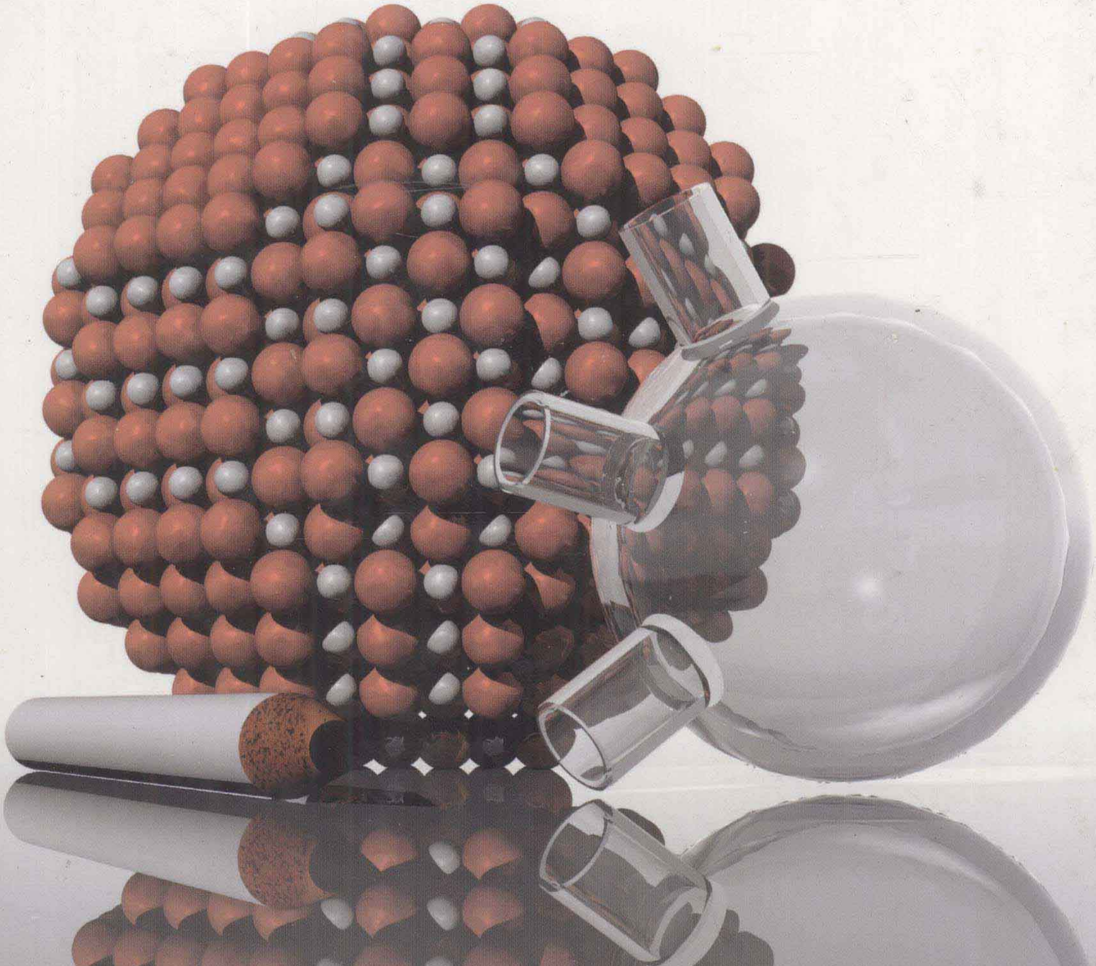
NANOCHEMISTRY

A Chemical Approach to Nanomaterials

Geoffrey A Ozin & André C Arsenault



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Dedication

We (Geoff and André) dedicate this book to our wives, Linda and Charlene. They are truly the inspiration, energy, and dedication contained in this text, for without them we would have none of these things

PREFACE

In the Beginning There was Nano...

