost, sunlight stable and non-toxic materials. Such materials would then be able to generate solar fuels and chemicals, such as carbon monoxide, methanol or methane, from carbon dioxide at a technologically significant rate and efficiency at global proportions.

The Payoff If this Utopian dream is realized it will forever change the way we see carbon dioxide: instead of a foe, it will become our greatest friend. The development of a practical artificial leaf will in turn seed the development of a global CO₂ economy that will provide a carbon neutral replacement for fossil fuels. Recycling carbon dioxide in our atmosphere and converting it to solar fuels and solar chemicals seems to be the only silver bullet solution to enable the human race to sustain its existence in a world depleted of fossil fuels.

What will it take? As the debate over greenhouse gas emissions and climate change intensifies with no signs of consensus being reached any time soon, governments in the United States, Europe and Asia have already determined the value of investing considerable funds in artificial photosynthesis research and development.

An impressively large global network of scientists working on artificial photosynthesis through team science and collaborative research emerged in 2012 (www.solar-fuels.org). This network is composed of a dozen European research partners, including the Solar-H₂ Network, supported by the European Union, and the Institute for Chemical Energy Conversion, a 100 million Euro foundation in Germany supported by Max-Planck Society. The US Department of Energy (DOE) Joint Center for Artificial Photosynthesis (JCAP), led by the California Institute of Technology (Caltech) and Lawrence Berkeley National

Laboratory, has been awarded US\$ 122 million over 5 years to demonstrate a scalable solar fuels generator using earth-abundant elements that robustly produces fuel from the sun at ten times the efficiency of current crops. Some Energy Frontier Research Centers (EFRCs) funded by the US DOE are focused on solar fuels-related endeavors, including the Argonne-Northwestern Solar Energy Research (ANSER) Center led by Northwestern University, the Center for Bio-inspired Solar Fuel Production (BISFuel) and Light-Speed Solutions and Light Works led by Arizona State University, and the Center for Solar Fuels led by the University of North Carolina. Other prominent international examples include the Energy Futures Lab at Imperial College London, the Australian Centre of Excellence on Electromaterials Science (ACES) Energy Research Program and the Solar Fuels Lab at Nanyang Technological University in Singapore. In Japan, the Advanced Low Carbon Technology Research and Development (ALCA) project aims to produce a carbon-free fuel based on hydrogen peroxide. In South Korea, the Pohang Steel Company is contributing to the Korea Center for Artificial Photosynthesis (KCAP). In China, the first national lab for clean energy research has been set up with the broader mission of also reducing carbon emissions.



Synergistic integration of research thrusts of the University of Toronto solar fuels team that embrace the design, synthesis, structure determination and properties measurements, computational modeling and reaction engineering of nano systems capable of carbon dioxide photo-reduction, - illustration courtesy of Chandra veer Singh.

At the University of Toronto a multidisciplinary solar fuels team was founded in 2012 and has been investigating a portfolio of nanostructured materials that are active for the gas-phase photo-reduction of carbon dioxide to solar fuels like carbon monoxide, methane or methanol.

The focus of the team's research on a gas-phase process is predicated upon their collected belief that the development of a global scale process capable of handling hundreds of billions of tons of carbon dioxide annually, which would represent the largest chemical factory ever on earth, for a host of practical and economical reasons is unlikely to

work in aqueous solution.

To embrace all aspects of the problem the expertise of the University of Toronto solar fuels team has been designed to crisscross the borders of experimental and theoretical materials chemistry and nanochemistry, chemical, materials, and optical and photonic engineering. Our collective skill-set and know-how enables us to effectively collaborate on the grand challenge of how to discover a champion artificial photosynthesis material that can transform gaseous carbon dioxide at a technologically meaningful efficiency and scale.

The thrust of our research is to understand at a fundamental level the relations between the synthesis, composition, structure and properties of champion nanostructured materials that confer upon them the capacity to function as efficient gas-phase carbon dioxide photocatalysts.

All of our experiments employ the full gamut of diffraction, microscopy, spectroscopy, electrical, optical, thermal and adsorption analytical techniques to define structure-property relations of photocatalysts. We use isotope-labeled reagents to identify reaction intermediates and products, to elucidate kinetics and mechanisms, and to distinguish real products from artifacts arising from ubiquitous carbon contamination problems.

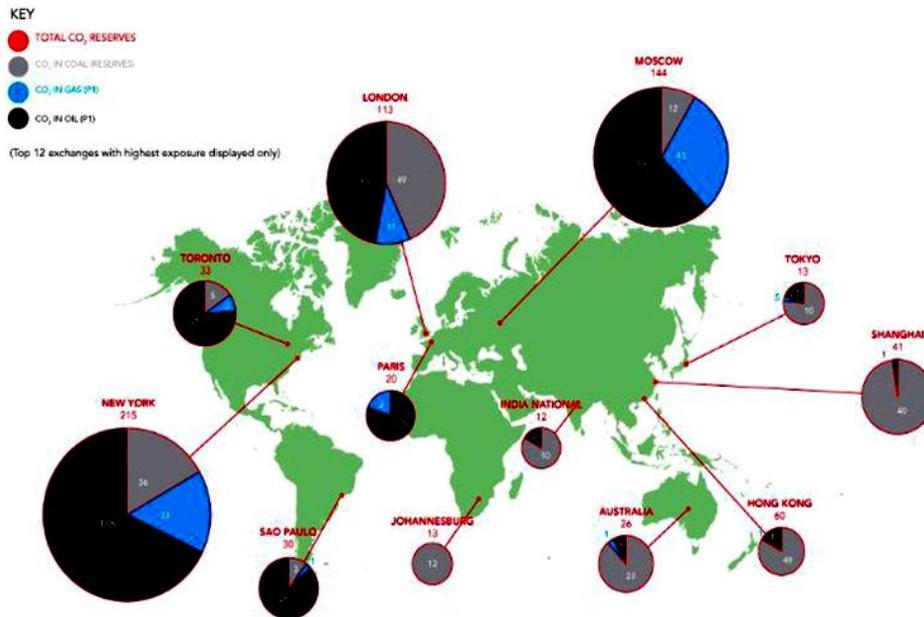
With this knowledge, photocatalytic conversion rates and efficiencies of materials can be engineered from a laboratory prototype and optimized to a technologically important archetype able to make solar fuels from carbon dioxide and sunlight at a globally significant scale.

We are all Passengers on Spaceship Earth It is clear from all the research activity on artificial photosynthesis that scientists understand the urgency of learning how to harness the energy of the sun to transform carbon dioxide into a renewable source of energy and chemicals to sustain life on earth. An equally important challenge is to change the perception of policy makers and the public in the fastest and most effective ways. We need to convince the world that carbon dioxide is a friend not a foe and can be used to carry and sustain our way of life long after the fossil fuel reserves have dried up.

By working together as a global community on the science and technology of artificial photosynthesis, carbon dioxide could be our savior rather than our downfall in the fossil fuel free world of the future.

