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NANO-CHEMISTRY*

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Nanotechnology is a highly interdisciplinary field, with contributions from all fields: physics, chemistry, biology, materials science, engineering, and others. The explosive number of publications in this field makes it nearly impossible to give an extensive review even in chemistry alone. Nonetheless, one may track its emergence and rapid advancement from the point of view of a chemist's. This paper aims to provide a conceptual overview of chemistry for nanotechnology, a brief classification of different approaches and applications, together with some sample cases.

1. Chemistry as nanochemistry

Is chemistry all along in the business of nanotechnology? Some might argue that it is, but on a practical level, it is not—not until about 20 years ago. For sure, it is contributing a lot to this new wave of technology.

In retrospect, chemistry is sometimes referred to as the central science, because one cannot escape the fact that to study nature one has to deal with the basic building blocks of matter, the atoms and molecules. In this author's opinion, the best definition for chemistry nowadays would be the answer to the question “what do chemists do?” Since the beginning, chemists (or alchemists) had been attempting to transform matter, but these attempts could not have progressed without a proper theory or model, at least in part, to help in the design of the method of transformation. The Greek Philosophers Leucippus and Democritus had proposed (450 B. C.) the idea that matter must be made of smaller building blocks, 'the *atomos*', a proposition which could have just been a rational extrapolation of the observation that the beach looks solid when viewed from afar, but is in fact granular on closer inspection. The atomic theory was developed by Dalton in his opus *A New System of Chemical Philosophy* (1808)[1] which explained very well those different transformations observed then for some of the known substances. Chemists, since then, have been involved in 'playing' with these atoms and molecules, transfiguring matter by combining atoms into various possibilities of atomic bonding combinations, permutations, configurations, and molecular arrangements. Nearly every general textbook in chemistry begins with the atomic concept —that all matter is made up of atoms. Learning more and more about the atoms and how to deal or 'play' with them is generally what chemists do.

Chemistry succeeded as a science because it was able to develop techniques for 'handling' atoms and molecules. The typical size of the atom? Order of magnitude, it is about 1 Angstrom (Å) in diameter or 0.0000001 of a millimeter. Clearly, too small to touch or handle individually. But how did chemists manage to do it? Well, the 'handling' is really a logical manipulation of the atomic model. By knowing the reactivities of the elements and compounds, chemists had a way of peering into the properties of the individual atoms or the molecules that they are made of. Chemistry owes a lot to thermodynamics (1800s) for providing a framework for accounting of all the energetics involved—and so, even before quantum theory, knowing relative bond strengths between carbon atoms and a bit of imagination such as Kekulé's dream, an accurate molecular model for the benzene was conjured (1872). It also owes a lot to quantum theory (early 1900s) for improving the model for the atom, which explained in further detail the observed chemical and physical properties of matter in terms of the electronic structure of the atom. Thus now, we have a clearer understanding of the chemical reactivities of atoms or molecules, are able to predict the molecular shape and electronic properties, or predict how they will interact with light, electricity, magnetism or with other atoms, assess their stabilities and reactivities, and all of these with fairly good accuracy. These molecular properties are, in turn, related to the observed property of bulk matter. Bulk matter here is made of at least 10^{16} atoms or molecules in an assemblage that has a size that can be manipulated and handled in glass vessels or crucibles typically found in a chemical laboratory; a typical lab specimen size being of micro- or milligrams, grams or even kilograms in quantity, which is readily weighed using a laboratory balance.

It is also no wonder why chemists often engage in discussions of structure-property relationships or in other words, in explaining an observed behavior of bulk matter in terms of the properties of the molecules that it is made of. For instance: this author overheard an auto-mechanic trying to explain why battery acid spills on polyester pants do not readily burn into holes—so he explained: “it is because the acid did not easily absorb into the polyester fabric, unlike in cotton.” A fine observation and a good explanation at that, but is still lacking of a molecular explanation. Chemists would prefer to explain the observation based on the molecular constitution of the fabric and what its properties are: “that polyester is made of molecules that are less polar than cotton, and are therefore less water-liking than cotton, among other things to be considered.” In this perspective, a chemist could therefore 'design' a molecule whose property will be of a particular wettability, in contrast to forming a blend of cotton and polyester. The point is, chemical intuition is synonymous to molecular level understanding, and this is routinely used to rationalize observed bulk properties of matter and in the design of molecules for desired bulk properties.

