

TOWARDS A MOLECULAR NANOTECHNOLOGY

**UNIVERSITY OF TORONTO CANADA RESEARCH
CHAIR IN MATERIALS CHEMISTRY**

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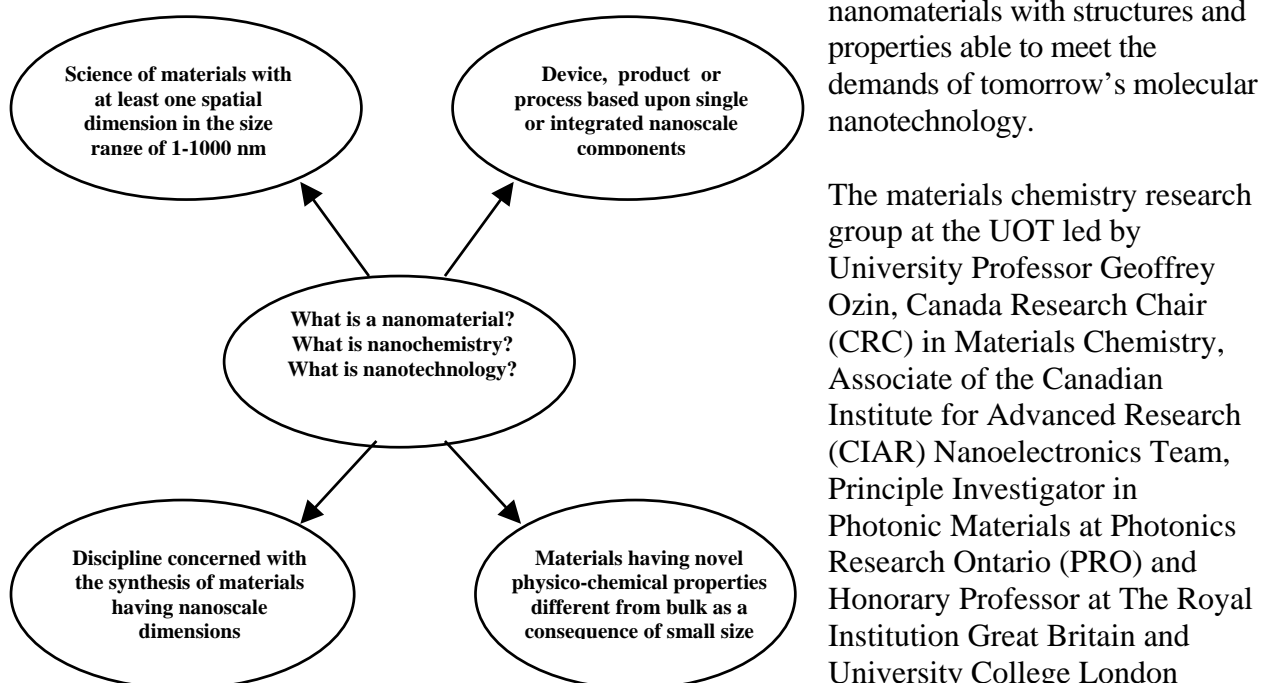
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TOWARDS A MOLECULAR NANOTECHNOLOGY: UNIVERSITY OF TORONTO CANADA RESEARCH CHAIR IN MATERIALS CHEMISTRY

In the *Solid State 20th Century*, where trial-and-error solid-state synthesis produced unique structures, structures produced new physics and physics produced novel devices, it has been the fields of materials science and engineering that have propelled materials technology to the spectacular heights that society accepts and enjoys today. As we enter the *Materials 21st Century*, where designed chemical synthesis creates original molecules, molecules produce new materials, materials produce novel structures and structures produce unique function and utility, it is the insatiable demand for new materials in emerging fields like nanotechnology and biotechnology that is now driving the fields of materials science and engineering. Materials chemists, the inventors and makers of new compositions of matter, will play a central role in the search for new classes of materials through planned synthesis of molecular building blocks for purposeful construction of



The materials chemistry research group at the UOT led by University Professor Geoffrey Ozin, Canada Research Chair (CRC) in Materials Chemistry, Associate of the Canadian Institute for Advanced Research (CIAR) Nanoelectronics Team, Principle Investigator in Photonic Materials at Photonics Research Ontario (PRO) and Honorary Professor at The Royal Institution Great Britain and University College London

