

## Nanochemistry

## Advancing Nanochemistry Education

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**Abstract:** The chemical approach to nanotechnology that has emerged in the last three decades has proved to be extremely fertile. As chemistry increasingly turns into nanochemistry, and renewable solar energy available in sunlight and in biomass emerges as the main energy and raw materials source available to mankind, effective teaching of nano-

chemistry becomes increasingly important. This Viewpoint identifies the requirements of a short course aimed to provide future scholars with the conceptual foundations, and a clear perspective, of an important discipline which turned out to be the enabler of nanotechnology.

## 1. Introduction

Nanochemistry, the chemical approach to nanotechnology, as first summarized by Ozin in 1992,<sup>[1]</sup> uses chemical synthesis to reproducibly afford nanomaterials from the atom “up”, as opposed to the nanoengineering and nanophysics approach which operates from the bulk “down”. Carried out under the mild and controlled conditions typical of synthetic organic chemistry, the nanochemical route affords nanostructured materials through the assembly of atoms or molecules in pieces of matter with nanometer sizes with new molecular organization affording special properties. In brief, nanochemistry becomes the “enabler of nanotechnology” yielding nanomaterials whose building blocks, with nanometer sizes in one, two, or three dimensions, produce novel structures which, in turn, produce unique function and utility, to meet today’s “insatiable demand”<sup>[2]</sup> for new functional materials in disparate areas of application.

In the typical pragmatic view of chemists, Ozin emphasized<sup>[1]</sup> that useful nanotechnology has to do with making *useful materials* with unique properties. The approach turned out to be dramatically fertile,<sup>[3]</sup> and in the subsequent two decades several new functional materials obtained via the nanochemical route have found application in areas as diverse as catalysis (including photocatalysis and electrocatalysis), functional coatings, biotechnology, chemical sensors, separation, environmental remediation, optical and photonic devices, photovoltaics, batteries, fuel cells, and microencapsulation for the controlled release of all sorts of functional ingredients including drugs, fragrance and flavor, and curing agents.<sup>[4]</sup> In satisfying the above “insatiable” demand for new functional materials, chemists play a central role analogous (but not identical) to that

played in the development of the iconic industry of the 20th century, the chemical industry.

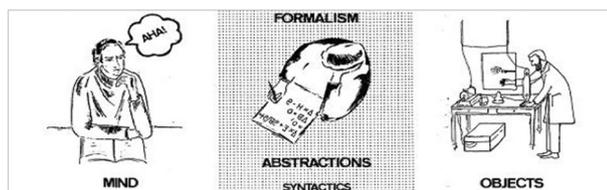
As chemistry turns into nanochemistry, therefore, the importance of education in nanochemistry becomes self-evident.<sup>[5]</sup> Blonder in Israel has investigated the crucial influence of models in teaching nanochemistry.<sup>[6]</sup> Her team developed specific models to advance the knowledge of nanochemistry and the teaching attitudes of chemistry teachers.<sup>[7]</sup> Ozin and his co-workers published the first comprehensive textbook<sup>[8]</sup> for teaching nanochemistry in 2005. A scientific Journal<sup>[9]</sup> was established in 2009 to discuss and advance the field of “nano education”, and numerous nanotechnology journals have more recently started to address the field, with some stating their intention to regularly feature a spotlight on education.<sup>[10]</sup>

The present Viewpoint addresses the issue of nanochemistry education in the context of the emerging, global transition of mankind from non-renewable to renewable sources of energy and materials, namely to solar energy either freely available in sunlight or accumulated in biomass. A short introduction to the chemical methodology is followed by an insight into the nanochemistry conceptual foundations. Aiming to shape scholars, rather than overspecialized researchers, the program of a short, advanced course on nanochemistry is identified, along with teaching materials and other educational tools and requirements.

## 2. The Chemical Methodology

Chemistry is a powerful, autonomous science with an intrinsic methodology of great utility<sup>[11]</sup> that continuously originates a cornucopia of ever new, artificial substances that largely benefit society, the economy, and the environment. At the core of the chemical methodology lies a powerful approach based on mental visualization and association of chemical *models* for substances. These models can be molecular structures. But they can also be synthetic “building blocks” of different size and shape, as the recent development of nanochemistry clearly shows. In brief, the chemist’s mind proceeds by self-creating

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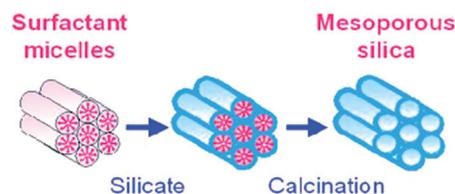
**Figure 1.** Chemists create mental images of the behavior of matter. And then go the laboratory to create their objects: the myriad substances benefiting society at large. (Reproduced from Ref. [12], with kind permission).

an image of how atoms, molecules, and other matter building blocks will actually behave, and then tries to mentally “push” them on the desired route (Figure 1).