In terms of forming new substances, synthetic chemists act like molecular engineers—designing and fabricating molecular structures of desired physico-chemical and electronic properties. They come up with steps to build a complex molecular structure in an atom-by-atom or molecular fragment-to-molecular fragment approach. Just this past week, one would read in the chemical news the complete synthesis of an antibiotic natural product plastensimycin, in just four months after its discovery was first reported![2] It just shows how much synthetic chemistry has matured.

So what makes chemistry nanochemistry? Whereas before, bulk behavior was routinely measured, nowadays, the observation data on properties of matter are not only limited to bulk behavior but also include those of matter made up of only a cluster of atoms—in the hundreds, thousands, or just a few million atoms bonded together in assembled structures whose final dimensions are only in the tens or hundreds of Angstroms. In other words, in the nanometer size regime. These structures—which we may refer to as *nanostructures*—are not like the molecules of old, but are materials yielding behavior unlike their bulk counterparts. And as more of them are cropping up these days, new phenomena are being observed, and in turn, there is more impetus to create new ones and innovate methodologies for making them into various morphologies or modes of molecular organization. The motivation is both fundamental and practical. Fundamental: to discover and understand new phenomena exhibited by matter at these newly accessible dimensions, and practical: to form them into useful somethings: as novel electronic devices, as efficient drug delivery systems, as ultrasensitive sensors, as ultra-lightweight structural materials, as highly efficient alternative energy sources, as environmentally benign materials, or as new materials for an entirely new application.

2. The Tipping Point for Nanotechnology

Many years before, there had been nanostructures formed, such as Faraday's gold colloids prepared in 1857, which remained stable for over a century until it was destroyed during World War II[3,4]. There was also the ultrathin films formed by Langmuir (1920) in his water trough, with thicknesses that span only one molecular length (~30 Å) or several layers of them (~100 Å).[5] In 1959, the Physics Nobel Laureate Richard Feynman made bold predictions for nanotechnology in his talk "There's Plenty of Room at the Bottom."[6] He even offered a US$1,000 reward for the first one to fabricate an operating electric motor not exceeding 1/64th inch cube in volume (not counting the lead-in wires)—which was promptly answered by a young engineer in the following year.[7] Therefore, many of the tools or incentives for nanotechnology are not really new, but the immediate spread and rapidity of its development in the past 20 years must have been brought about by a 'tipping point,' (borrowing Gladwell's idea that a confluence of events must produce a tipping point that allows for fashion, fads, or trends to spread).[8] Nanotechnology probably hit its tipping point just before 1990: due to breakthroughs such as the invention of the scanning probe microscope, the successful synthesis and isolation of the fullerenes and carbon nanotubes, and at the same time, the rapid progress in the personal computing industry and its drive towards further miniaturization of the microchip (now it's a nanochip). The semiconductor industry is fervently conforming with Moore's Law—which states that the size of the computer chip decreases by half every one-and-a-half years.[9]

The scanning tunneling microscope and atomic force microscope,[10-11] which are also generically referred to as scanning probe microscopies (SPM), are relatively new imaging tools then that allowed visualization of solid surfaces at atomic-level or Angstrom resolutions. Similar resolutions were already possible by high resolution electron microscopy even long before, but the SPM provided chemists and other researchers with a more readily accessible instrumentation for viewing surfaces and ultrathin molecular films. The instrument is relatively easy to operate and the interpretation of its images is almost straightforward—the image produced is what you have (well, there were some problems with interpretation of some artifacts produced, but this was resolved early on, and researchers now knew better). SPM works much like how a phonograph works, by 'feeling' the atomic or molecular bumps on a solid surface by moving a probe tip (a metal or inorganic wire) in a raster pattern on a flat solid surface. The moving probe's minute deflections are then translated into a 3-D, topographic image of the surface. Key to the SPM's invention were the ability to move the probe in tiny nanometer steps by attaching it to a piezoelectric crystal whose X-Y-Z expansion, upon application of a voltage, is readily calculable; and also the stabilization of the base on which the sample is placed, which eliminates possible blurring of the image due to ground or surrounding vibrations. An analogy can also be made with a blind person reading a Braille book—by scanning by touch the bumps on the pages of the book.