"Imagination is more important than knowledge"
Albert Einstein (1879–1955)

1 Nano – The Interdisciplinary Science

In December of 1959, the eminent physicist Richard Feynman described the future in a groundbreaking talk about the physical possibilities for "making, manipulating, visualizing and controlling things on a small scale," and imagining that in decades to come, it might be possible to arrange atoms "the way we want." As an example of what would be possible, Feynman used physics to demonstrate theoretically that all of the accumulated information in all of the books in the world could be written "in a cube of material one two-hundredth of an inch wide – which is the barest piece of dust that can be made out by the human eye." Feynman did not suggest how this might be done, that task would have to be left to others as nanoscience evolved over the next 40 years, overcoming the early skepticism of much of the scientific community.

You might imagine nanoscience as a pretty specialized field, when in reality it is quite the opposite. In nano, the idea is to do something really big and important with objects that are really small and distinct in their properties and behavior from the large objects with which we are all familiar. It is a field full of enormous challenges that cannot be met by any one specialist. It requires collaboration on the part of many specialists, just as fashion designers rely on weavers, tailors, and cutters to accomplish their designs.

Nano is a word that has now left the science reservation and entered the public consciousness. The field of nanoscience with its promise of amazing nanotechnologies is one of today's most challenging, exciting, mutli-disciplinary and competitive fields, and one of the most highly funded. It is considered poised to revolutionize the world as we know it, and transform in into something better.

Some researchers still argue that nanotech, as a coherent field with clear goals, does not actually exist. The current leap of faith by so many ill-informed folk into a new field seemingly fraught with so much uncertainty can create fear of the unknown. This is clearly the case with nano, and it is what lends it a science fiction quality. Recently, in some circles, a dread of nanotechnology has emerged. This hysteria is not unlike the fears surrounding biotechnology when it first gained public attention. We believe that it is very important to counter this type of paranoia, especially in a field with such potential to do good for society. We must use effective means of communication to educate the public about the scientific and technological issues of nano, as well as the ramifications of nano for the social sciences and humanities, biology and medicine. It is up to us, scientists, to dissuade the public that the ultimate goal of nanotechnology is to fabricate self-replicating nanorobots which will overrun the earth.

In order to be globally competitive, emerging nanotechnology companies and universities need creative and competent personnel who "know it all." These are the people who in their education and training have been wise and brave enough to cross borders between fields. By doing so, they can really identify and understand what the problems are and how to solve them. Moreover, they can communicate them, not just to other scientists, but also to those in the social sciences, health sciences, humanities, the business world and the media, so that they too can get a perspective on the problem and how it affects their fields.

2 Plenty of Room at the Top and Bottom

To gain perspective of the nature and scope of the field of nanochemistry it is important to recognize the evolution of materials science with respect to the creation of new technologies. In the latter half of the 20th century, materials engineering science enabled innovations in electronics, communications, construction, transportation, energy, biomedicine and space research. Here for instance, the synthesis of solid-state materials led both to a new brand of physics and electronic devices. However, to satisfy the 21st century demand for new materials in fields like nanotechnology, information technology and biotechnology, solid-state synthesis approaches to preparing materials are gradually being supplanted by molecular methodologies, particularly the self-assembly of materials with structures that can approach the complexity of those observed in nature.

In *Nanochemistry* the authors describe how recent research in materials synthesis and self-assembly has helped fuse "top–down" solid-state physics ways of making structures and "bottom–up" molecular-chemistry methods of making materials. They show how the integration of materials chemistry, self-assembly, templating and chemical patterning strategies, from nm to μm length scales, is being actively pursued in university and industrial laboratories to make new materials having structures, properties and functions suited to a range of nascent technologies.

An attempt is made in this textbook to paint a picture of modern materials research founded upon a building block approach to materials synthesis through the paradigm of self-assembly, comprising shape controlled nanometer to micron scale objects, such as spheres and wires, tubes and sheets, made of organic and inorganic, organometallic and coordination, polymer and ceramic compounds. These are orchestrated through chemistry to auto-construct into functional architectures with designed utility. This approach to making materials fuses "top–down" solid-state engineering physics ways of making structures, and "bottom–up" molecular-chemistry methods.

One of the main challenges in this new approach to making materials is the actual synthesis of the building blocks with pre-determined bulk and surface composition, and shape, and in a size regime straddled between that of molecules and bulk matter. The building blocks, making and perfecting them, are the key to success. By having access to them through the amalgamation of organic and polymer, inorganic and organometallic chemistry one is able to develop a new way of doing solid-state chemistry that is distinctive to what has emerged over the past 50 years. It is no longer the structure and composition of the material that is new, but rather its form and scale, and guiding its arrangement and integration, that is new and which yields new materials with new function and new utility.