What chemists really *do* is to create mental images of the substances they wish to create; and then manipulate these shapes in a rational manner to verify if they could fit to afford the desired substance; a process vividly illustrated by a famous speech by Kekulé at a dinner commemorating his “discovery” of benzene’s structure in 1865.<sup>[13]</sup> Put another way, what chemists actually do practicing their science is to mentally play with these representations *before* entering the laboratory. In this sense, chemistry constitutes a *language*, and thus learning chemistry is analogous to learning a language. In each language, there are rules to combine the elementary units (words), which, in turn, represent objects and ideas. The result of the combination is a meaningful language that enables people to communicate. In chemistry, the units are the chemist’s building blocks (the pure substances whose chemical formula is like a word),<sup>[14]</sup> and the outcome is a new substance whose structure and functions are to be discovered.

### 3. The Nanochemistry Methodology

In short, nanochemistry *expands* the reach of the chemical approach extending the chemical methodology to materials synthesis. The result is a physico-chemical handling of matter relying on secondary valences, the adjustment of geometrical shape and interface energies, and self-organization, rather than classical synthesis.<sup>[15]</sup> Materials self-assembly, for instance, has introduced an entirely new way of thinking about *how to make* materials. In a self-organizing system of materials a particular architecture forms spontaneously with a structural design determined by the size and shape of the individual nanocomponents, and by the spontaneous organization of building blocks into assemblies due to molecular forces that operate at length scales beyond the molecular, between the building blocks, and over different scales.<sup>[8]</sup> Figure 2, for example, shows the schematic drawing of the liquid-crystal templating mechanism. Hexagonal arrays of cylindrical micelles are formed in solution, and silicate species occupy the spaces between the cylinders. A new form of mesoporous silica structure is thus obtained showing an organized, periodic structure despite the amorphous character of the silica walls (see below the concept of functional randomness). These silica structures have found great utility as catalysts and adsorbents because of the regular arrays of uniform pore channels.



**Figure 2.** Materials synthesis by self-assembly can easily be carried out growing, for example, the material around the structure of a micelle in solution. Here the hexagonal arrays of cylindrical micelles formed in the solution dictate the growth of hexagonal silicate cylinders to give periodic mesoporous organosilica.

Chemists, in practice, create new nanomaterials through the utilization of planned synthetic chemistry to produce molecular building blocks, bridging between the worlds of molecules connected by molecular bonds and the chemical engineering of micron-sized structures (lithography, chemical vapor deposition, coating techniques, etc.). Such nanoscale building blocks of different size and shape, composition and surface structure can be useful in their own right, or in a self-assembled structure. In general, however, for nanomaterials size and shape are *as important* as structure and composition. Or, as put it by an officer of the US Environmental Protection Agency “... *properties change with size alone, not just composition. New tools and approaches are necessary to show that the phenomena were real. We have never actually believed it before.*”<sup>[16]</sup> Beyond composition, shape, and size, imperfection in the assembly structure of nanostructured materials is the other important factor which provides them with interesting properties, and ultimately with function.

Disordered sol–gel glasses doped with organic molecules,<sup>[17]</sup> for example, are a celebrated example of an enormously large class of functional materials in which function is eminently due to the imperfect and tuneable geometry of the encapsulating glassy matrix. “*In practice*”, Avnir explains, “*we are learning to master functional randomness, namely the teaching of Nature that is much more efficient to construct complicated systems by allowing disorder and correlations to compete and to come to terms with each other through an optimal solution.*”

Now, a brief analysis of the historic development of materials chemistry starting, for instance, from Harting’s work with biomineral formation (1873) through the classic *Of Growth and Form* of D’Arcy Thomson (1917), shows how the effort to apply physico-geometrical principles to explain morphogenesis in the study of natural materials, has been a constant driving force of scientific thought. Nanochemistry-enabled nanotechnology is a continuation of this intellectual endeavour, and another surprising example of *historical hysteresis*, for which the revival of interest in areas of research such as materials morphogenesis described in *Of Growth and Form* has led to dramatic advances creating one of the most active and interesting fields in contemporary chemistry and materials science, out of a research field considered as completely closed until the late 1980s.