SPM provided a rapid and new way of 'looking' at properties exhibited by materials with dimensions that are in the nanometer range. It provided a tool with which scientists could probe properties observable or manifested in nanometer dimensions. When IBM spelled its company name by picking up and laying down single atoms of Xe on a surface using an SPM probe tip—it demonstrated to the world that indeed, there is a tool that can literally handle individual atoms![12] What makes this tool especially more powerful, aside from using it to image or to pick-up and deposit atoms from one location to another, is that it can change its mode of action by changing the probe tip or the type of forces that it measures. For example, one can measure the stretching of a single strand of a polysaccharide molecule tethered between the probe tip and a surface, in a new technique called single-molecule force spectroscopy;[13] or measure thermal, magnetic, or frictional forces on a surface; or replace the tip with an optic fiber to allow optical imaging at very close spaces eliminating diffraction effects, in a technique called near-field scanning optical microscopy (NSOM).[14] Each technique is an avenue for investigating phenomena at the nanometer scale that was not available before.

The fullerenes and carbon nanotubes are a class in itself—these are new allotropes of carbon and they present many interesting properties and possibilities for nanotechnology. Whereas Kekulé dreamt of the ring structure of the benzene molecule, Richard Smalley (1996 co-winner of the Nobel Prize in Chemistry) pasted pieces of paper cut outs, hexagons and pentagons, to form the buckyball shape of a C_{60} molecule. Who would have taught that by burning carbon rods (or graphite) in an arc discharge in a glass chamber with argon gas, one would form a black soot composed of these interestingly shaped molecules? In 1991, Iijima reported that in the same soot, one would find rolled up sheets of carbon that are now called carbon nanotubes (CNTs)—there were earlier reports of the discovery of these carbon fibrils, as early as 1952 which went largely unnoticed. The CNTs are like molecular fibrils of about 1 nm diameter, with tensile strength that is 60 times that of steel, the electronic property can vary from semiconducting to conducting just like a metal, and its periphery amenable to functionalization with molecular moieties.[4] Thus, there is also an explosive growth in research on these forms of carbon, because of the exciting properties and its potential applications in electronics, structural materials, and many others.

Around the same period of time, the silicon industry is keeping up with Moore's Law, which in turn produced cheaper and faster computing hardware. The newest computer silicon chip processors today are built using less than 100-nm manufacturing technology. Some say that as this pace continues, the device on the silicon chip will hit its physical size limit soon enough (~2016). Therefore, there is also increasing trend in finding alternative electronic device structures, designs and materials, and perhaps a new paradigm for computing that is based on quantum theory.[15] These future nano-scaled electronics could be composed of molecules or clusters of atoms that are able to function just like its silicon-based counterparts or that may work using new quantum computing algorithms.

In summary, the drive towards electronic device miniaturization, the invention of a new tool for studying nanostructures, and the discovery of a new class of carbon materials provided a tipping point for the hype and frenzy, widespread research interest, and worldwide investment in nanotechnology today. In the U. S. alone, a total of about US$ 4 billion investment comes from government, small business and industry to support efforts towards nanotechnology.[16]

3. Approaches to Nanochemistry

And so, what do nanochemists do? The answer would depend on whether the goal is fundamental or practical. We can start with the fundamental, such as the question of fabrication or synthesis, and discuss possible applications. Or alternatively, we can target the application, and concern ourselves with how to do it, nano-wise. Generally, the former is the approach to science, because the more that we understand the system (first), and then it is easier for us to predict where and what they may be good for. We shall use this approach in our discussion.

If one is to study properties of nanostructured systems, then one must find ways to synthesize or fabricate them. The problem can be posed this way: if given 1 million atoms, each with a radius of about 1 Å, what type of nanomaterial can be made out of these and how would one do it? (A million sounds a lot, but actually, this is too small to weigh in a laboratory balance—but there are ways to prepare this number, of course. Anyway, we can just think hypothetically to illustrate some of the approaches to nanochemistry or nanotechnology.) The type of nanomaterial that can be formed will depend on its dimensionality.

Ultrathin films (Two-Dimensional Nanostructures)

We can try to spread the atoms on a flat surface to form a single layer, and thus we would have constructed an ultrathin film (or coating, if you will) which is only 1 Å thick and can cover roughly a square area of 1000 Å^2 or 1 μm^2 when compacted. The covered area is not nanometer-sized, but the film thickness is sub-nanometer, and thus, this film is within the realm of nanotechnology. This may be done in the lab by vaporizing the 10^6 atoms and allow them to adhere onto a solid substrate. In the lab, this technique is called atomic layer deposition.[17] It is important to note, however, that to form a single layer of atoms on a flat substrate is not trivial, because it may not be stable. Atoms at a surface or interface experience an imbalance of forces. Below and beside them, they have other atoms that pull them inward due to bonding interactions, and above them it is just air or vacuum. Nature abhors this imbalance—it is unstable, and thus, ordinarily, the surface atoms would seek ways to minimize this imbalance, to lower the surface energy. Clustering is one way to minimize surface energy. In fact, the growth of our film formed by vapor deposition would most likely start with clustering of atoms (nucleation) and this growing cluster may begin to coalesce with the other clusters to eventually form a continuous film. In this case, our film may not be mono-atomic in thickness but would turn out to be several atomic layers thick. Nonetheless, it may still be nanometer-thin and so we have a nanostructured system. The preparation of ultrathin films poses experimental and theoretical challenges, and thus many scientists are busying themselves with these concerns.