Nanochemistry presents a blueprint for the future development of an exciting teaching and research program in materials chemistry that is organized around the theme of tailored materials and the tenet that "all matter has a shape and all shapes matter." The central idea for developing a new materials chemistry with a bright future is that it is pivotal to know which size and shape a material must have for it to exhibit a particular property, function and utility, and that designing and synthesizing a shaped material with the right length scale can be just as important as selecting its structure and composition. However, synthesizing a material with particular forms and dimensions requires a different way of thinking than synthesizing matter with a specific structure and composition.

The latter approach that focuses just on structure and composition of a material represents the classical way of making materials, whose properties and function relate to structure and composition with size and shape as an afterthought. It has worked well for more than half a century during which time the development of solid-state materials synthesis, X-ray diffraction structure of solids, electronic properties of solids and function of defects in solids, have enabled utility of solid-state materials in a myriad of advanced technologies – almost everything around us these days! This is however, the old way of thinking about and acting upon the relations between the synthesis, structure, property, function and utility of materials. The challenge of this classical approach for making materials has always been how to choose a synthetic method that targets a product with structure and composition, to provide materials properties and functions that can be orchestrated to create utility when made into a suitable shape.

In this textbook, the authors make it clear that the approach of making materials where size and shape are a "fore thought" rather than a "postscript" is just as important in synthetic design as the structure and composition of the material. They present a "bottom–up" chemistry approach to synthetic size and form rather than a "top–down" engineering physics way of sculpting the shape. In many of today's advanced technologies, it is not just choosing the right process for synthesizing the material that counts, but also making sure that the synthesis can also form the material into the desired shape and at the appropriate length scale. It is always surprising to realize that a material of the proper composition can be totally useless if not fashioned into exactly the right form. To be successful in this new approach to making materials, one needs to have wide-ranging skills in chemical synthesis, traversing organic and polymer, inorganic and organometallic chemistry, together with a deeply analytical appreciation of materials diagnostics using the methods of modern diffraction, microscopy, spectroscopy and thermal, electrical and optical, magnetic and mechanical methods.

One should ask, is this approach to synthetic shape new, or is it just an obvious, incremental and natural extension of the classical way of making and forming materials into functional shapes? Traditional methods for synthesizing solids often involve direct reaction of solid precursors. Their chemical reactivity mainly depends on their form and physical size as well as their structure and defects. As-synthesized materials made in this way are often crystalline or glassy micron scale powders, which may need to be post-engineered into pellet, plate, tube, rod or wire shapes. If the material needs to be fashioned as a single crystal with specific dimensions and orientations, special growth processes have to be devised. These crystals may be polished or cut to expose particular faces and cut into wafers. If single crystal or polycrystalline films are required special deposition processes must be formulated. Films may be grown on lattice-matched substrates to create epitaxial films or artificial superlattice films. All of these materials' morphologies can be accessed by classical methods. However, when the physical size of shaped materials, like spheres and clusters, wires and rods, tubes and sheets, drops down to the nanoscale where their properties vary with size according to mathematically defined quantum mechanical scaling laws, then new approaches have to be devised. Both the synthesis of materials on this minute length scale, their size tunable properties and surface functionalization, as well as their organization and interconnection into functional constructs, can pose unexpected difficulties.

The ramifications of reconstructing matter into shaped building blocks has profound scientific and technological ramifications in application areas that include batteries, fuel cells and photovoltaics, digital imaging and printing, microelectronic packaging and controlled chemical release, chemical sensing and molecule separations, catalysis and photocatalysis, combinatorial materials chemistry, microfluidics and lab-on-chip, nanoelectronics, nanophotonics and nanomagnetics. In fact, one would be quite hard pressed to find a field which nanotechnology will not influence.