Similarly, for that matter, it is enough to consider the discovery that organized organic molecules such as micelles actually

direct the growth of inorganic oxides in solution. This single finding, indeed, brought about a revolution in the preparation of new porous materials.

Barrer and Denny (1961) first showed how quaternary allylammonium cations in the synthesis media dictate the assembly of microporous aluminosilicates, establishing the organic structure-directing agent concept.<sup>[18]</sup> Flanigen and Bedard (1989) demonstrated how to go beyond aluminosilicates, and how silicas as microporous materials can be templated from many elements of the periodic table;<sup>[19]</sup> Kresge and co-workers (1992) demonstrate how to extend the method, achieving length scale well beyond the molecular scale;<sup>[20]</sup> Takahashi and his team (1998) showed how to use an O/W microemulsion to afford hollow mesoporous silica spheres;<sup>[21]</sup> and finally Ozin and co-workers (1999) introduced periodic mesoporous organosilicas,<sup>[22]</sup> in an intellectual and chemical *tour-de-force* that Ozin aptly termed “full escape from the 10 Å prison”,<sup>[23]</sup> and with it the birth of the nanochemistry of mesoporous materials.

The richness of the above chemical approach to nanotechnology—bottom-up, from the atoms to the nanoscale objects—has led to the creation of a multiplicity of nanostructured materials, eventually providing the long-awaited practical benefits envisaged by Feynman in his celebrated “There is plenty of room at the bottom” lecture at the 1959 meeting of the American Physical Society. In this lecture, Feynman devised what was later called the nanophysics approach to nanotechnology, claiming that a physicist could “in principle synthesize any chemical substance that the chemist writes down”.<sup>[24]</sup>

“A chemist comes to us and says, “Look, I want a molecule that has the atoms arranged thus and so; make me that molecule.” The chemist does a mysterious thing when he wants to make a molecule. He sees that it has got that ring, so he mixes this and that, and he shakes it, and he fiddles around. And, at the end of a difficult process, he usually does succeed in synthesizing what he wants. By the time I get my devices working, so that we can do it by physics, he will have figured out how to synthesize absolutely anything, so that this will really be useless.

“But it is interesting that it would be, in principle, possible (I think) for a physicist to synthesize any chemical substance that the chemist writes down. Give the orders and the physicist synthesizes it. How? Put the atoms down where the chemist says, and so you make the substance. The problems of chemistry and biology can be greatly helped if our ability to see what we are doing, and to do things on an atomic level, is ultimately developed—a development which I think cannot be avoided”.

#### 4. Shaping Scholars

Often promoted with sensation-seeking claims according to which nanotech should have impacted “life science, information technology, energy-related sciences, and materials science”<sup>[25]</sup> through new technical solutions such as novel drug delivery methods, tiny motors for robotics/medicine, new computer memory platforms and highly efficient solar panels, the

first commercial products on the market after more than two decades (1985–2009), were stain-resistant pants, scratch-proof paint and bouncier tennis balls.<sup>[4]</sup> The situation, since then, has certainly evolved, with many nanomaterials which have entered daily life;<sup>[26]</sup> but not yet to the extent and with the large-scale impact envisaged in the early days of nanotechnology.

It is appropriate, then, to look back at past decades remembering the promises made by scientists. A theme on which physicist and epistemologist Lévy-Leblond has appropriately written that:<sup>[27]</sup> “Society remembers promises made in the past, especially when they are not kept. In particular, it is interesting to review what physics promised in the 1950s and 1960s.” ...“We promised nuclear power would provide free energy for all. Basing their opinion on experts’ views, popular magazines of the time seriously predicted that before the end of the century everyone would have a small nuclear reactor in their own home and car (*sic*), and that large-scale thermonuclear fusion would be mastered.”... “Obviously, anyone can see we are not even close to achieving these goals.”

One can easily realize that the claims made by physicists in the 1950s are similar to those made by nanotechnology advocates today, with frequent abuse of language borrowed from marketing.<sup>[28]</sup> To separate the realistic prospects from the hype surrounding this important domain of contemporary research, it is important to understand that nanotechnology is a multidisciplinary discipline with the hallmark of a true *chemistry of materials* at the nanoscale.