Another way would be for us to disperse the atoms into a solvent to form a solution, and from there, allow the atoms to spontaneously organize onto a solid substrate. Obviously, gravity would not do it—because they are too small to be settling down; there are other forces in solution that will keep them dissolved. The formation of our thin film will happen if there is a strong preferential attraction of our atoms to the substrate. What we hope to do here is to spontaneously crystallize our atoms onto a surface or interface: a self-assembling technique. Self-assembly is a generic term for forming nanostructures from a disordered state. This is a major technique, actually, that is widely used because it offers a generally straightforward manner of building nanostructures, and is amenable to mass production of the nano-material for commercial purposes. This is a bottom-up approach to nano-synthesis, because the structure is built in a manner that is one atom-at-a-time. If self-assembly were not possible, a bottom-up approach is not going to be efficient, if one is to build atom-by-atom mechanically. This methodology is opposed to the top-down approach, wherein one first makes a bulk material, and then its size is decreased by mechanical or some other means until the material is divided or fabricated into the nanometer size range.

One example of self-assembly is Langmuir's technique—here, one spreads a very dilute solution of amphiphilic molecules (e.g., surfactants) on a water surface. The amphiphilic molecules will not quite dissolve into the water, and once its solvent evaporated, they are left floating at the water-air interface. The molecules at the surface may be compressed to occupy a smaller area using a non-sticky barrier such as a Teflon™ sheet. Compression will form a two-dimensional condensed, monomolecular layer at the water-air interface. The use of the dilute solution allows one to limit and calculate the number of dissolved molecules that will be covering a given area of the water interface. The stability and integrity of the film depends also on the interaction between molecules. The formed films at the interface may subsequently be transferred onto a solid substrate by dipping the latter through the film/interface. These are called Langmuir-Boldgett films,[18-19] and one can make single- or muti-molecular layers on glass and others substrates. This procedure was developed way back in the 1920s and is still being used today using other types of molecules to prepare various films of different properties. At least nowadays, the film structure and morphology can be routinely imaged by SPM and other advanced characterization tools.

Another similar-type film is the so-called self-assembled monolayer (SAM), which is formed by allowing molecules with a dangling sulfur atom at one end (these molecules are called thiols) to stick onto a flat gold surface. This procedure is much easier than Langmuir-Blodgett's technique. The formed film is stable because of the chemical bond between the sulfur and gold, and the attraction between the alkyl chains of the thiol molecules allows the formation of a *pseudo*-two-dimensional crystal at the gold surface. One of the very first papers published by Whitesides *et al.* of Harvard University on SAMs is one of the most cited research papers in Chemistry today.[20-21] Because of the ability of chemists to modify molecular structures, various SAMs have been formed with all sorts of molecular groups attached onto gold.[22] It also paved way for such new techniques for creating patterned nanostructures (called soft-lithography), wherein nanosized SAMs features are 'imprinted' on a gold surface by micro-stamping a solution of thiols on gold.[23] A recent review of the uses of SAMs for nanofabrication is given in reference 22. SAMs were also used as 'ink' for writing on gold in what is called dip-pen nanolithography (DPN)—here the probe of the SPM is wet with thiols and the SPM probe is programmed to 'write' patterns across the gold surface, depositing a layer of SAMs on the gold as it moves. The DPN technique proved useful for other molecules as well.[24] This approach promises to be a way to build nanostructures on a surface, and by using a multi-probe writing device (e.g., one with 55,000 pen tips) it was demonstrated that one can write massively on a surface, which makes it feasible for mass production of the nanostructured system.[25]

Nanoparticles (Zero-Dimensional Nanostructures)

If the 10^6 atoms that we have are all in one solid mass, and are closed-packed in a particle, it will occupy a volume of about 6000 nm^3 with a width or diameter of only about 18 nm. A million atoms make a nanoparticle! Many everyday-life particles that we encounter are already nanometer in dimensions, such as the micelles formed by soap molecules in water, smoke particulates, or clay particles. In fact, nanoparticles were used hundreds of years ago as colorants in Chinese vases or pigments in the stained glass windows of cathedrals in Europe. There is much renewed interests in nanoparticles because chemists and other researchers are able to characterize their behavior at higher precision using the advanced tools that are now available. There are also various ways to synthesize and stabilize them, and new possible applications are discovered.