The authors of *Nanochemistry* present a basic chemistry approach for making nanomaterials and describe some of the principles of materials self-assembly over "all" scales. It is demonstrated how nm to μm scale building blocks with a wide range of shapes, compositions and surface functionalities can be coerced through chemistry to organize spontaneously into unprecedented structures, which can serve as tailored functional materials. This approach to materials discovery utilizes modular synthesis of hierarchical materials, according to which molecular-scale building blocks self organize into complex structures that span the entire hierarchy of length scales. Through a series of purposeful synthesis strategies, the authors illustrate how truly revolutionary advances in nanoscience and nanotechnology can result from this approach to materials discovery.

Nanochemistry research is showing the way to a world of materials that had not previously existed. The work surveyed by the authors involves a "global" way of thinking about solid-state materials that introduces the notions of complexity and hierarchy into materials chemistry, which not so long ago were deemed appropriate only for the incredible mineral-based materials made by living organisms. In essence, the authors show that the self-assembly of inorganic, organic and polymeric building blocks may occur spontaneously or be directed by molecules, aggregations of molecules, microphase-separated block copolymers, colloidal crystals or a variety of forces. Self-assembly can provide an effective pathway to new materials whose structure at "all" levels of construction, from the nanoscale to the overall macroscopic form determine materials properties, desired function and practical utility. The broadly tunable length scales and dimensionalities, platonic and curved morphologies, close-packed and open-framework structures, elemental compositions and physicochemical properties of solid-state materials to emerge from this work are of interest in a myriad of areas as diverse as those mentioned above.

But truly the greatest contributions still lay dormant in the thoughts of the students training right now, those brave enough to cross disciplines, entice collaborators, be creative, and Go Nano!

3 Nano Safety

No chemical is safe unless proven otherwise; even water can be dangerous when experienced in the wrong quantities! There are national and global regulated standards in health and safety for chemicals by which all governments, industries and universities abide. Every laboratory working with chemicals must have a comprehensive and current laboratory safety manual that describes recommended protocols for safe handling, storing and disposing of chemicals as well as access to materials safety data sheets (MSDS) that document toxicology of chemicals and recommended treatment for exposure.

Do we need to treat nanomaterials differently than other chemicals? Some might argue that nanomaterials are only versions of already classified chemicals and can be treated with the same caution. Others recognize the added fact that nanomaterials, particularly nanochemicals, are not only characterized by their chemical composition but also by their special physical dimensions, which are below the micron scale of common particles (*i.e.*, sizes between a nanometer and a micrometer). This means that the toxicity of both the bulk forms and the activity and interactions of these nanomaterials, or their intermediates, need rigorous testing. Therefore, to ensure safety to our health and our environment, new protocols on how to work safely with nanomaterials need to be developed and we should evaluate and test nanomaterials under new safety criteria (Figure 1).[1–3] Any new nanomaterial, with known or unknown composition, should be treated with as much caution as any new and untested "non-nano" chemical. Paradoxically, since the concept of nanomaterials are quite new to the field of toxicology, it is the emerging field of "bionanochemistry," an area concerned primarily with bioassays,