A Burning Closing Thought Last year the International Energy Agency cautioned that a [third of the world's fossil fuel reserves must be put off limits](#) until 2050 if

humanity is to stand a chance of avoiding catastrophic climate change (<http://www.worldenergyoutlook.org/publications/weo-2012/>).



Map showing the distribution of fossil fuel reserves distributed between the top twelve stock exchanges in the world together with their respective listed number of Giga Tons equivalents of carbon dioxide of current coal, oil and gas reserves – <http://www.carbontracker.org/wastedcapital>

<http://www.carbontracker.org/wastedcapital> and trillions of dollars in revenues, <http://www.carbontracker.org/wastedcapital>. Investors are rightly concerned about the risks associated with multinational oil, coal and gas companies that could be left with trillions of dollars of stranded assets if carbon taxes and other emission limits reduce the demand for fossil fuels (<https://www.ceres.org/files/car-mats/car-release/companies-that-received-car-letter/>). Why, then, would they invest in climate catastrophe?

In a fossil fuel world whose unmitigated freedom to operate as usual is curtailed by the threat of climate devastation, a carbon dioxide economy based on artificial photosynthesis can come to the rescue not only to the benefit of all those who believe and invest in the initiative, but also to sustain the health and well-being of humankind.

In this context it is worth noting that a recent report claimed if governments ever issued an edict to curb the use of fossil fuels because of climate change it could put \$6 trillion in fossil fuel reserves in jeopardy (<http://gofossilfree.org/files/2013/>).

In this scenario it has been [estimated that a](#)

32. Real or Artifact: CO₂ Photo-Catalysis versus Carbon Contamination

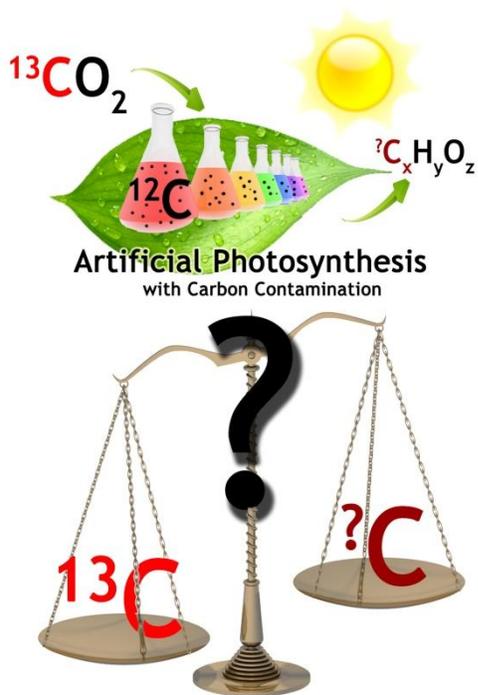
Because of energy and climate concerns, research into carbon dioxide capture and utilization has skyrocketed in the past decade. Of all the different approaches proposed to solve this problem the only one that appears to offer the capacity to have a significant impact on greenhouse gas emissions, is a solar-to-chemical conversion gas-phase artificial photosynthesis process with an efficiency that can surpass natural photosynthesis. The goal is to sequester carbon dioxide either from concentrated sources and/or thin air and transform it to an organic fuel or chemical feedstock using sunlight as the only energy input.

The intergovernmental panel on climate change, the trillion tonne communiqué and the carbon exchange in 2014 aptly put the intertwined climate and energy conundrum into stark perspective with some key facts and messages that include:

- Consensus on a trillion tonne carbon limit to prevent global warming above 2°C
- Fossil fuel share of that limit = 2,900 Gt CO₂
- Current total CO₂ emissions = 1,430 Gt CO₂
- 50% of troposphere space for CO₂ is used up
- 66% chance at keeping global temperature rise $\Delta T < 2^\circ\text{C}$
- Remaining fossil fuels should stay in the ground
- Stranded carbon assets have created a carbon bubble for global investments
- Regulation, guidance, transparency needed to shift capital market carbon practices
- The world needs to get to net zero annual emissions by 2050 or shortly thereafter

Clearly we need an economically competitive global artificial photosynthesis silver bullet initiative to help solve this problem.

To amplify on the science and technology of artificial photosynthesis, the Holy Grail is to discover a carbon dioxide photo-catalyst that is at least an order of magnitude more efficient than natural photosynthesis, one that can convert at least 10% of sunlight into organic fuels or chemicals.



Leaf Mimic - Fact or Fiction. Graphic illustration courtesy of Chenxi Qian

Translated into the recommended United States Department of Energy metric of 10% efficiency for the solar powered transformation of carbon dioxide to carbon monoxide, methane or methanol requires the discovery of a photo-catalyst that can achieve conversion rates of millimoles per gram of catalyst per hour at a solar irradiance of AM 1.5.

Research on photo-catalytic water splitting into hydrogen and oxygen greatly outweighs that on carbon dioxide reduction to organic chemicals and fuels where the bulk of the work today is conducted in the aqueous phase with relatively little effort being expended on the more practical gas phase process. For water splitting in the aqueous phase state-of-the-art photo-catalysts achieve rates of $10 \text{ mmol gcat}^{-1} \text{ hour}^{-1}$ with photonic efficiencies of 56%

Of the dozen or so reports that do describe gas phase carbon dioxide photo-reduction the photo-catalyst is based on single or multi-component nano-structured materials, mainly metals and metal oxides, and organic products are usually characterized by gas-chromatography.

Generally speaking the majority of reported carbon dioxide conversion rates and efficiencies are currently well below the US Department of Energy 10% target required for a practical artificial photosynthesis process that could be engineered at a large enough scale to have a meaningful effect on the reduction of greenhouse gas emissions.

Even though valiant measures are taken through solvent and chemical removal, oxygen plasma and high temperature oxidation post-treatment methods to strip nano-structured photocatalysts of adventitious carbon, the problem of artifacts arising from such carbon residues can remain.

The main concern comes from carbon contamination on the surface and within the bulk of photo-catalysts. This kind of carbon residue, which can originate from organics in the environment as well as from incomplete removal of solvents, precursors, surfactants and additives and their decomposition products, can complicate the analysis of organic products by gas-chromatography, giving artificially elevated rates of photo-conversion.

This is a problem that can arise from carbon residues as low as 0.001- 0.1 wt % of the photo-catalyst, which can only be revealed and quantified by $^{13}\text{CO}_2$ isotope tracer

experiments best analyzed by on-line and coupled gas-chromatography mass-spectroscopy.

Very few literature reports have included this kind of isotope tracing data so any conclusions drawn about photo-catalysts boasting champion photo-conversion efficiencies that lack this information must be considered dubious at best.

Of the very few that have employed $^{13}\text{CO}_2$ isotope labeling it is important to realize that it is not only evidence of ^{13}C labeling that matters but also the $^{12}\text{C}/^{13}\text{C}$ ratio of unlabelled to labeled organic photo-products, enabling one to define the selectivity towards real products of carbon dioxide photo-catalysis relative to artifacts of deleterious carbon contamination.