Because of its small size, the number of surface atoms becomes significant. The smaller the radius of the particle, the bigger the fraction of surface atoms. For a spherical particle, the surface area $A_s = 4\pi r^2$, whereas the volume of the particle is $V = (4/3)\pi r^3$. Thus, the surface area-to-volume ratio is $A_s/V = 3/r$, and since the number of surface atoms is proportional to the area exposed, then this ratio is proportional to the fraction of surface atoms in the particle. The smallest closed-packed cluster of spherical atoms is a 13-atom cluster wherein one atom is surrounded by 12 surface atoms (its coordination number). Here, the surface-to-volume ratio of atoms is very large at 92.3% (or 12/13). A 100-particle cluster will have a surface-to-volume ratio of 68.0%; a thousand, 38.4 %; and a million, 4.4%. For a micron-sized particle composed of 10^{11} atoms, the surface-to-volume ratio is 0.10%. Indeed, the nanometer-sized cluster will have significant surface energy. Recall that our surface atoms experience an imbalance of forces around them creating a surface energy that seeks to be minimized. Therefore, the surface energy and surface curvature become dominant factors that affect the overall shape, stability, and property of the nanoparticle. Generally, the particle will be stable at or above a critical radius wherein the effects of surface energy is compensated by the overall free energy of the entire particle. Any smaller size, means the surface atoms will have to reconstruct, melt away, or seek other ways to minimize surface energy. For example, the melting point for gold crystals was shown to have a dramatic decrease with decreasing radius of the crystal, especially right around 3-4 nm radius.[26]

This discussion of stability of a cluster generally applies to metal or semiconductor nanoparticles which form tiny crystallites or nanocrystals. (A review of nanocrystal chemistry is published by El-Sayed *et al.*[26]) In general, the synthesis goal is to produce stable nanoparticles of uniform size, shape, and properties. The nanocrystals may be synthesized from the vapor phase by crystallization onto a substrate through heterogeneous nucleation, or by controlled homogeneous nucleation in a liquid phase that is usually a supersaturated solution.[4] In solution crystallization, stabilization of the nanoparticles is generally achieved by lowering the surface free energy through bonding with organic molecules that passivate the surface atoms. For example, nanocrystalline or colloidal gold is typically formed by reduction of gold ions in solution by citrate ions producing typically ~20 nm particles. The agglomeration of the colloidal gold is prevented by electrostatic repulsion between the Au particles that are flanked by negatively charged citrate ions. The size of gold particles can also be controlled to be 1.5 nm to 20.0 nm radius by 'capping' it with thiol molecules to thermodynamically stabilize and stop further growth of the nanocrystals.[27] Stabilization of the nanoparticles is also done using polymers, which was found to also influence the resulting size and shape of the nanocrystals that are formed. In our lab, for example, we were able to grow CdS nanoparticles *in situ* a carrageenan polymer which was previously impregnated with cadmium ions. Here, the growth of the crystal occurred by slow precipitation upon diffusion of hydrogen sulfide into the Cd^{2+}-polysaccharide matrix.[28] Bawendi *et al.*[29] found a procedure for synthesis of semiconductor nanoparticles of CdSe in a 'wet laboratory' technique, which involved controlled precipitation and stabilization using small organic ligands. They can prepare CdSe particle sizes between 1.5 nm to 11.5 nm with very narrow size distributions (monodisperse).

Semiconductor nanoparticles are also sometimes referred to as quantum dots or 'synthetic atoms' because of quantum confinement effects. When a particle is energetically excited, an electron leaves a hole creating an electron-hole pair that is called an exciton. Because of the small size of the particle, the electron-hole pair may still be 'bound' to each other thus creating electronic energy levels that are modeled after the electron-proton pair of a hydrogen atom. This is theoretically and experimentally observable for cases when the size of the nanocrystal is less than the corresponding Bohr radius of the bulk crystal. For nanocrystals, electronic properties become size-dependent, because the electronic energy level structure is quantized or discrete as opposed to the electronic band structures exhibited by bulk crystals. Therefore, nanocrystals are tunable opto-electronic elements. This is dramatically exhibited by the varying colors of CdSe solutions (or colloidal dispersion), due to the sharp absorption lines of the excitons in the visible region of light.[31] Another very interesting property in this size regime is the discreteness of electron conductivity, wherein the observed current-voltage characteristics produce a staircase-like pattern due to individual tunneling of single electrons.[26] This is different from the continuous curve predicted by Ohm's Law. Measurement of this effect may be done by connecting an