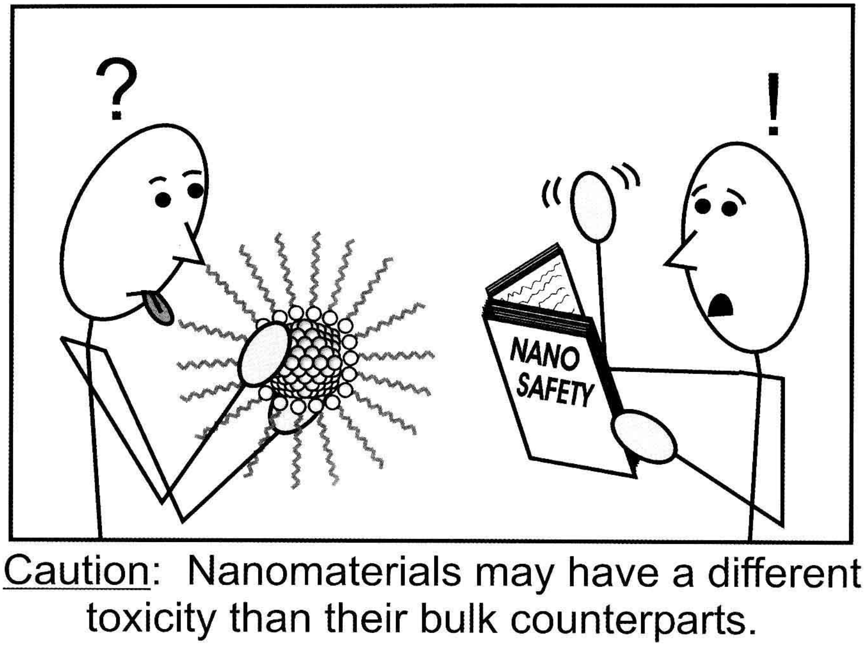
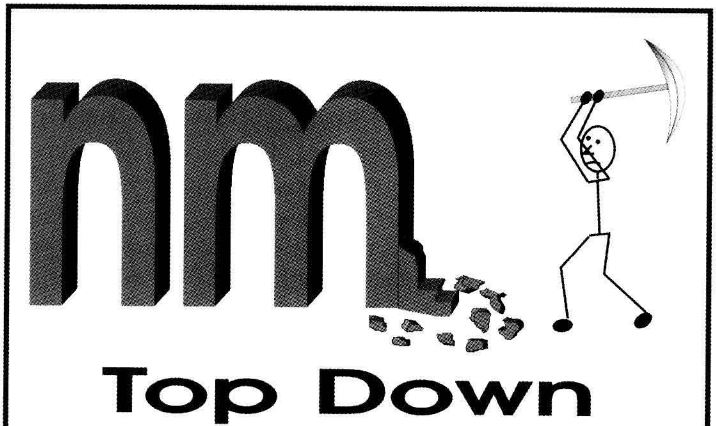


Figure 1 *Even well known compounds may present unexpected health risks when they are fashioned as nanoscale building blocks*

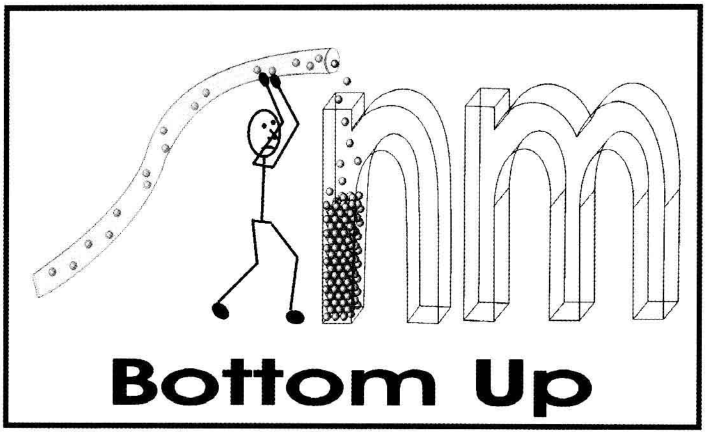
biolabels and bioelectronics, which will likely provide useful knowledge and technology to address such safety issues and other questions central to issues of nanotoxicity. For some very recent work on this subject see Appendix B, Cytotoxicity of Nanoparticles.

Aims of this Book

About half a century ago, Richard Feynman gave his prophetic lecture "*Plenty of Room at the Bottom.*" He outlined in this talk the foundations of nanoscience, and the promise that totally synthetic constructions could eventually be built with molecular scale precision. Nanoscience research has been rapidly increasing across the globe during the past decade. It is now widely accepted by the scientific, industrial, government and business communities, that nanoscience will be of integral importance in the development of future technologies. Nanoscience is being touted as the engine that will drive the next industrial revolution.



One of the hallmarks of nanoscience is its interdisciplinary nature – its practice requires chemists, physicists, materials scientists, engineers and biologists to work together in close-knit teams. Communication and collaboration between disciplines will enable the most challenging scientific problems to be tackled, those that are most pressing in the successful exploitation of nanotechnology. This is a daunting challenge for students, researchers, managers, funding agencies and politicians, as the field of nanoscience is so diverse and evolving rapidly. These difficulties are exacerbated by the fact that few textbooks on nanoscience have existed that bring together the vast range of published work in an accessible primer for students and practitioners of this topic.



"*Nanochemistry – A Chemical Approach to Nanomaterials*," has been written through the eye of chemistry in an attempt to fill this void. The content of the book has been selected and organized to establish the basic principles of nanoscience through the subject of nanochemistry. Because of the interdisciplinary approach adopted by the authors, the book should be useful to a broad readership even though the fundamental science and applications will continue to change almost on a daily basis.