Another pitfall that can go unrecognized with $^{13}\text{CO}_2$ isotope labeling experiments which are required to differentiate reality from artifact in the formation of solar fuels is the specified purity of the $^{13}\text{CO}_2$ from the supplier, which for the cheaper lower grade ^{13}C enriched carbon dioxide often contains significant amounts of $^{13}\text{CH}_4$, so buyer beware!

Without this pivotal isotope tracer confirmatory information it is exceptionally hard to judge fact from fiction in the burgeoning field of gas-phase carbon dioxide photo-catalysis, a difficulty which is severely impeding the rate of progress towards the vision of global artificial photosynthesis. Hopefully practitioners in this vitally important and rapidly expanding field will realize this predicament exists and will make every effort to improve the current situation.

On closing it is worth mentioning that unrecognized carbon contaminations of carbon dioxide reduction nano-structured photo-catalysts can have a disastrous affect on the work and lives of researchers and students who expect published work in the literature to be reliable and reproducible. My solar fuels group knows firsthand how much time, effort and money can be wasted pursuing promising leads published in top-rank, peer-reviewed journals that prove to be specious. Unfortunately such false positives can terribly mislead newcomers trying to enter the field with similarly devastating consequences.

It is instructive to recognize however that water splitting photo-catalysts have evolved from conversion rates of nanomoles to milimoles per gram of catalyst per hour within a decade, so there is no reason to believe carbon dioxide photo-catalysts cannot follow suit.

33. Is Semiconductor Photocatalysis Photochemical or Thermochemical or Both and Do We Care?

Around 35 years ago in a classic paper (Journal of Catalysis, 1980, 66, 383-390), Childs and Ollis asked a profound question: 'Is Photocatalysis Catalytic?'

They wanted to understand (i) whether or not a photocatalytic reaction was truly catalytic rather than stoichiometric from knowledge of turnover numbers or turnover frequencies and (ii) how these photocatalytic reactions compare to thermocatalytic ones, accessed from reaction rates per unit surface area.

This question is just as applicable today, even after the publication of more than 17,000 papers on semiconductor-based organic photooxidation, water photolysis and carbon dioxide photoreduction reactions.

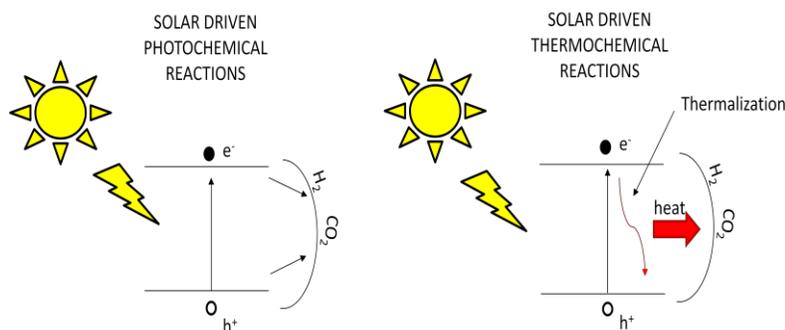


Figure 1 Photocatalysis: light, heat or a combination of both?

This important issue is encapsulated in Figure 1 which illustrates light driven versus heat driven contributions to these 'light-assisted' processes. On the left side of Figure 1, excited charge carriers interact with adsorbed surface species to enhance reaction rates. On the right side of Figure 1, excited charge carriers thermalize and supply heat energy to enhance reaction rates. The questions are which of these processes dominate and what their contributions are? This is especially pertinent for the case of gas-phase photocatalysis where conduction and convection heat losses are expected to be small compared to the aqueous phase analogue.

The efficiency of most photocatalytic reactions will increase with the intensity of the light and the number of photogenerated electron-hole pairs. This implies the requirement of strong absorption of light by the photocatalyst. Subsequently, photoexcitation at energies

An equally important question relevant today, especially in the rapidly emerging field of solar fuels and solar chemicals, is what proportion of a claimed photocatalytic reaction is light driven, heat powered or a combination of both?

This important issue is encapsulated in Figure 1

higher than the electronic band-gap will result in heating of the photocatalyst from rapid phonon relaxation, with an accompanying increase in the local temperature. Excitation below the energy of the band-gap should have no effect unless sub-gap defect states abound. This is likely the scenario operating in reported research of CO₂ photoreduction on 'black' catalysts, exemplified by Ru-RuO_x and Ni-NiO_x nanomaterials, which begs the question whether they are light powered or heat driven or both?

As most photocatalysts these days are high surface area nanoscale particulate materials, it may be the local temperature of the nanoparticle that controls the reaction rate and efficiency rather than the global temperature of the support of nanoparticle film. The latter is usually measured with a thermocouple and can be very different from the local temperature.

An especially pressing question is how to decide on the best way to go scientifically, technologically and economically in the production of solar fuels and solar chemicals using greenhouse gas (CO₂) as the feedstock. This is particularly urgent as we are currently in the midst of an intense international effort to develop technologies capable of converting CO₂ into a fuel or a chemical. Discovering materials able to positively improve this process on a large scale, driven thermochemically and/or photochemically, is a critical step towards ameliorating greenhouse gas emissions and enabling a carbon-neutral, renewable energy, sustainable economy.

In current industry practice there are many catalysts and processes known for making fuels and chemicals from CO₂ some of which are shown below:

Sabatier Reaction: $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$

Methanol Synthesis: $\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$

Reverse Water Gas Shift: $\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$

Methane Synthesis: $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2$

Methanol Synthesis: $\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 3/2\text{O}_2$

Carbon Dioxide Splitting: $\text{CO}_2 \rightarrow \text{CO} + 1/2\text{O}_2$

Methane can power electricity-generating stations and provide heating for buildings. Methanol can drive fuel cells, run automobiles and act as a precursor for ~30% of industrial chemicals. Lastly, carbon monoxide can be used as a precursor for making hydrogen, methanol and liquid hydrocarbons according to the reactions:

Water Gas Shift: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

Methanol Synthesis: $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$

Fischer-Tropsch Synthesis: $(2n + 1)\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$

The energy required to drive these processes is dominated by fossil fuels. However, increasing amounts of renewable energy, from wind and solar, tidal and hydroelectric, nuclear and geothermal are coming on stream to minimize the depletion of legacy resources and cut back on associated carbon dioxide emissions.

The idea of utilizing power from the sun to make electricity has a long history in the annals of solar cells whereas the vision of making solar fuels and chemicals from the sun is of a more recent vintage. While great scientific and technological strides have been made over the past four decades towards the realization of a renewable energy resource from the photolysis of H_2O to H_2 , the photocatalytic reduction of CO_2 remains a significant challenge and has been studied to a much lesser extent. This is especially true for gas-phase CO_2 photoreduction, which is increasingly being considered as the only practical way of scaling the process to sufficient proportions to have a significant impact on decreasing global greenhouse gas emissions.