University, has over a period of nearly three decades developed molecular and modular self-assembly approaches to nanomaterials for a future molecular nanotechnology. The group's research in materials self-assembly has been instrumental in enabling the transition between traditional *top-down* solid-state physics ways of making nanostructures and new *bottom-up* molecular and modular chemistry methods of making nanomaterials. Their speciality is self-assembly of photonic, electronic, optical, magnetic, catalytic, electrocatalytic, separation, composite and sensor nanomaterials and bionanomaterials through the utilization of supramolecular and biomimetic chemistry. These are rapidly expanding and highly competitive fields of contemporary materials research and the UOT materials group has made groundbreaking developments to the field since the early 70's and continues to show the way to a world of self-assembling nanomaterials that had not previously existed – considered to be enabling nanoscience for a molecular nanotechnology.

The UOT materials chemistry group has pioneered innovative synthetic chemistry approaches to

functional nanomaterials and nanostructures whose properties are intentionally designed to scale with and depend upon their physical size. A blueprint for a molecular nanotechnology through materials self-assembly was laid out in their paper Nanochemistry: Synthesis in Diminishing Dimensions *Advanced Materials* **4**, 612-649, 1992. It inspired a *bottom-up* chemistry approach to a myriad of novel nanomaterials and nanostructures and helped establish a scientific foundation on which to base research and development and ultimately an economy fashioned on nanoelectronic, nanoionic, nanophotonic, nanomagnetic and nanomechanical components.

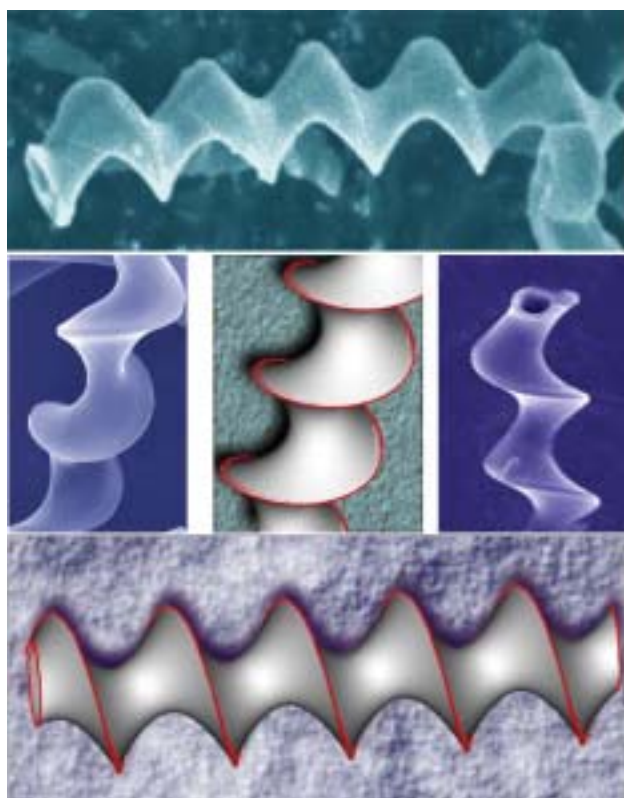


Figure 1. Self-assembled hollow helicoids – Archimedian spirals made of periodic mesoporous silica

Nanochemistry contributions first emerged from the UOT materials chemistry group in the 70's where early developments towards a molecular nanotechnology include their experimental and theoretical studies of *ligand-free* controlled nuclearity metal atoms and clusters M_n where $n = 1, 2, 3, 4 \dots$ and $M = Na, Cu, Ag, Au, Sc, Ti, V, Cr, Mo \dots$, unraveling of metal atom-cluster-bulk geometric-electronic structure relations and quantum size effects in metal clusters, development of metal cluster localized bonding models of chemisorption and catalysis M_nL_m where $L = CO, N_2, O_2, CS, CH_4, SiH_4, C_2H_6, C_2H_4, C_2H_2$ and $n, m = 1, 2, 3, 4 \dots$, explorations of the metal cluster-metal surface analogy, investigations of *naked* metal atom and metal cluster photo-processes like the nuclearity dependence of metal atom aggregation and metal cluster dissociation and isomerization reactions, and selective insertion of photo-excited transition metal atoms like Cu, Ag, Mn, Fe, Co, Ni, Zn into the C-H bond of methane and ethane, the Si-H bond of silane and the H-H bond of dihydrogen to make RMH and HMH. Notable early papers from the group on these topics include Transition

