

Pores for Thought

RSC 2011 Barrer Award Lecture

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Inspiration



It is an incredible honour to receive the RSC Barrer Award for my contributions to the field of porous materials. 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 O_2 and N_2 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 indeed a great honour to receive the RSC Barrer award that recognizes meritorious recent pure or applied research in the field of porous inorganic materials and in my lecture on this special occasion I will present personal recollections of my explorations of 'materials filled with holes', the dimensions of which traverse length scales from nanometers to microns, the scale of molecules to the light scale, a 'panoscopic' vision of this fascinating class of solids.

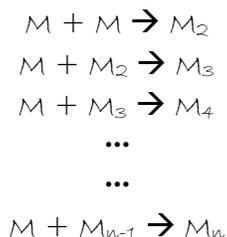
Where Did It Begin?

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-Craft 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 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.

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 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 promising 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].

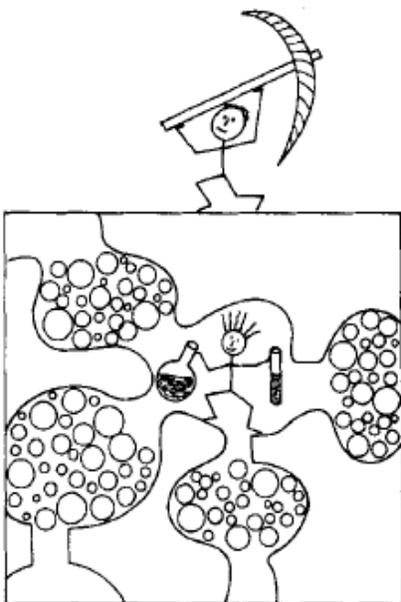
Escape from the 10 Å Prison



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

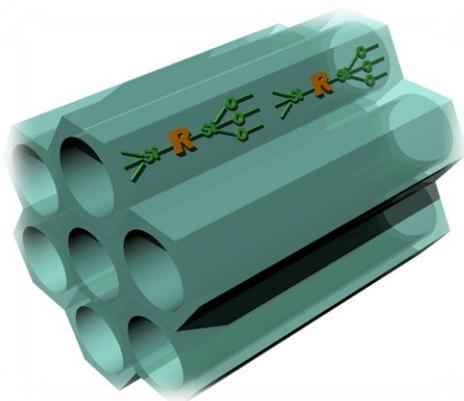
unabated today [6]. In this paper I envisioned the novel world of nanochemistry with its 0-D dots, 1-D wires, 2-D layers, and 3-D open frames, configurations that surprised, shape- and size-dependent behaviors that startled. Here were the conceptual foundations, the description

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!

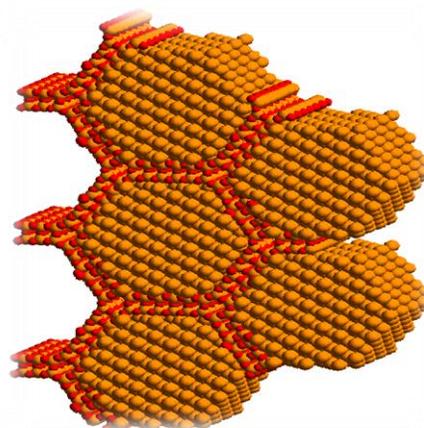
Micropores to Mesopores to Macropores

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



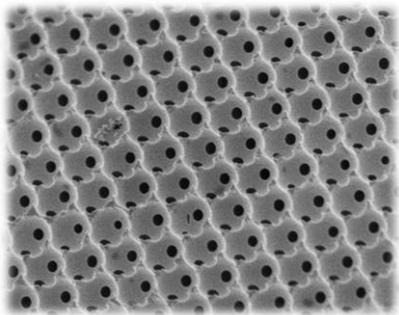
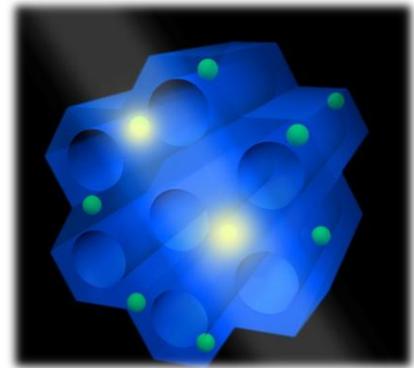
aromatics, dendrimers, fullerenes, and silicon-based polyhedral oligomeric silsesquioxanes and nanocrystals, delivering properties that transcend the sum of their inorganic and organic components, and currently finding widespread interest in microelectronic packaging, chromatography stationary phases, 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].

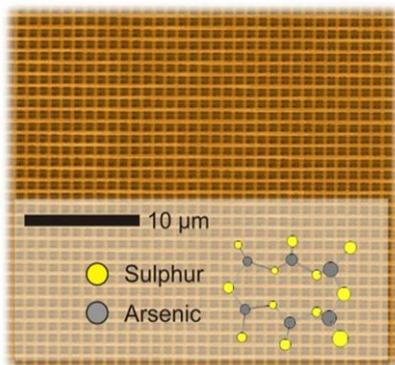


6. Photonic crystal materials - a bottom-up chemical approach to the world's first 3D silicon photonic crystal with a complete photonic bandgap operating at optical telecom wavelengths - this research enabled the full gamut structural color and slow light amplified absorption and emission attributes 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, As₂S₃, 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].

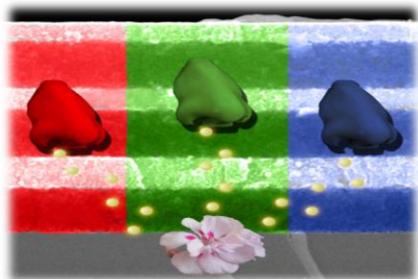
8. Photonic crystal technology - research on different kinds of photonic crystals led to the invention of actively tuned photonic color systems that include full colour displays, authentication devices for anti-counterfeiting, and colour sensors for food and water quality control and pathogen detection 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

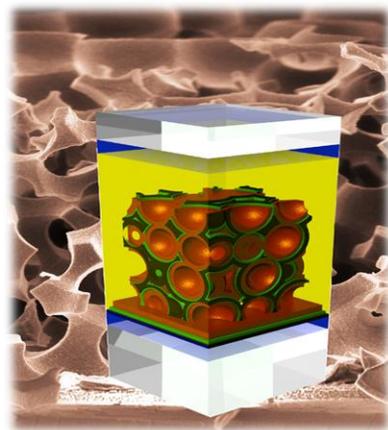
develop, manufacture, and commercialize photonic color technology, and has readied three unique manifestations of the technology for the market mentioned below.

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:

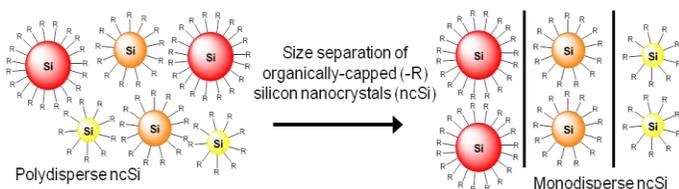
1. Enhanced efficiency light harvesting solar cells -

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 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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