As the heterogeneous catalytic reactions listed above for converting CO_2 to fuels and chemicals are thermally activated, the pursuit of using light and/or heat from the sun to drive these reactions has become an active area of research. In both cases, research has been aimed at the development of optimized photochemical or photothermal catalytic materials, photo-thermal reactors and solar-light concentrators.

While the construction of the most efficient reactors and concentrators are engineering obstacles, the ongoing process of discovery for the most active materials is a chemical challenge. Hence, deciding whether the chemical reactions are light driven, heat driven or both is an important issue, as illustrated in Figure 2. In this respect, experiments need to be devised that would permit the disentanglement of photochemical and thermochemical contributions to observed heterogeneous reaction rates and efficiencies. This can be done by monitoring the temperature, wavelength and intensity dependence of the reactions in the dark versus in the light.

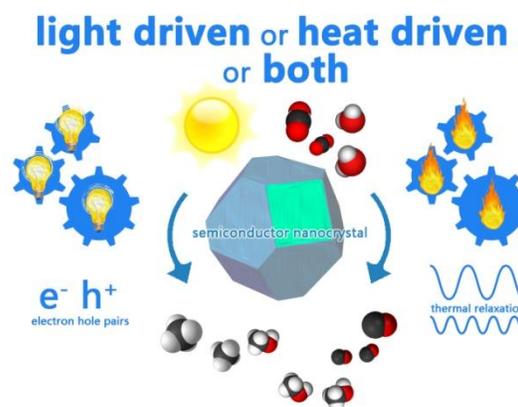


Figure 2 Is your photocatalytic reaction powered by light or heat or both? Graphical illustration courtesy of Chenxi Qian

It is worth noting photon to chemical conversion efficiency in principle can reach 10-20 % whereas thermal to chemical conversion efficiency is usually lower, so from this point of view photocatalysis is advantageous. Also exothermic reactions can be easily catalyzed thermally whereas for endothermic ones catalysis by light can be an efficient way to supply the energy needed to drive the reaction.

The heat is now on the implementation of a new CO₂ economy for the production of solar fuels and solar chemicals using light from the sun!

34. This is your Brain on Art: Metaforming Nature

Boulder Museum of Contemporary Art Lecture Series



The collaboration between arts scientist Todd Siler and nanoscientist Geoffrey Ozin www.artnanoinnovations.com began with a shared interest in how the integration of art and science can generate innovative frameworks for a sustainable future. With the global population predicted to reach 9.6 billion by 2050 accompanied by mounting demand for fossil fuels to spur economic growth, the fate of humankind seems tenuous at best.

Ozin's research into nanochemistry, however, suggests an antidote to the fear of environmental collapse and mass extinction. If nanotechnology can mimic a process like photosynthesis in plants then carbon dioxide ceases to be a noxious gas and becomes a resource. Siler's art gives form to these concepts, particularly how the brain interacts with nature as it connects and transforms everything nature creates in personally meaningful and purposeful ways.

At the CU Art Museum, Siler's large-scale installation *Metaphorming Nature* features a selection of artworks that interpret what nature makes and what we make of nature, Figure 1. The installation replicates the limbic system - the heart of the human brain - where intuitions, feelings and emotions, including fear, are integrated and interpreted. The immersive environment presents a mosaic of interrelated paintings, sculptures, drawings, and photomontages produced over the last four decades. Other artworks visualize nano-scale and macro-scale processes and physical matter,

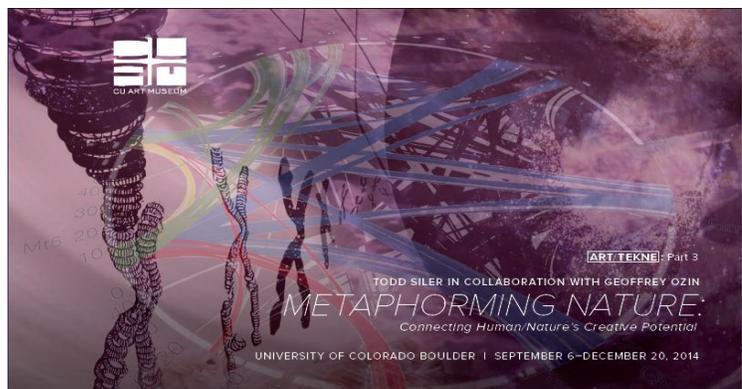


Figure 1 Courtesy of the Colorado Museum of Modern Art

in which sparks between atoms seem to transform into a cosmos of possibilities. With no stabilizing horizon line, the large swathes of fiery reds and cool blues at play in these paintings impact cognition and also activate in the mind fear of the unknown and the boundless represented by the infinitesimal and infinite. Likewise, Ozin's research into new nanotechnology with global ramifications on renewable energy solutions to climate change through the paradigm of a new carbon dioxide economy is at once hopeful and a little bit scary.

35. Do We Have a Plan B?

The Intergovernmental Panel on Climate Change (IPCC) reported in October 2013 that it is 95% certain humans are the cause of anthropogenic climate change from the increasing concentrations of carbon dioxide greenhouse gas emitted into the atmosphere from the combustion of fossil fuels. In March 2014 the IPCC announced that our planet now faces irreversible climate change and our only choice going forward is an assessment of risk, vulnerability, mitigation, adaptation and cost (see reference: <http://www.ipcc.ch/>).

Let's refer to this 'burn-and-adapt' scenario as Plan A. It appears to me that what is missing from the ongoing greenhouse gas climate-change debate, is a credible Plan B, namely an alternative course of action for use if Plan A should fail.

What I mean by Plan B is a science-based solution with an accompanying action road-map to enable a global scale energy transition from our current one – which is dependent on the finite supply of oil, coal and gas - to one founded on a new energy source that would be able to sustain a global society; particularly after the emission of an estimated Trillion tons of CO₂ into the atmosphere through the burning of fossil fuels (see references: <http://trillionthtonne.org/>, <http://www.climatecommuniques.com/>, <http://www.carbontracker.org/>).

CO₂ is the thermodynamic 'default molecule' of fossil fuel combustion. Hence, I believe a Plan B strategy can be built around a 'New CO₂ Economy', the premise of which is (i) CO₂ is not a waste product to fear, (ii) CO₂ is a bounteous carbon resource, (iii) CO₂ belongs to all and (iv) through innovative chemistry CO₂ could provide a sustainable supply of fuels and chemicals for the rest of time.

In the energy transition to Plan B, the fossil fuel industries can continue their exploration for oil, gas and coal in order to replenish the atmospheric CO₂ feedstock. These CO₂ emissions are needed for Plan B in order to maintain sustained petrochemical and chemical production using CO₂ driven by light and heat from the sun. Once this transition is completed, atmospheric CO₂ can provide a sustained source of feedstock for fuel production via sunlight and depletion of legacy fossil fuels from the earth could then be stopped. At steady state, a closed energy cycle can be reached whereby CO₂ is converted to solar fuels, which is consumed to produce CO₂, which then can be used to convert to solar fuels again.