Metal Atom Inorganic Synthesis in Matrices *Accounts of Chemical Research* **6**, 313-318, 1973, Matrix Synthesis and Characterization of Dichromium Cr_2 *Nature* **254**, 503-504, 1975, Transition Metal Atoms in the Synthesis of Binuclear Complexes *Angewandte Chemie International Edition* **14**, 292-303, 1975, Metal Atom Matrix Chemistry - Correlation of Bonding with Chemisorbed Molecules *Accounts of Chemical Research* **10**, 21, 1977, Relative Extinction Coefficient Measurements for Naked Silver Atom Clusters $Ag_{1,2,3}$ by Photoaggregation Techniques *Journal of the American Chemical Society* **100**, 6776-77, 1978, Cobalt, Nickel and Copper Naked Metal Clusters and Olefin Chemisorption Models *Coordination Chemistry Reviews* **28**, 117-47, 1979, Selective Photoaggregation of Metal Atoms to Small, Bimetallic Clusters of Known Size - The Chromium-Molybdenum System Cr_nMo_m *Journal of the American Chemical Society* **100**, 2262-64, 1978, Silver Atom Cryophotoaggregation - Optical Emission and

Absorption Spectroscopic Studies *Journal of the American Chemical Society* 102, 7702-9, 1980, Spectroscopy, Chemistry and Catalysis of Metal Atoms, Metal Dimers and Metal Clusters *Faraday Society Symposia of the Chemical Society* 14, 7-64, 1980, Metal Atom to Cluster to Bulk Transformations - Electron Spin Resonance Studies of Silver Atoms in Rare Gas Matrices at 12K - The Quantum Size Effect *Journal of the American Chemical Society* 102, 3301-03, 1980, Methane Activation - Photochemical Reactions of Copper Atoms in Solid Methane *Journal of the American Chemical Society* 103, 1574-5, 1981, Photoinduced Reductive-Elimination of Iron Atoms and Methane from CH_3FeH *Journal of the American Chemical Society* 104, 7351-52, 1982, Ligand-Free Metal Clusters *Angewandte Chemie International Edition* 22, 674-94, 1983.

In the 80's the UOT materials chemistry group embarked on the development of chemical vapor deposition synthetic methods for the growth of controlled nuclearity metal clusters in alkane, wax, liquid and solid polymer, metal oxide and carbon matrices, and semiconductor cluster and cluster superlattices in zeolite matrices. The driving force for the group's work was the obtainment of well-defined, catalytic and electro-catalytic, electronic and optical nanomaterials through nanochemistry. The rapid global development of the field of nanocluster science and technology that ensued in the 80's and 90's, highlighted by the discovery of supersonic and aerosol cluster molecular beams, and capped cluster and cluster superlattices, was stimulated by the UOT materials groups early metal and semiconductor cluster research contributions in the 70's and 80's aspects of which are recorded in their papers Very Small Metallic and Bimetallic Clusters - The Metal Cluster-Metal Surface Analogy in Catalysis and Chemisorption Processes *Catalysis Reviews* 16, 191-260, 1977, New Materials From Metal Vapor Chemistry *Chemtech* 488-496, 1985, Properties of Dispersed Metal Clusters, in *Metal Clusters in Catalysis Studies in Surface Science and Catalysis*, Elsevier, pp. 265-391, 1986 and Advanced Zeolite Materials Science *Angewandte Chemie International Edition* 101, 373-90, 1989. The UOTs materials chemistry work in the 70's and 80's pointed the way to a molecular nanotechnology through nanochemistry.