Nanoscience today is a creative amalgamation of bottom–up chemistry and top–down engineering techniques. We are currently witnessing an explosion of novel ideas and strategies for making and manipulating, visualizing and interrogating nanoscale materials and structures. An aim of the book is to describe the concepts and methods developed for synthesizing a range of nanoscale building blocks with strictly controlled size, shape, bulk and surface structure and composition, and properties. A further aim is to explain how these nanoscale construction units can be organized and integrated into functional architectures using a combination of self-assembly, templating, chemical lithography and other patterning methods.

Nanochemistry will be a valuable textbook for students planning an academic or industrial research career in any area related to nanoscience and nanotechnology. It provides a global perspective of the subject of nanochemistry, written with sufficient breadth and depth to make it suitable as the basis of an advanced undergraduate course in chemistry or a graduate course in materials chemistry, engineering materials science, solid-state physics and nanoscience. Much of the subject matter presented in the book can be readily adapted to introduce chemical aspects of nanoscience to a broad audience of undergraduates in their first 3 years at university. This text should provide a readily accessible road map of nanochemistry, beginning with its roots and extending to its branches, emphasizing throughout the connection of ideas from discovery to application from within and between the science disciplines. It provides a unique perspective on nanoscience and nanotechnology, an attribute which will make it invaluable for those witnessing, participating in, and trying to remain at the leading-edge of the nanoscience explosion. These include scientists, managers in university and industry, government workers, business people, even the media.

Structure of this Book

In the first textbook on nanochemistry, Arsenault and Ozin describe the methods used by chemists to make nanoscale building blocks and the techniques that can arrange them into functional architectures. Primary building blocks have dimensions spanning nanometers to micrometers, and can be made of almost all conceivable materials. Their assembly into a particular arrangement can be driven by forces acting between them, or directed by specific interactions with a structure-guiding template or patterned substrate. Like Nature's biomineral construction units, these primary building blocks can associate into secondary structures and this organization scheme can continue until the highest level of complexity is reached. This introduces the notion of building blocks assembling over multiple length scales as a way of making materials with hierarchical structures and complex form. Hierarchy allows a material to satisfy several, sometimes conflicting, sets of conditions and demands in a single material. How this relates to Nature's way of creating structures introduces important connections between molecular recognition and epitaxy, crystal growth and form, unifying ideas in coordination, bioinorganic, materials and solid-state chemistry.

The book *Nanochemistry* begins by exploring the basic tenets of self-assembly, and continues into some insightful 19th century research of Pieter Harting on synthetic morphology, Ernst Haeckel and D'Arcy Thompson on morphogenesis and Emil Fischer on the lock-and-key principle of molecular recognition. These classic studies relate in turn to 20th century research of Richard Barrer on template directed self-assembly of microporous materials, Hientz Lowenstam on organic matrix mediated formation of biominerals and Jean-Marie Lehn on supramolecular chemistry. Ideas and methods stemming from this pioneering work provide a springboard for the development of the 21st century emerging field of nanochemistry.

Continuing on this flow of ideas, the book explores the genealogy of chemical discoveries that lead to the development of nanochemistry. The toolkit of nanochemistry is described in terms of the integration of concepts and methods in chemical lithography, templating, materials chemistry and self-assembly. The underlying theme is how different patterning and templating methods spanning the scale of microns to nanometers can be creatively fused with synthesis and self-assembly of sheet, wire, tube, rod, cluster, solid and hollow sphere and hemisphere, spiral and ring building blocks to make new materials and structures. The goal is to create functional nanostructures with perceived utility in such areas as electronics, magnetics and photonics, batteries, solar cells and fuel cells, catalysis and sensing, chemical storage and release. In fact, in a few years time it will be difficult to find products and technologies that have not been significantly advanced by nanoscience.

At the end of every chapter the reader is challenged with "*Nanofood for thought*," a collection of questions often without clear-cut answers that have been designed to inspire creative and holistic thought and facilitate a connection of ideas about the materials and methods described throughout the book. "*Nanofood for thought*" will hopefully serve not only to enhance the readers' understanding of the underlying physicochemical principles of nanochemistry but also suggest new ways and means for the reader to approach and solve basic and directed research problems in their own area of nanoscience.