In order to expand upon the above statement, we direct our attention to well-documented large scale, gas-phase, heterogeneous catalytic processes which are already able to convert CO₂ into fuels and value-added chemicals in the petrochemical and chemical industries. However, these processes are invariably thermally driven and require an initial input of

energy. More often than not, the energy used to power these processes are usually generated through the burning of fossil fuels, either to produce electricity or heat, which in themselves produce more CO₂.

I would argue therefore that the infrastructure exists for the development of a global scale CO₂ capture and conversion economy, which leads to recycling of CO₂ from the atmosphere to fuels and value-added chemicals. It can however only be sustained until the point in time when fossil fuels are depleted and the only thing left is a plentiful supply of CO₂ in the atmosphere.

What is missing in the transition from a fossil fuel based economy to one based on CO₂ is a globally sustainable supply of clean energy to enable the heterogeneous catalytic processes that can transform CO₂ into fuels and value-added chemicals. In this, nothing can match the massive scale, pristine nature and essentially infinite lifetime of Nature's fusion reactor, the sun.

The grand challenge for science and engineering is to discover novel materials and processes that can efficiently and economically capture CO₂ and harvest both light and heat from the sun and convert CO₂ into fuels and chemical feed stocks. This can be exemplified by the economically viable production of CO, CH₄ and CH₃OH at a relevant rate and scale.

To place this grand challenge into perspective, a conversion rate of 10 moles of CO₂ per hour per gram of catalyst translates into a conversion rate of 1 Gigaton of CO₂ per year per ton of catalyst when placed in 250 sunny locations. In practical terms, this can be achieved through the use of 20,000 solar panels with an area of one square meter, containing a 10 micron thick catalyst film made from a MO_x nanomaterial with average density of 5 g.cm⁻³.

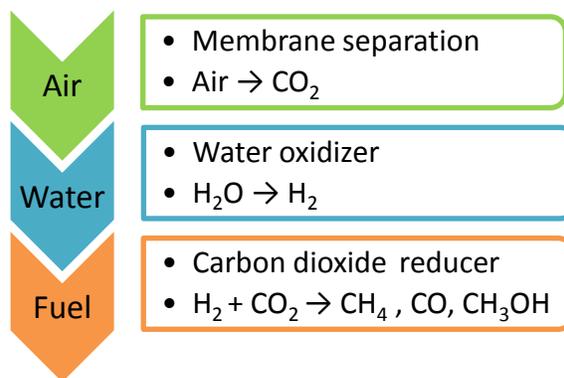
One can appreciate from this 'back-of-the-envelope' calculation that the development of a global scale CO₂ economy could readily handle the yearly global emission of 40 to 50 Gigaton of CO₂. This conversion rate is sufficiently high in that it can maintain a steady-state concentration of CO₂ in the atmosphere as well as produce the carbon equivalent of fuels and chemicals, thereby solving our climate and energy dilemma in one fell swoop.

In this context it is worth noting that Ivanpah - the world's largest solar thermal power station located in the Mojave Desert (<http://www.brightsourceenergy.com/>) - is currently producing high-value electricity and steam from sunlight. Their product is used in power, petroleum and industrial-process markets worldwide. Its deployment area of 330,000 mirrors is roughly equivalent to the surface area calculated for the envisioned CO₂ conversion process mentioned above.

Integrating an earth abundant and cost effective catalyst with existing chemical and petrochemical industrial infrastructure could provide a practical, economical and

sustainable alternative to fossil fuels and its perceived climate change consequences. The beneficiaries of this will be the oil, coal, gas, and chemical and petrochemical industries, the engines of our global economy.

To further build upon this proposal, a Plan B vision for a sustainable future is to make the solar fuels technology (i.e. capturing and utilizing CO₂ in both air and in concentrated localized sources) compatible with existing infrastructure on land and sea around the world. The scheme illustrates the envisioned Air-to-Fuel technology, which utilizes solar-assisted heterogeneous catalysis materials science and chemical engineering methods. The three-step process involves CO₂ separation or capture. Next gaseous water is split into H₂. Then this H₂ is utilized to reduce gaseous CO₂ to CO, CH₄ and CH₃OH fuels and chemicals. This model provides an example of how we can transition the most promising solar fuels materials from a laboratory scale prototype to a CO₂ capture and conversion technology that will enable the creation of a new and sustainable CO₂ economy. If the economics (energy and cost) and the timeline (lab-to-market) of the process both work, we may be able to circumvent the predicted consequences of greenhouse gas climate change.



What will it take to make this energy transition a reality? I believe what I have proposed is a positive message that circumvents the controversy and negativity of the climate debate. It is an appealing vision and a scientifically plausible idea that everyone would appreciate, from high school students to academics, from industrialists to investors and from economists to policy makers.

A solar fuels technology that would enable an energy transition to a sustainable future would begin as a small piece of the energy puzzle that is expected to grow overtime. The end goal is to power the world using renewable energy, with solar fuels generated from CO₂ being a critical component of the energy endgame.

The goal of a new CO₂ economy envisioned in this article presents a credible science and engineering paradigm, with a calculable cost, assessable risk and definable benefit over a quantifiable development time period. By contrast, the protracted climate change debate with its opposing forces appears to be grid-locked, increasing the economic and human cost of not having a credible Plan B.

36. Jarring Fears – Have We Covered Everything



Jarring Fears, Courtesy of Todd Siler

We are sensing increasingly escalating fear and angst amongst the public about the environmental uncertainties they must face in the next 10-20 years as a consequence of the relentless emission of carbon dioxide (CO₂) from the combustion of legacy fossil fuels into our atmosphere, and the havoc the global temperature rise, caused by the associated greenhouse gas effect, is expected to wreak on the climate and their fragile existence.

In 2011 the International Panel on Climate Control (IPCC) announced a “carbon budget” for our atmosphere that was calculated to keep the rise in

global temperatures to no greater than 2°C above pre-industrial levels; in 2011 they announced we have used up 67% of that budget!

Todd Siler’s transparent artwork “Jarring Fears” shows a glass jar of potentially deadly weather conditions, which contrasts with Roz Chast’s insightful cartoon “Is Everybody Happy?”, (Fuzzy Logic, in *Scientific American*, 2003), which depicts a tin can full of some unknown, but, presumably, “safe,” consumable goods that’s smothered with popular health-conscious labels, designed to give us a peace of mind.

Crammed within this jar of fears are all the terrifying weather conditions that we dread will result from greenhouse gas climate change. The conditions range from more forceful and frequent hurricanes to record-breaking tornadoes; from rising temperatures to relentless forest fires, famine, drought and disease; from ice cap melting that causes loss of permafrost and the escape of methane, exacerbating sea level rise with ensuing floods of epic proportions. Picture this disquieting image looming over our heads like some proverbial black cloud. That’s the public’s perception of the state of the world that we would be wise to better understand.