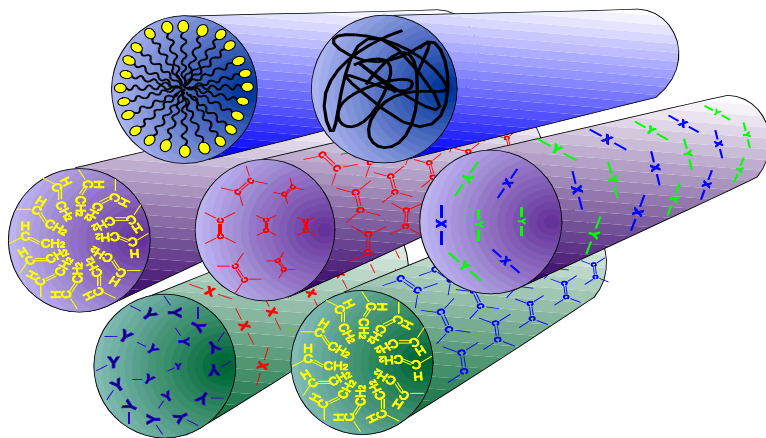


Figure 2. Classes of self-assembled periodic mesoporous organosilica hybrid materials, organic-inorganic nanocomposites

new classes of nanomaterials having crystalline mesoporosity using supramolecular templates

Trend setting contributions to a future molecular nanotechnology from the UOTs materials chemistry research group appeared in the early 90's. They include self-assembly synthetic approaches to photonic, separation, battery, fuel cell, bone replacement and sensor nanomaterials through supramolecular and biomimetic chemistry. Synthetic methodologies developed by the group have embraced structure-determined self-assembly with morphology control as fibers, rods, films, gyroids, spheres, hollow helicoids and soft lithographically defined micron scale patterns of

and summarized in their paper *Curves in Chemistry - Supramolecular Materials Taking Shape Canadian Journal of Chemistry* **77**, 2001-2014, 1999 - see Figure 1. This work was first described in their article *Morphogenesis of Shapes and Surface Patterns in Mesoporous Silica Nature* **386**, 692-695, 1997, and expanded upon in their paper *Defects in Silicate Liquid Crystals - Role in the Formation of Mesoporous Silica Fibers, Films and Curved Shapes Advanced Materials* **10**, 883-887, 1998, which led to an understanding of how topological defects in silicatropic liquid crystal templates controlled the morphology of highly curved mesoporous silica shapes.

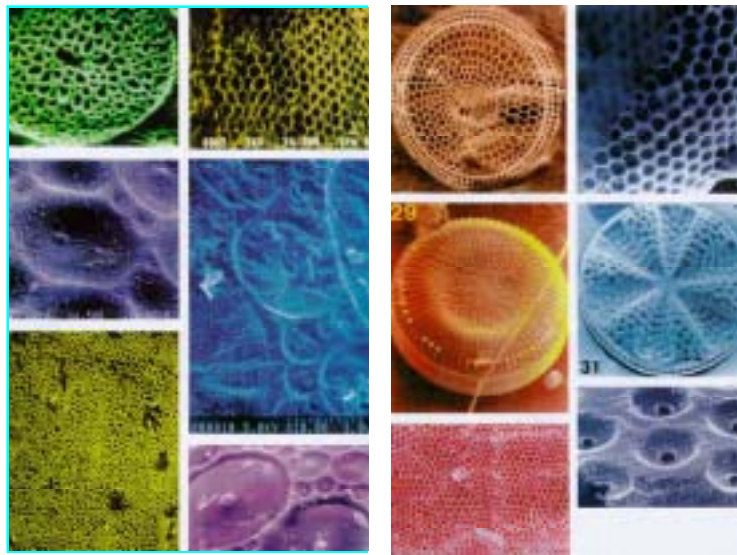


Figure 3. Diatoms and radiolaria – which ones are natural and which are synthetic?