The boundaries that have separated these traditional chemistry disciplines in the 20th century have broken down. One large multidisciplinary community with a keen scientific and technological interest in “all” aspects of chemistry at the nanoscale has emerged in the last 20 years, as scientists from all corners of the older sub-disciplines of chemistry have learned how to synthesize from the bottom-up, tailor-made (nano)materials from individual or groups of nanoscale building-blocks that have been intentionally designed to exhibit useful properties with purposeful function and utility.

In brief, the very intrinsic cross-disciplinary nature of nanoscale science requires the shaping of scholars, getting back to a fertile past when universities shaped scholars (and not “researchers”), whose activity consisted not only in *doing research*, but also in *teaching, disseminating* and *applying science*.<sup>[27]</sup> The ultimate aim of these newly educated scientific professionals will not be to get the next paper published or grant approved, but rather to conceive and develop breakthrough technologies capable of solving a number of global challenges; the most relevant of which is likely to be the continuing dependence of mankind for energy and goods on non-renewable energy and materials sources.<sup>[29]</sup>

#### 5. The New Nanochemistry Curriculum

Along with Jones and other scholars, Blonder has recently (2013) reviewed the current research on nanotechnology education including curricula, and educational programs for both high school and university undergraduates.<sup>[7]</sup> As expected for a relatively new field, many differences were found among dif-

ferent countries, and even within the same country. No standards of learning for nanotechnology have yet been created. Even focusing on undergraduate education, the educational offer varies from four-week to four-year courses. For example, educators in the US have shown that a four-week nanotechnology course for first-year undergraduate students was effective for students to assemble key concepts about nanotechnology in a meaningful way.<sup>[30]</sup> On the other hand, Dublin's Trinity College offers a four-year degree programme ("*Nanoscience - Physics and Chemistry of Advanced Materials*"), aimed to "build a deep and lasting understanding" of nanoscience.

In agreement with the above findings that a short-course time frame may be effective to educate students about advancements in instrumentation and processes used in nanoscale science and technology, herein we outline the requirements of an intensive course lasting six weeks comprising five modules (6 h per week), including one full module of laboratory training (Table 1). Owing to the short duration of the course, the students should be knowledgeable in chemistry, physics, and mathematics, namely undergraduate students who have completed the second year of their MSci studies in chemistry, physics, biology or engineering.

The course employs four renowned textbooks as teaching materials, including one of Ozin's pioneering texts. Rather than starting with theory, the course is opened with three examples of successful nanoproducts with large-scale utilization. We verified that this choice makes the instruction personally relevant to each student's life, as previously reported for similar nanotechnology courses.<sup>[31]</sup> The interdisciplinary nature of nanochemistry requires an educational offer that encompasses several diverse topics in the new curriculum. Following education on the foundations of nanochemistry and on specific nanomaterials, students will receive classes on the impact of nanoma-

terials on human health and the environment, since it is now well known that the small size and high surface area of nanomaterials may cause numerous negative health and environmental effects.

Students are confronted, for example, with the necessity to use new classification systems, capable of taking into account the fact that the toxicological effects of nanomaterials considerably differ depending on the degree and type of functionalization. Dedicated laboratory training is aimed at developing basic skills in synthesizing selected nanomaterials, and in evaluating their efficacy in selected applications from the technical and environmental viewpoints.

Finally, the need for effective continuous learning is addressed by presenting the nanomaterials "genome" initiative<sup>[32]</sup> as one of the emerging resources to effectively innovate in the field of nanomaterials. The course is concluded with classes in written and oral communication to advance the skills required to effectively communicate outwardly the relevance of the students' future work,<sup>[33]</sup> (to investors and funding agencies, to the public, to policy makers and to interest groups).

Students continuously get feedback on their learning with written exercises and works during the course. After concluding the first half of the course, each student is asked to effectively present a scientific article in nanotechnology. The average grade of the ongoing evaluation will account for 50% of the final mark. At the end of the course, a final oral exam is used to assign the rest of the overall mark. Students successfully completing the course will be able to master synthetic methods to afford functionalized nanomaterials, as well as to discuss the applications and the large applicative potential of manufactured nanomaterials taking into account technical, economic, health and safety, and environmental aspects.