SPM probe tip (specifically STM) on top of a nanoparticle adsorbed on a metal. This behavior which is also known as Coulomb blockade or 'Coulombic staircase' offers a possibility for single electron transistors that may be part of future computing devices. Because of the availability of a method to synthesize monodisperse CdSe nanocrystals, many researchers have incorporated them into other nanostructured systems for various applications: nanoelectronics, optoelectronics, photonics, catalysis, snesors, etc.[30] There are of course many other types of semiconducting systems: CdS, PbS, ZnS, TiO_2, ZnO, etc., but to review them is beyond the scope of this paper, and the reader is referred to the review given by reference 26.

Metallic nanoparticles exhibit strong surface plasmon absorption that give them the characteristic deep red color, such as Faraday's colloidal gold dispersion. Surface plasmon resonance arises from the coherent motion of electrons in the conduction band of the metal, which 'resonates' with light.[26] This is another 'tunable' property, because the absorption band can shift in wavelength depending on the size of the metallic nanoparticle. Because colloidal gold is easily synthesized, and they are amenable to self-assembly interactions with molecules with thiol groups, they have been used a lot in various functionalized forms. In fact, the test strip used in pregnancy or rapid drug screening comprise of a dispersion of gold colloids that are bioconjugates with antibodies that can selectively bind with a target compound—when a sufficient number of these gold clusters are concentrated (and not a lot is needed because of the strong surface plasmon absorption of light) on a part of the strip, one sees the development of a purple or reddish line which can indicate presence or absence of the compound; the level of detection can be as low as 50 parts per billion (ppb) or even lower.[31] Thus, metallic nanoparticles have found use in biomedical diagnostics.[32-33] Other applications reported are for medical purposes, using the catalytic properties of these particles, that can have antimicrobial and possibly anti-HIV properties.[34]

Of course, atoms can also bond with other atoms covalently to make molecules, and in this way, the bonding requirement by each atom is satisfied, that is, there is no dangling bond left at the surface. Nonmetallic elements generally do these to form a molecular species—small molecules or very large ones (polymers) which have extensive covalent bonding. Polymers are large molecules wherein each atom is covalently bonded to each other in a particular way, such as to form a very long chain that can fold into a random coil. The radius of the coil can go as high as several microns. Polymers are not new, but they also figure in a lot in nanochemistry because they make interesting nanostructures, may be used as agents to stabilize the system, as templates for nanostructure fabrication, and many other uses. The folded helical DNA molecule, for example, is comprised of strands of a nature-designed polymer.

Nanowires (One-Dimensional Nanostructures)

Going back to our starting 1 million atoms, we know that to produce a one-dimensional structure, we will need to align the atoms unidirectionally to make elongated structures. Based on the length of the nanostructure, it could be a nanowire or a nanorod. Bonding the atoms to make a linear polymer chain is not new, but this is possible only with elements that are amenable to extensive covalent linkages, otherwise, the structure will be unstable. For semiconductor or metallic elements, nanowires are made with nanometer-sized radii, such that the cross-section of the wire consists of hundreds or thousands of atoms. They may be formed by controlling the growth process, usually along preferred directions of crystallization or using a template to align the process. There are various techniques for making nanowires, which may be from the vapor phase such as the nanobelts of the semiconducting ZnO produced by Wang *et al.*[35]: by evaporating the oxide under vacuum and condensing them on alumina substrate (~30 nm diameter and several hundred nm long). Or from solution, such as the silver nanowires (30-40 nm diameters, ~50 μm long) grown by reduction of silver nitrate with ethylene glycol and allowing the metal to grow from Pt seed nanoparticles, and inducing unidirectional growth using a polymer polyvinyl pyrrolidone as surfactant that adsorb on the growth surfaces.[36] Of course, present-day photolithographic techniques (more of a top-down approach) allow 'printing' of lines that are less than 100 nm in width, and are used now in the manufacture of computer processors. The most recent processors released by Intel™ are based on the so-called 65-nm production process which have transistor gates about 35 nm in width; this is about a 100 times smaller in diameter than a red blood cell.[37-38] As pointed out earlier, one of the most interesting nanowires nowadays are those of carbon nanotubes.