The double-entendre title on the lid of this jar "Have we covered everything?" aims to prompt politicians and policy-makers to learn more about the complexity of this whole messy climate change challenge. Currently, they seem not to be "covering" the complexity - or simply fearing it - like so many world citizens experience who feel overwhelmed and frightened by the prospect of living on an ecologically bleak planet.

It humbles and saddens us all just imagining the extinction of the human race.

Is this really what we can look forward to understanding, by accepting the severity, pervasiveness and irreversibility of climate change, its impact on people and the ecosystem and adopting Plan A? This plan implies a global strategy whereby the finite supply of legacy fossil fuels will continue to be combusted and depleted with its associated emissions of CO₂ spewed into our atmosphere. The cost of the risk against the benefits will be estimated and appropriate measures will be put in place to reduce the effects of the vulnerabilities and prepare for the consequences of CO₂ driven climate change. In the absence of any aspirations on mitigation of CO₂ emissions the future appears bleak.

Our most trusted experts assure us that our most well-established advanced technologies (wind, solar cells, biomass and geothermal) will save-the-day. But how exactly they'll fulfill this promise remains a deep source of anxiety for many people who follow this developmental work closely. These experts assure us that hopefully very shortly we'll have the ways and means to create a sustainable future with these renewable forms of energy operating synergistically. To date, these renewable forms of energy continue their remarkable growth and are becoming cost competitive with fossil fuels.

In 2012 global power generation from the four renewable forms of energy mentioned above provided nearly 0.5GW with almost \$250B in investments, ahead of fossil fuels for the third year running. This begs the question; will the current targets for the proportion of renewable forms of energy versus the total energy demand be met? While 0.5GW sounds impressive, keep in mind the 20-30TW global demand for energy, which amounts to about 50 times the energy generated by renewable, most of which still comes from gas, oil and coal. This means current carbon dioxide emissions of around 40-50Gtons per year continue unabated and will most likely continue for the foreseeable future.

Some would like us to believe natural gas will rescue us from the abyss as we are told there is plenty of it for at least 250 years. Is this "really" the best we can do for Plan B?

Burning natural gas adds 0.2kg CO₂/kWh into our atmosphere compared to 0.4kg CO₂/kWh from coal, 0.28kg CO₂/kWh from oil, 0.05kg CO₂/kWh from biomethane, and from wind and solar a mere 0.01kg CO₂/kWh. Moreover, natural gas provides a stable energy supply, which integrates well with intermittent renewable forms of energy. Natural gas and biomethane can be readily stored, easily transported and is able to power our homes, industries and transportation.

While this all sounds quite promising it does not solve the problem of our burgeoning obsession with burning fossil fuels and the incessant emissions of greenhouse gas CO₂ it churns out into our atmosphere.

In the future, excess electricity from wind and solar can be stored as synthetic natural gas obtained through electrolysis of H₂O where the H₂ so produced can be used to reduce CO₂ to CH₄ with known thermally powered heterogeneous catalytic industrial processes.

So the conversion of renewable electricity to natural gas does seem to integrate seamlessly into the existing gas infrastructure and might reduce some of the CO₂ emissions in the process but globally CO₂ from the combustion of fossil fuels will continue to be disgorged into our atmosphere.

The big question is whether natural gas and its synthetic replacement built into an integrated energy system will in the foreseeable future be enough to stop climate change in its tracks? In this context, the recently published book, *Sustainable Energy: Without the Hot Air* by Cambridge University Professor of Engineering, David MacKay, quantitatively defines the enormity of the challenge of replacing fossil fuels by renewable forms of energy. Clearly, the current plan to burn the estimated 24 trillion tons of CO₂ equivalents of fossil fuels that remain in the ground is neither desirable nor sustainable.

MacKay makes it clear in his reality study of a sustainable future that in order to address the crucial issues of climate change and energy security, new global scale renewable energy technologies beyond those mentioned above must be discovered and implemented to achieve CO₂ emission targets and energy demands.

We believe a viable Plan B could be based on a materials technology that can simultaneously harness abundant solar energy - capturing and reducing gaseous carbon dioxide into fuels and chemical feed stocks, while addressing issues of energy security and climate change.

An appealing vision is an energy transition from one based on unsustainable fossil fuels to a sustainable solar fuels energy technology founded on capturing and utilizing CO₂ – from both thin air and more concentrated localized sources. This strategy could be made compatible with existing CO₂ emitting industries around the world.

Achieving this vision of a carbon-neutral-cycle technology necessitates developing compact, tandem, concentrated solar powered photochemical reactors for efficiently splitting gaseous water into H₂ and then using the H₂ to reduce gaseous CO₂ to fuels and chemicals.

With major breakthroughs in conversion rates and efficiencies anticipated over the next five years, the time it should take to transform solar fuels laboratory-scale science to a

global technology could be short enough to circumvent the predicted adverse consequences of greenhouse gas climate change. More to the point: this strategy will enable a timely energy transition from unsustainable fossil fuels to sustainable solar fuels.

Is this a credible Plan B? Does it deserve strong support from the fossil fuel producing and consuming industries around the world? Will countries with major concentrated sources of CO₂ be among the main benefactors of Plan B?

If we adopt Plan B, a key question that will be raised, is at what point in time would the total amount of CO₂ in the atmosphere start to reduce; when would the crossover point occur? This calculation would likely depend on how quickly the scaled-up solar fuels plants could be built around the world. Even at the crossover point, we may not see an immediate change in the climate – it might take some further time before an observable change in the climate takes place or the detrimental effects of climate change are halted. We also have to accept that even if climate change is halted, the climate at that point may not be the same as the climate we experience now because of changes which have occurred, such as icecaps and tundra melting.

We think Plan B could prove to be an important component of the renewable energy mix. And we're certain it's worth "covering" in-depth.

37. CO₂: War and Peace



Figure 3 Every day we influence the dynamic balance between The CO₂ War and Peace, by messing with the equilibrium level and steady-state concentration of CO₂ and O₂ in the atmosphere through the relentless combustion of fossil fuels. If left unchecked and out of balance, this fragile equilibrium - by virtue of photosynthetic bacteria, algae, and plants - can become our nemesis, rather than sustain our genesis and growth. Our well-being and health of collective future now rests on some basic choices and conscious civil actions. Will we choose to flow with Nature, or not, and if not, why not? Choose wisely, and be at peace. Courtesy Todd Siler, www.artnanoinnovations.com

bacteria that evolved to utilize energy absorbed from ambient sunlight to oxidize water to form molecular oxygen. As a result of this astonishing event, a symbiotic balance and synergy evolved between the O₂ required to sustain life and the life needed to sustain O₂. In this biological era - and up until recent times - a delicate equilibrium was established that maintained a steady-state concentration of CO₂ and O₂ in the atmosphere. This equilibrium enabled all life processes to flourish on Earth. Essentially, **life was at peace with CO₂**, and has remained so ever since, **Figure 1**.