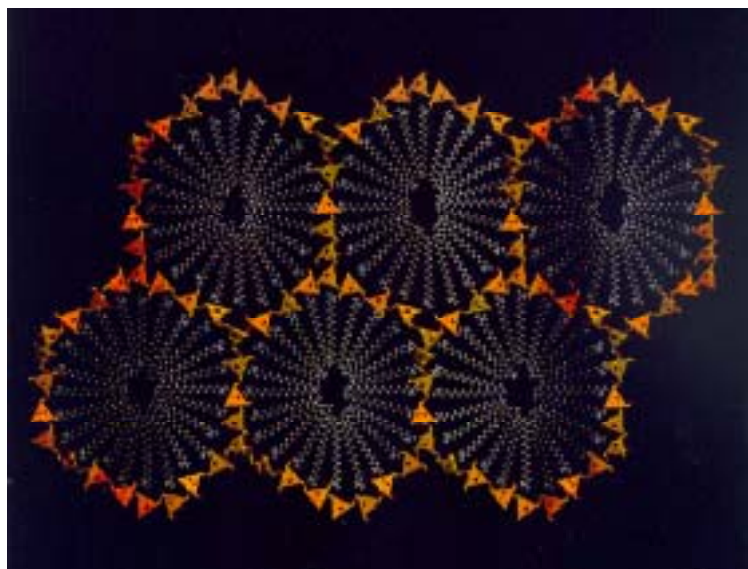


Figure 4. Modular self-assembly of a periodic mesostructured metal germanium sulfide made of adamantanoid germanium sulfide building blocks.

This work proved fundamental to the development of the science and technology of this novel and important class of nanomaterials. The groups groundbreaking papers on the *Synthesis of Oriented Mesoporous Silica Film on Mica Nature* **379**, 703-705, 1996 and *Free-Standing and Oriented Mesoporous Silica Films Grown at the Interface Between Air and Water Nature* **381**, 589-592, 1996 proved for the first time that periodic mesoporous silica could be synthesized as oriented supported and oriented free-standing film thereby laying the foundation for the development of these nanomaterials as membranes for large molecule catalysis, separation and sensing, templates for the assembly of nanostructures, masks for high-resolution lithography, low refractive index cladding for optical waveguides and dye lasers, coatings for bone implants and low dielectric constant film for packaging smaller and faster microelectronic circuitry.

The group's work on supramolecular synthesis of mesostructured silica and aluminum phosphate materials with morphologies that resemble biomineralized structures such as diatoms and radiolaria - Figure 3 - coined morphosynthesis - represented a first for materials chemistry. This discovery led to inorganic materials with hierarchical

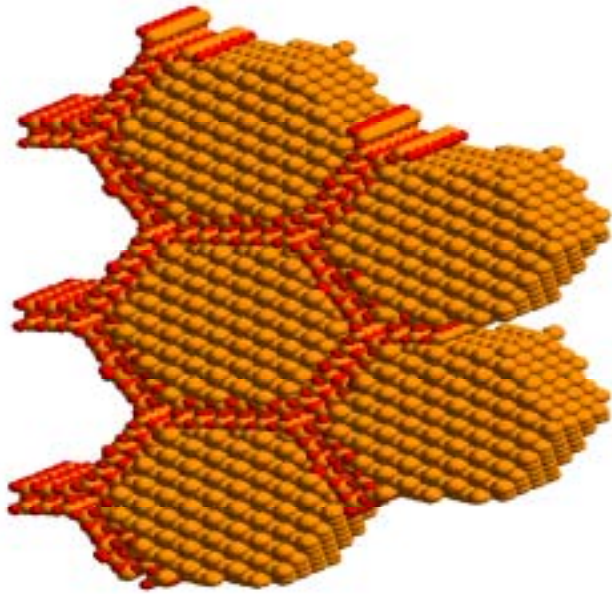


Figure 5. Self-assembled photoluminescent silicon nanocluster – mesostructured silica nano-composite film

influencing current thinking in the field of biomimetic materials chemistry and is envisioned to