Supramolecular assemblies

What was discussed so far are nanostructures that can be formed based on the dimensionality of the material that is produced. However, nanotechnology or nanochemistry is not limited to these types, and more often than not, the nanostructured system or material is a composite of various types. Ultimately, nanotechnology will approach molecular-level control of the device or material architecture. What is uniquely nanotechnology today is that the design is molecular in approach to form materials that are supramolecular assemblies.[39] Much of what is happening in biological cells, for example, is a molecular machinery of sorts that is responsible for the spontaneous copying, transcription, and reproduction of the DNA and proteins, for example. And some researchers have also begun to look at nature to come up with biologically-inspired nanomaterials. One example is a nacre-like nanostructured composite formed by layer-by-layer assembly of polymers and clay materials that are nanometer-spaced —the resulting structure is brickwork in the nanometer scale.[40] Those engaged in nanocrystal research, for example, also discovered that nanoparticles can form superlattices, and a group of researchers has already begun forming various types based on binary nanoparticle superlattices.[41] Polymers also form nanostructure assemblies such as those used in nano-patterning using block copolymers (or polymers with two parts of the chain that are different in chemical composition) in a self-assembly approach.[42]

It is not necessary to just form nanostructures to be working in the realm of nanotechnology. An effect that is manifested in nanometer dimensions is also considered part of this field. The semiconductor properties of some inorganic materials, such as titania (TiO_2), for instance, had found applications as nano-photocatalysts, and are now currently used as coatings in ceramic tiles which are 'self-cleaning' and anti-microbial. UV light can produce an exciton in TiO_2 nanoparticles which are trapped as electrons (which form radicals) and holes at the surface, in turn acting as reducing or oxidizing agents, respectively. These catalyze the degradation of organics to carbon dioxide and water—the self-cleaning effect, and they also find use in the remediation of pollutants such as dioxins.[43] In our lab, we have found, for example, that a thin TiO_2 coating, when etched to nanoscale roughness will have increased anti-microbial properties.[44] Nanostructured TiO_2, after dye-sensitization, is also useful for solar cell devices.[45-46] Another nano-sized manifestation is the wettability of a surface, which is usually attributed to its polarity, but can be made super-hydrophobic or super-hydrophilic (or in other words, super non-stick or super-wettable by water) by varying the surface nanostructures.[47] These surfaces improve the self-cleaning properties because of lowered adhesion of surface impurities.

4. Concluding Remarks

Nanotechnology is here. Today, we are at the building-box age of nanotechnology moving on towards integration of nanosystems to existing products (such as the computer processor). And it is just a matter of time when we fully grow into the age of nanomanufacturing wherein researchers and engineers have come up with ways to mass-produce functional nanostructured systems for specific applications. Here, nano-chemistry makes its contribution as that science that investigates, designs, synthesizes, and fabricates matter that are in the nanometer-size regime through molecular control of these systems.

5. Literature Cited

1 Holton, G. and S. G. Brush. *Introduction to Concepts and Theories in Physical Science, 2/e* (Princeton University Press, 1985).

2 Borman, S. *Chemical & Engineering News* **84** (2006) 12 .

3 Turkevich, J., *Gold Bull.* **18** (1985) 86 as cited in reference 4.

4 Cao, G. *Nanostructures & Nanomaterials: Synthesis, Properties, & Applications* (Imperial College Press, 2004).

5 Langmuir, I. *J. Faraday Soc.* **15** (1920) 6.

6 http://www.zyvex.com/nanotech/feynman.html (accessed 12 October 2006)

7 Waterman, A. T. *American Scientist*, March 1961, 1-8.

8 Gladwell, M. *The Tipping Point: How Little Things Can Make a Difference* (Back Bay Books, 2002).

9 http://www.intel.com/technology/silicon/mooreslaw/ (accessed 12 October 2006)

10 Binnig, G. and H. Rohrer. *Rev. Mod. Phys.* 59 (1987) 615-625.

11 Meyer, E., H. J. Hug, and R. Bennewitz. *Scanning Probe Microscopy: The Lab on A Tip* (Springer, 2003).

12 Eigler, D. M. and E. K. Schweizer. *Nature* **344** (1990) 524.

13 Rief, M., F. Oesterhelt, B. Heymann, and H. E. Gaub. *Science* **275** (1997) 1295-7.

14 Harris, C. *Anal. Chem.* **75** (2003) 223A-228A.

15 Schulz, M. *Nature* **399** (1999) 729-730.

16 http://www.nano.gov/ (accessed 12 October 2006)

17 George, S. M., A. W. Ott, and J. W. Klaus. *J. Phys. Chem.* **100** (1996) 13121-13131.

18 Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-assembl*y (Academic Press, N. Y., 1991).