At War with CO₂ It started around the period of the industrial revolution (1760-1840) as the concentration of CO₂ in the Earth's atmosphere, which had remained at a stable concentration of around 300 ppm for about 2 billion years, began to be disturbed by the combustion of fossil fuels. At this time coal, oil and natural gas harvested from the earth's crust was regarded as a miraculous and seemingly infinite supply of stored chemical energy and certainly have proven to be an able provider of power for a growing global population.

This event, which may be referred to as the "Carbon Dioxide Catastrophe", has caused the concentration of CO₂ in the Earth's atmosphere to gradually increase from its equilibrium

At Peace with CO₂ Over its 4.7 billion year history the chemical composition of the Earth's atmosphere has changed a number of times from its inhospitable chemical origin into the pre-biological era through the microbial era to the biological era that created an atmospheric environment and ecology suitable for sustaining the co-existence of all life forms on earth today.

About 2 billion years ago, oxygen appeared in the earth's atmosphere for the first time, produced by photosynthetic

level of around 300 ppm to the current level of around 400 ppm. And there is no sign of its abatement in the foreseeable future.

The human race has recently been issued an ultimatum by the United Nations Intergovernmental Panel on Climate Change, IPCC. Science has spoken. Pump no more than a trillion tons of CO₂ into the atmosphere to keep global warming below 2°C or face the consequences (note that by 2011 we had pumped 1.9 trillion tons of CO₂ into the atmosphere and at today's increased emission rate of 40-50 billion tons of CO₂ per year we are on track for a 2°C rise). Cut global CO₂ emissions by half within the next fifteen years or be prepared for a temperature rise of between 2-5°C. At that dire level, we'll all be forced by nature to face the resulting dangerous effects of climate change.

In this context, the IPCC strongly recommended that low carbon sources must be used to generate the majority of the world's electricity by 2050. They insist on seeing rapid growth of renewables from their current 30% share of the power sector to 80% by 2050. And they believe electricity from fossil fuels - minus carbon capture and storage - should be essentially eliminated by 2100.

Of course, there will always be climate change skeptics who will hawk the heterodox view arguing the massive cost of the transition from fossil fuels to renewable forms of energy and the adverse effects this will have on national and global economies.

Naturally all sorts of economics and ethics related questions will be raised, such as who should pay for climate cleanup and who should welcome climate refugees forced to relocate because of extreme weather conditions: Those countries that have put most of the CO₂ into the atmosphere since the industrial revolution or those nations currently emitting the greatest amount of CO₂ per capita with willful blindness?

The consensus in the scientific community is crystal clear: If we want to avoid the risk of climate change from a greenhouse gas induced 2-5°C temperature rise our addiction to fossil fuels must be curbed immediately; the pumping of CO₂ into the atmosphere must be reduced immediately, and it must be done fast, effectively and efficiently - global emissions must be cut by half in the next fifteen years in the view of the IPCC!

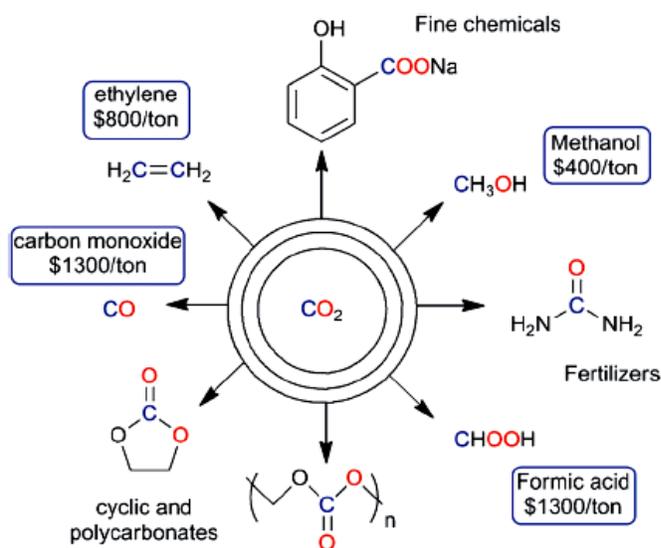
The big challenge for the global community is whether we have the scientific, technological, economic and political means and motivations for commercial implementations to agree upon an approach to accelerate the transition of fossil fuels to renewable forms of energy fast enough to avoid the ramifications of a CO₂ calamity?

At first sight this does seem like an almost impossible challenge if for example we look at the slow progress of carbon capture and storage worldwide with only one commercial plant on line in Canada (www.saskpower.com) While the storage element of this procedure

is likely to be different if CO₂ is used as a feedstock, the time scale for carbon conversion seems an almost herculean task if a 2-5°C temperature rise is to be avoided.

The big problem in convincing all countries to work together to achieve a rapid decrease in global CO₂ emissions, is that the “have and have not” fossil fuel countries have starkly different perspectives on the benefits of curtailing emissions *versus* the detrimental effects it will have on their economies. In essence, capitalism and the climate are in conflict. It's self-evident to see that, today, **life is at war with CO₂**, **Figure 1**.

At Peace Again with CO₂ Perhaps the toughest challenge of ameliorating climate change and facilitating a sustainable energy future, in which life is at peace with CO₂, is stopping ourselves from treating CO₂ as a waste product endangering life on Earth. Instead we need to utilize CO₂ as an abundant, non-toxic and low cost feed stock for making fuels and chemicals, enabling life to flourish indefinitely.



Scheme CO₂ is not a waste product to fear, it is an abundant, non-toxic, low cost C₁ chemical feed stock for making fuels and chemicals, Love, J.B. Chemical Communications, 2012, 48, 1392

use the CO₂ we have in a synthetic carbon cycle, not dig up fossil fuels any more.

Sounds too good to be true, hardly, this is not a new problem. Large scale chemical processes have been known for more than a century for making fuels and chemicals using CO₂ as the feed stock from direct air capture and fossil fuel burning electricity generating stations, steel, aluminum, cement and bio-ethanol industry sources.

This is a solvable chemical problem; if the rate of transformation of CO₂ to useful molecules and materials can be made to match its rate of production from the combustion of fossil fuels, then our greenhouse gas problem would be resolved and our war with CO₂ would be over.

In actualizing this possible reality, CO₂ is captured and converted in a carbon neutral cycle to provide fuels and chemicals forever, circumventing the specter of climate change. Essentially the goal is to short circuit the natural carbon cycle, basically doing what nature takes billions of years to do on a much shorter timescale. So now we just

Even though there has been a significant amount of research and development, considerably more effort and money needs to be spent to improve the performance of CO₂ conversion to technologically practical rates and efficiencies on an industrial scale and to integrate it into existing chemical and petrochemical industrial processes. Industry road maps show milestones and timelines as to why-how-when-where CO₂ conversion fits into their projected carbon fuels and chemicals pipeline.