The book culminates by posing the provocative question "*What comes next?*." Some fanciful thoughts are offered on how to think about assembling the future beyond the nanochemistry presented in this textbook.

Finally, a series of practical experiment outlines in nanochemistry is explored, to enable students and researchers to roll up their sleeves in the "*Nanolab*," make matter that matters, and invent materials of the next kind!

List of Acronyms

5CB	4-pentyl-4′-CyanoBiphenyl
AAO	Anodized Aluminum Oxide
ACC	Amorphous Calcium Carbonate
AFM	Atomic Force Microscopy
ALD	Atomic Layer Deposition
APS	AminoPropyltrimethoxySilane
ATO	Antimony Tin Oxide
BDC	1,4-Benzene-DiCarboxylate
BPEI	Branched PolyEthyleneImine
BZ	Belousov-Zhabotinsky
CVD	Chemical Vapor Deposition
CC	Colloidal Crystal
CCMV	Cowpea Chlorotic Mottle Virus
CFM	Chemical Force Microscopy
CPC	Colloidal Photonic Crystal
CPMV	CowPea Mosaic Virus
CSS	Core-Shell-Shell
DDP	Decylammonium-DihydrogenPhosphate
DEISA	Directed Evaporation-Induced Self-Assembly
DLVO	Derjaguin Landau Verwey Overbeek
DNA	DeoxyriboNucleic Acid
DOS	Density Of States
DPN	Dip-Pen Nanolithography
DPPE	DiPalmitoyl PhosphatidylEthanol
DX	Double-crossover
EBG	Electronic Band Gap
EDS	Energy Dispersive Spectroscopy
EDX	Energy Dispersive X-ray analysis
EELS	Electron Energy-Loss Spectroscopy
EG	Ethylene Glycol
EISA	Evaporation Induced Self-Assembly
EMR	ElectroMagnetic Radiation

ESA	Electrostatic Self-Assembly
ESL	Edge-Spreading Lithography
EXAFS	Extended X-ray Absorption Fine Structure
FESEM	Field-Emission Scanning Electron Microscopy
FET	Field-Effect Transistor
FTO	Fluorine-doped Tin Oxide
GLYMO	(3-GLYcidyloxypropyl)-triMethOxysilane
GMR	Giant MagnetoResistance
HMDS	HexaMethylDiSilazane
HREM	High-Resolution Electron Microscopy
HRSEM	High-Resolution Scanning Electron Microscopy
HRTEM	High-Resolution Transmission Electron Microscopy
IR	InfraRed
IRRS	InfraRed Reflection Spectroscopy
ITO	Indium-Tin Oxide
IUPAC	International Union of Pure and Applied Chemistry
LbL	Layer-by-Layer
LCD	Liquid Crystal Display
LED	Light-Emitting Diode
LFM	Lateral Force Microscopy
MALDI	Matrix-Assisted Laser Desorption Ionization
MAS NMR	Magic Angle Spinning Nuclear Magnetic Resonance
MBE	Molecular Beam Epitaxy
MCP	MicroContact Printing
MEMS	MicroElectroMechanical Systems
MFM	Magnetic Force Microscopy
MHA	16-MercaptoHexadecanoic Acid
MIMIC	MIcroMolding In Capillaries
MINIM	Metal-Insulator-Nanocluster-Insulator-Metal
MIPO	Micromolding in Inverse Polymer Opals
MOCVD	Metal Organic Chemical Vapor Deposition
MOF	Metal-Organic Framework
MOSFET	Metal-Oxide-Semiconductor Field-Effect Transistor
MPP	Microscope Projection Photolithography
MS	Mass Spectroscopy
MSA	Mesoscale Self-Assembly
MTP	MicroTransfer Printing
MWNT	Multi-Walled carbon NanoTube
NCA	N-CarboxyAnhydride
NCP	NanoContact Printing
NDR	Negative Differential Resistance
NEMS	NanoElectroMechanical Systems
NIR	Near InfraRed
NLO	Non-Linear Optical
NMR	Nuclear Magnetic Resonance
NSL	NanoSphere Lithography