19 Enriquez, E. P. *Kimika* **14** (1998) 1-9.

20 Bain, C. D. , D. B. Troughton, Y. Tao, J. Evall, R. G. Nuzzo, and G. M. Whitesides. *J. Am. Chem. Soc.* **111** (1989) 321.

21 Borman, S. *Chemical & Engineering News* **81** (2003) 54.

22 Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-assembl*y (Academic Press, N. Y., 1991).

23 Gates, B., Q. Xu, M. Stewart, D. Ryan, C. Grant Wilson, and G. M. Whitesides. *Chem. Rev.* **105** (2004) 1171-1196.

24 Ginger, D. S., H. Zhang, and C. A. Mirkin. *Angewandte Chemie Int'l Ed.* **43** (2003) 30-45.

25 Salaita, K., Y. Huang, J. Fragala, R. A. Vega, C. Lui, and C. A. Mirkin. *Angewandte Chemie*, 26 Sep 2006 (on line).

26 Burda, C., X. Chen, R. Narayanan, and M. A. El-Sayed. *Chem. Rev.* **105** (2005) 1025-1102.

27 Leff, D. V., P. C. Ohara, J. R. Heath, and W. M. Gelbart. *J. Phys. Chem.* **99** (1995) 7036-7041.

28 Enriquez, E. P. and A. K. A. Aliganga, in *Proceedings of the DOST-JSPS Workshop on Polymers and Materials Chemistry* (Ateneo Office of Research and Publications, 1998).

29 Murray, C. B., D. J. Norris, and M. G. Bawendi. *J. Am. Chem. Soc.* **115** (1993) 8706-8715.

30 Murray, C. B., C. R. Kagan, M. G. Bawendi. *Annu. Rev. Mater. Sci.* **30** (2000) 545 as cited in reference 4.

31 http://www.homehealth-uk.com/index.html (accessed 12 October 2006). See for example: http://www.homehealth-uk.com/medical/pregnancytest.htm.

32 Daniel, M-C., D. Astruc. Chem. Rev. **104** (2004) 293-346.

33 Han, M. S., A. K. R. Lytton-Jean, and C. A. Mirkin. *J. Am. Chem. Soc.* **128** (2006) 4954-4955.

34 Elechiguerra, J. L., J. L. Burt, J. R. Morones, A. C-Bragado, X. Gao, H. H. Lara, and M. J. Yacaman. *J. Nanobiotechnology* **3:6** (2005).

35 Pan, Z. W., Z. R. Dai, and Z. L. Wang. *Science* **291** (2001) 1947-1948.

36 Sun, Y., B. Gates, B. Mayers, and Y. Xia. *Nano Lett.* 2 (2002) 165-168.

37 http://www.intel.com/technology/silicon/si08042.htm (accessed 12 October 2006).

38 Bjorkholm, J. E. “EUV Lithography—The Successor to Optical Lithography? In http://www.intel.com/technology/itj/q31998/pdf/euv.pdf (accessed 12 October 2006).

39 Schneider, H. J. and A. K. Yatsimirski. *Principles and Methods in Supramolecular Chemistry* (Wiley, 2000).

40 Podsiadlo, P., S. Paternel, J. M. Rouillard, Z. Zhang, J. Lee, J. W. Lee, E. Gulari, and N. A. Kotov. *Langmuir* **21** (2005) 11915-11921.

41 Schevchengko, E. V., D. V. Talapin, C. B. Murray, and S. O.'Brien. *J. Am. Chem. Soc.* **128** (2006) 3627.

42 Krishnamoorthy, S., C. Hinderling, and H. Heinzelmann. *Materials Today* **9** (2006) 40-47.

43 Choi, W., S. J. Hong, Y-S. Chang, and Y. Cho. *Environ. Sci. Technol.* **34** (2000) 4810-4815.

44 A. K. Aliganga and E. P. Enriquez, *Proceedings of the16th Philippine Chemistry Congress*, 2000.

45 Bisquert, J., D. Cahen, G. Hodes, S. Rühle, and A. Zaban. *J. Phys. Chem.* B **108** (2004) 8106-8118.

46 Mor, G. K., K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes. *Nano Lett.* **6** (2006) 215-218.

47 Martines, E., K. Suenarine, H. Morgan, N. Gadegaard, C. D. W. Wilkinson, and M. O. Riehle. *Nano Lett* **5** (2005) 2097-2103.