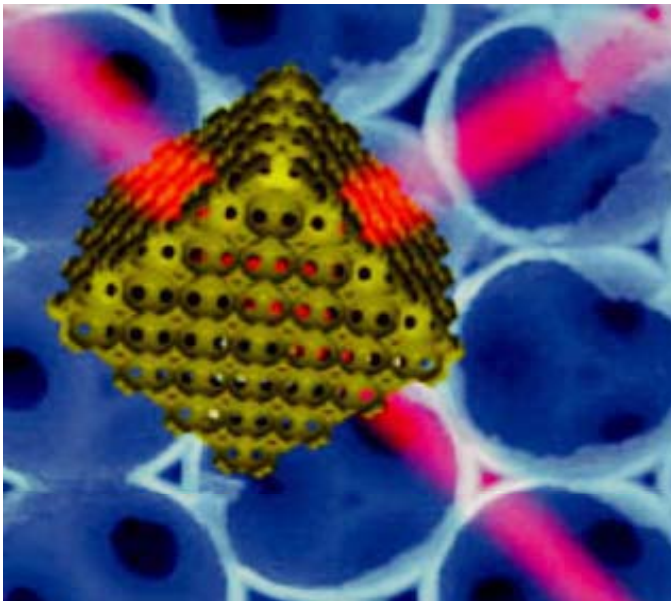


Figure 6. Computer graphical representation of a 3-D Si inverse opal with a full photonic band gap in the near infrared around $1.5 \mu\text{m}$ superimposed on top of a SEM of a synthetic facsimile made by opal templated silicon CVD.

structures and complex form - it introduced to materials chemistry a new language of shape as described in their papers Synthesis of Inorganic Materials with Complex Form *Nature* 382, 313-318, 1996, Lamellar Aluminophosphates that Mimic Radiolaria and Diatom Skeletons *Nature* 378, 47-51, 1995, Morphogenesis of Biomineral and Morphosynthesis of Biomimetic Forms *Accounts of Chemical Research* 30, 17-27, 1997 and Blueprints for Inorganic Materials with Natural Form - Inorganic Liquid Crystals and a Language of Inorganic Shape *Dalton Transactions* 3941-3952, 1997. The group's work in this field provided useful insight into how biominerals assemble in the natural world and suggested interesting biomimetic ways of synthesizing materials where form controls function and end-use. What one has here is something amazingly simple given its scope and power yet something very complex as it challenges out notion of growth and form. It is profoundly influencing current thinking in the field of biomimetic materials chemistry and is envisioned to have considerable impact, for example on the development of structural nanocomposites and bone replacement nanomaterials.

This research was a precursor to the group's work that enabled fusion of organic synthesis with inorganic materials chemistry to create a new class of nanocomposites with molecular scale control of the interface between the organic and inorganic parts. This breakthrough was first described in their paper Periodic Mesoporous Organosilicas with Organic Groups Inside the Channel Walls *Nature* 402, 867-871, 1999 and in their concept articles Writing on the Wall with a New Synthetic Quill *Chemistry: A European Journal* 6, 2507-2511, 2000 and New Nanocomposites - Putting Organic Function "Inside" the Channel Walls of Periodic Mesoporous Silica *Journal of Materials Chemistry* 10, 1751-1755, 2000 – see Figure 2. These

organosilica hybrid materials with crystalline mesoporosity, tailored through organic chemistry to be mono-, bi- or tri-functional, offer unique potential for scientific and technological advances in numerous application areas because the organic function and the inorganic framework can be tailored through chemistry to tune their mechanical, electrical, optical, magnetic, catalytic, separation and chemical reactivity properties – see the groups recent paper Novel Bifunctional Periodic Mesoporous Silicas, BPMOs - Synthesis, Characterization, Properties and In situ Selective Hydroboration – Alcoholysis of Functional Groups *Journal of the American Chemical Society* Web ASAP 14 August 2001.

The group further expanded the element composition field of periodic mesoporous materials beyond silica with their paper on modular-assembly of well-defined metal-sulfide cluster precursors to form periodic mesostructured metal sulfides first outlined in their paper Non-Aqueous Supramolecular Assembly of Metal Germanium Sulfide Mesostructures from $\text{Ge}_4\text{S}_{10}^{4-}$ Clusters *Nature* **397**, 681-684, 1999- see Figure 4. This breakthrough described a new class of mesoscale open-frameworks with a structure based upon the linkage of M^{2+} or metal-metal bonded M_2^{2+} units and adamantanoid $\text{Ge}_4\text{S}_{10}^{4-}$ building-blocks and considered as contenders as heavy metal sponges for environmental clean-up applications. In this genre is the group's work on the synthesis, structure and properties of a new class of mesostructured metal sulfide and phosphate thermotropic inorganic liquid crystals. Materials of this type are rare because they combine the fluid properties of liquid crystals with for instance the semiconducting and optical properties of inorganic materials. This unusual combination of behaviors makes them attractive for a range of display and optical technologies, a representative example is found in their paper Tin(IV) Sulfide-Alkylamine Composite Mesophase - A New Class of Thermotropic Liquid Crystals *Journal of Materials Chemistry* **7**, 2213-2222, 1997. In this same vein is the group's work on self-assembly of porous hydroxyapatite-dodecylphosphate composite film on a substrate comprised