Some examples of this paradigm are shown above in the **Scheme** that illustrates industry examples currently being practiced at the Megaton per year production scale for pharmaceuticals (Aspirin), liquid fuels (methanol), hydrogen storage and transportation (formic acid), polymers (ethylene, polycarbonates), fertilizers (urea) and carbon monoxide, which can be used as a feed stock for making myriad fuels and chemicals, such as gasoline, methanol and hydrogen. In principle, these kinds of industrial processes have the capacity to transform CO₂ to useful products around the world and could be scaled to produce Gigatons per year, thus making a pretty big dent in the CO₂ footprint.

The main contenders under active investigation for CO₂ conversion to fuels and chemicals include homogenous and heterogeneous catalysis, biomass, electrochemistry, photoelectrochemistry, solar thermal and photocatalysis. Although there are technical and economic pros and cons for each of these approaches, with continued research and development, there will likely emerge a creative mix of CO₂ conversion processes with the overall capacity of utilizing Gigaton amounts of CO₂ per annum for making fuels and chemicals. That sure beats storing it in the ground or emitting it into the atmosphere.

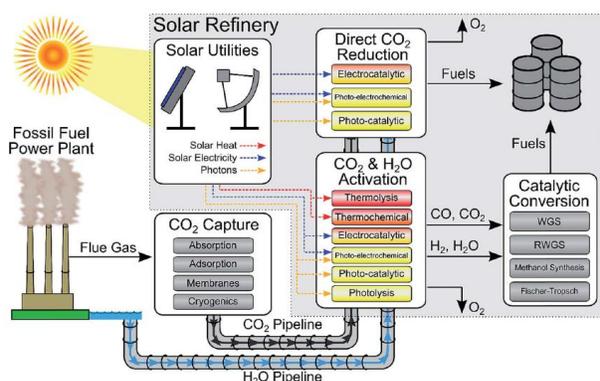
A real hurdle that must be overcome for any approach is that it must be cost effective. The cost of the production of fuels and chemicals must be cheaper than existing costs using fossil fuels. If cost effective conversion on an industrial scale can be demonstrated then the people that matter will start taking a real interest. It is noteworthy that CO₂ conversion to fuels and chemicals does not seem to be in the conversation at the moment for the IPCC, political leaders or the public.



Figure 4 Peace → War → Peace with CO₂ again enabled by the endeavors of chemists and chemical engineers; Courtesy of Chenxi Qian

Can we look forward to this “New CO₂ Economy” and a sustainable climate and energy future? With all the new solar fuels science and technology in the pipeline and poised to take off, could this “sleeping giant” emerge more quickly than industry, government, business stakeholders imagine? It seems possible, providing these processes are powered by renewable forms of energy (electricity and sunlight) and not fossil fuels. Any emissions of CO₂ into the atmosphere should be strongly regulated by a global CO₂ watchdog commission. In this way again, **life at peace with CO₂**, will become an ‘ideal made real’, **Figure 2.**

38 Solar Refinery: Can we have our Carbon Cake and Eat It ?



Scheme Futuristic 'solar refinery' for making fuels and chemicals from CO₂, H₂O and sunlight, Energy and Environmental Science, 2014, DOI: 10.1039/c4ee1958j

There is a global effort underway to discover advanced engineering materials and processes to stock the solar refinery of the future.

Key modules of the solar refinery, include materials and processes for (i) harvesting sunlight, (ii) capturing, purifying and releasing CO₂, and (iii) converting CO₂ and H₂O directly or indirectly to fuels. A flow diagram of how these modules are integrated in a solar refinery is illustrated in the **Scheme**.

There is nothing too surprising contained within each module of the solar refinery: (i) A solar utility harvests sunlight in the form of heat, light or electricity; (ii) A CO₂ facility uses absorption, adsorption, membrane or cryogenic techniques for capturing, purifying and releasing CO₂ on demand; (iii) The CO₂ is piped with H₂O and (a) directly transformed to fuels using electrochemical, photoelectrochemical and photocatalytic methods or (b) indirectly converted to CO and H₂ by thermochemical, electrochemical, photoelectrochemical and photocatalytic means which are subsequently made into fuels by well known industrial heterogeneous catalytic processes, including Fischer-Tropsch, methanol synthesis, water gas shift and reverse water gas shift.

What has been sorely missing however, to assist teams of materials chemists, scientists and engineers around the world, raring to contribute to the development of a solar refinery, is a cradle-to-grave technoeconomic analysis of the energy and economic costs of the alternative technologies contained within each module. These teams also need to know, how the ultimate price tag of fuels produced in the solar driven refinery compare with those generated in a fossil fuels powered refinery.

In a chemical engineering tour-de-force, Christos Maravelias and colleagues from the University of Wisconsin have recently modeled and analyzed the energy and economic cost of every step and each alternative technology in the solar refinery (Energy and Environmental Science, 2014, DOI: 10.1039/c4ee1958j). Their analysis encompasses all scales and all parameters of the problem to create a general framework that will allow scientists and engineers to evaluate how

various materials and processing technology improvements of solar and CO₂ capture and conversion would accelerate the development and impact the vision of the solar refinery.

The view that emerges from this techno-economic evaluation of the solar refinery is one of guarded optimism. On the subject of energy efficiency, it is clear that solar powered CO₂ reduction is currently lagging far behind that of H₂O splitting. In the indirect process of transforming CO₂/H₂O to fuels, if the >10% currently achievable solar H₂O-to-H₂ conversion efficiencies can be matched by solar CO₂/H₂-to-fuel conversion, through creative catalyst design and reaction engineering, this would represent a promising step towards an energetically viable solar refinery. For the direct process of transforming CO₂/H₂O to fuels, improvements in conversion rates and product selectivity are key requirements for achieving energy efficiency in the solar refinery.

Economic efficiency is also a key to the success of the solar refinery of the future and for currently achievable CO₂ reduction rates and efficiencies the cost of fuels evaluated by the techno-economic analysis, in the case of methanol, turned out to be about three times greater than the industrial selling price. Improvement in the activity of CO₂ reduction photocatalysts by several orders of magnitude would have a significant impact on the energy and economic costs of operating the solar refinery. It is anticipated that these developments are in the pipeline!

Additional improvements in the energy and economic efficiency of CO₂ capture and purification using specialized sorbents and of CO₂ release using solar power, exemplified by systems under development at www.Climeworks.com, together with advances in CO₂ photo-reduction rates, efficiencies and product selectivities, could enable positive energy incorporation efficiencies in a solar refinery, a prerequisite for commercialization.

Returning to the question in the title of this article: can we have our carbon cake and eat it? Multidisciplinary teams of materials chemists, materials scientists, and materials engineers across the globe believe in the dream of the solar refinery and a sustainable CO₂ based economy. It is abundantly clear from the energy and financial analysis of the solar refinery by Christos Maravelias and his colleagues that modeling and evaluating cradle-to-grave technical and economic hurdles involved in solar fuels processing, will continue to play a crucial role in the development of these technologies. They will serve to identify key aspects of materials and process design that are required to facilitate the transformation of ongoing solar fuels research and development into the solar refinery of the future.