**Table 1.** Nanochemistry: The route to functional materials to solve global challenges.

Content	Duration	Teaching materials
1. <i>Why nano is different</i> Fundamentals of nanoscale science and technology	three lectures (6 h)	L. Cademartiri, G. A. Ozin, <i>Concepts of Nanochemistry</i> , Wiley-VCH, <b>2009</b>
2. <i>The nanochemical route to nanomaterials</i> Basic and advanced methods for the synthesis and assembly of nanomaterials	three lectures (6 h)	
3. <i>Nanomaterials</i> Porous nanomaterials, nanocomposites, polymeric nanomaterials, biomimetic nanomaterials	six lectures (12 h)	G. Cao, <i>Nanostructures and Nanomaterials: Synthesis, Properties and Applications</i> , Imperial College Press, London, <b>2004</b>
4. <i>Nanomaterials in action</i> Energy storage, catalysis, functional coatings	three laboratory training sessions (6 h)	M. Pagliaro, <i>Nano-Age: How Nanotechnology Changes our Future</i> , Wiley-VCH, <b>2010</b>
5. <i>Resources for life-long learning and communicating nanochemistry</i> The nanomaterials genome initiative, effective nanoscience and technology communication	three lectures (6 h)	M. Tomczyk, <i>NanoInnovation: What Every Manager Needs to Know</i> , Wiley-VCH, <b>2014</b> C. Qian, T. Siler, G. A. Ozin, <i>Exploring the Possibilities and Limitations of a Nanomaterials Genome: Small</i> , <b>2015</b> , <i>11</i> , 64

## 6. Outlook and Conclusion

Chemistry-enabled nanotechnology has the potential to solve the environmental crisis due to the increasing consumption of non-renewable resources such as oil, natural gas, coal, and uranium to make energy and goods.<sup>[34]</sup> Evident global trends suggest that in the near future (within the next two decades), Ciamician's vision of 1912<sup>[35]</sup> will become a reality; that is, mankind will use renewable solar energy available in sunlight and in biomass to make useful energy, chemicals, materials, fuels, and polymers, as well as to remediate the poor environmental status of many areas.

For instance, 20% efficient photovoltaic (PV) modules with thirty-year lifespan currently sold by photovoltaic manufacturing companies at <\$0.6 per W, have lowered the cost of solar electricity to such an extent to reach the "grid parity" with fossil electricity in practically most countries of the world.<sup>[36]</sup> Accordingly, as of early 2015 the overall PV power installed worldwide exceeded 180 GW,<sup>[37]</sup> whereas in 2000 the world's cumulative solar PV power was only 1.4 GW. There are no shortage issues, as silicon is among the most abundant elements on Earth, and the PV industry is thriving making the 300 GW yearly installation threshold a reasonable objective. Silicon-enabled PV power is fully scalable with the energy needs of mankind. Yet, sunlight is heavily intermittent. Especially during autumn and winter seasons, the actual production of electricity is up to 90% lower than during the summer. This obviously places demands on new electricity storage (and release) solutions, capable of efficiently accumulating and then readily making available huge amounts of solar electricity at low cost.

New high energy density batteries, water electrolyzers, fuel cells, and supercapacitors are the technologies that nanochemistry research must target and make available in the near term. Whether batteries or fuel cells, these devices will need to rely on nanomaterials comprising abundant elements (and thus, not on Pt, In, or other rare and costly metals). We therefore need educated nanochemists capable of creating and developing these technologies up to the level required for large-scale adoption.

This study identifies the requirements of a brief, advanced course in nanochemistry for undergraduate students at the end of their second year of studies. Clearly, many other courses, and obviously full degrees in nanochemistry and nanotechnology, are equally suited to providing such education in a meaningful way.

For example, Ozin at the University of Toronto currently teaches 12 lectures of two hours to about 25–30 students registered for credit.<sup>[38]</sup> Following the first six basic lectures given by the lecturer, the students team up to teach the last six lectures using the remainder chapters of *Nanochemistry*, which accounts for 50% of the course mark for the students. Aiming to stimulate creativity in the words of Pauling ("it's what's in your head that counts, not that you have to look it up in a library"),<sup>[39]</sup> Ozin then asks students to provide the classroom with a surprise with an original proposal in the form of three

slides and 5 min including questions where they have to defend the innovation in their proposed ideas.

What is specific to the present course, however, are i) the diverse topics encompassed in the curriculum, so as to conform to the intrinsic interdisciplinary nature of nanoscale science and technology; ii) the emphasis on the conceptual foundations of nanochemistry; and, iii) the suggested approach to continuous learning and innovating in environmentally responsible ways, aiming at changing the prevailing view in their chosen field through creative thinking.

As continuously improving the educational offer is an eminent part of the activities of every academic institution fulfilling its mission and pursuing scientific excellence, the outcomes of this study should be useful to nanoscience educators as well as to senior faculties in older and newer institutions.

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