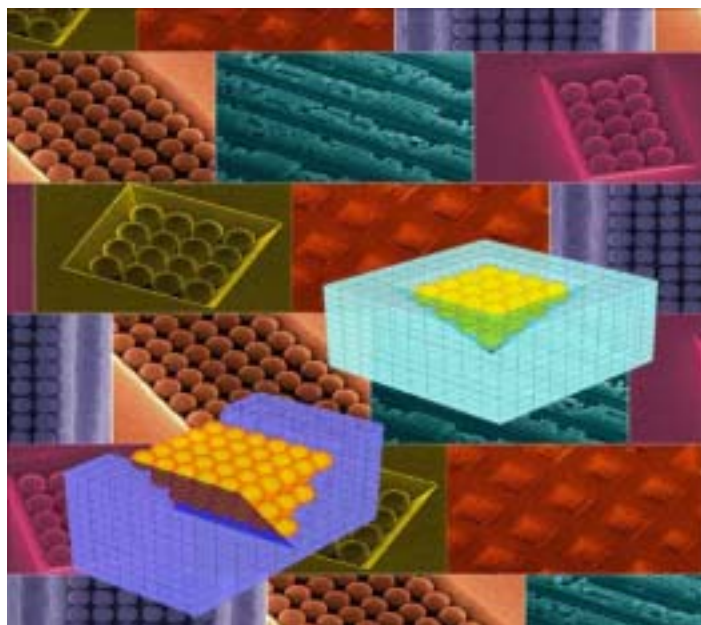


Figure 7. Planarized micro-photonic crystal chip made by directed self-assembly.

of titania-titanium first described in their paper Porous Hydroxyapatite-Dodecylphosphate Composite Film on Titania as a Bone Analogue *Journal of Materials Chemistry* **9**, 703-710, 1999 and expanded upon in Bone Mimetics *Journal of Materials Chemistry* **7**, 1601-1607, 1997. This work represents a novel materials chemistry approach to a smart mesostructured bone implant material capable of integrating and delivering bioeffector and drug molecules at a bone repair site of interest to bone biologists for potential biomedical applications.

With materials at hand offering crystalline mesoporosity, the UOT materials group developed topotactic chemical deposition synthetic strategies to host-guest nanocomposites based

upon quantum confined semiconductor nanoclusters, which have proven to be very interesting in electronic, optical and data storage applications. An example is fast and intense visible photoluminescence from silicon nanoclusters, self-assembled by chemical vapor deposition within the channels of oriented mesoporous silica film. This work is described in their paper Photoluminescent Silicon Clusters in Oriented Hexagonal Mesoporous Silica Film *Advanced Materials* 11, 474-480, 1999 and first outlined in their article New Forms of Luminescent Silicon - Silicon-Silica Composite Mesostructures *Advanced Materials Chemical Vapor Deposition* 2, 8-13, 1996– see Figure 5. This approach may provide a mild and straightforward synthetic route to luminescent silicon for making spin-on light emitting diodes in a silicon microfabrication facility.

Another self-assembly synthetic strategy utilized by the group involves colloidal crystal templating of silicon photonic crystals for optical telecommunications first described in their paper Self-Assembly of a Silicon Photonic Bandgap Material with a Complete Three-Dimensional Gap at 1.5 Microns *Nature* 405, 437-440, 2000 – see Figure 6. The group has also employed directed self-assembly, an amalgamation of micro-fabrication and self-assembly methods, to make the first examples of planarized microphotonic crystal chips summarized in their paper The Race for the Photonic Chip, Opal-Patterned Chips *Advanced Functional Materials* 11, 1-10, 2001 – see Figure 7. This work described simple, quick, reproducible and inexpensive methods for making opal-patterned chips with potential applications in photonic chip as well as lab-on-chip technologies. An attractive feature of this approach is that it is easily integrated into existing chip microfabrication facilities – see Opal Chips: Photonic Jewels *Chemical and Engineering News* 79, 55-58, 2001.

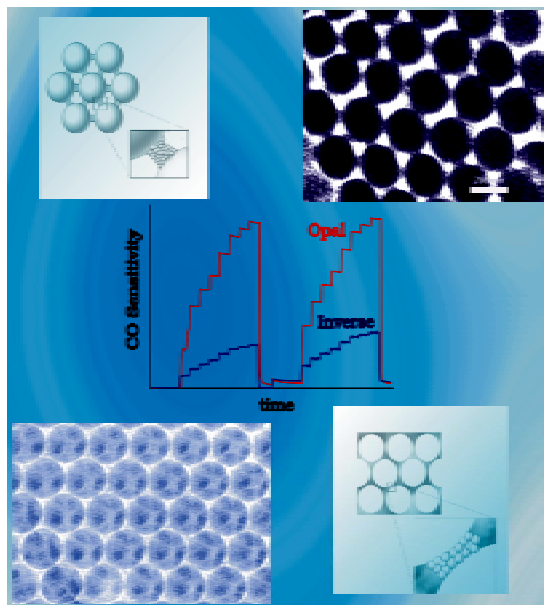


Figure 8. Tin dioxide opal and inverse opal gas sensors.

Three decades of nanomaterials research enabled the UOT materials chemistry team to develop a panoscopic vision of the synthesis of materials with structural features that traversed length scales from nanometers to microns. Their ideas on this subject have been presented in an article entitled Panoscopic Materials - Synthesis over “All” Dimensions *Chemical Communications* 419-432, 1999 and more recently Panoscopic Silicon – A Material for “All” Length Scales *Advanced Materials* 12, 1071-1078, 2000.

In the context of the nanomaterials research of the UOT group it is worth noting that nanoscience emerged from the discovery that materials properties alter with size in distinct ways that obey scaling laws. This is one of the defining features of a nanomaterial but as one can tell from the micron scale opal templated photonic crystals whose optical properties scale with the photonic lattice size, not all nanostructures are that small. In fact, *large*

nanomaterials with crystal lattices fashioned at the light scale represent a new dimension in

nanoscience and portend new opportunities for nanotechnology. Such micrometer periodic dielectrics, the most well know class being photonic crystals, are renown for their ability to function as semiconductors for light. The UOT materials group has shown that there are however a myriad of other prospects for micrometer crystal lattices made of spherical building blocks. In this context, the focus on their recent synthetic work has been aimed at fashioning materials like ferroelectric barium titanate, nanocrystalline tin dioxide, mesoporous silica, photoactive titanium dioxide, and redox active and semiconductive poly(ferrocenylsilanes) as opal and inverse opal architectures, made of solid or hollow micro-spheres, with perceived utility that include optoelectronics, chemical sensing, chromatography, catalysis, microelectronics packaging, chemical delivery, acoustic insulation, light harvesting solar cells and magnetic data storage – see Figure 8 . An example in this vein is described in their recent paper Tin Dioxide Opals and Inverted Opals: Near-Ideal Microstructures for Gas Sensors, *Advanced Materials* September 2001.

The UOT research in nanochemistry has established a *panoscopic* way of thinking about nanomaterials having structure over “all” length scales. It has introduced complexity and hierarchy into materials chemistry, which until their work was reserved for nature's incredible biominerals. The UOT research has shown that *directed self-assembly* of molecular and modular construction units provides an effective pathway to new materials whose structure from the nanometer scale to the overall macroscopic form, determine materials properties, purpose and utility. The group’s work is considered to provide an enabling step towards a molecular nanotechnology and constitutes an integral part of the strategic plan of the UOT in teaching and research in nanoscience. The recent award of the Canada Research Chair in Materials Chemistry to University Professor Geoffrey Ozin will enable him and his team to expand and intensify their effort in the global race for new nanomaterials and nanostructures for a future nanotechnology.

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