Nanoscience and Technology: A Chemical Engineer's Perspective[#]

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Introduction

A nanometer is 10 Å or 10^{-9} m. Broadly speaking, nanoscience and nanotechnology can be defined as science and technology (S&T) that manipulate materials with at least one dimension being of the order of a nanometer. Miniaturisation has always fascinated humanity and making things smaller than what was possible has been a challenge. Nano S&T is a natural consequence of this. It is being talked about a lot now since the means for planned synthesis and manipulating materials of these dimensions have become available in the last couple of decades. The growth of this field is also due to the discovery of many special properties that materials possess in this finely divided state. Some of the notable milestones that led to the rise of nano S&T are the invention of scanning tunneling microscope (STM) in 1981 and atomic force microscope (AFM) in 1986, as well as discovery of fullerenes in 1984 and carbon nanotubes (CNTs) in 1991. Nanomaterials had been made in ancient times also, but the ability to manipulate materials and synthesize them in a planned way at the nanoscale is very recent. This ability has given rise to very novel and new ideas. In this paper, an attempt has been made to give a flavour of nano S&T by presenting some of the applications already in practice, some of the developments in the process of making, and some of the work in which the author has been involved.

Dream of Nanotechnology

Small devices have been made in many ways. Semiconductor industry has been making small devices at submicron level for many years, and at the tens of nanometer level in the last decade. This has been achieved by the processes of etching – i.e., removal of material – and deposition. Deposition is done by the usual diffusion and reaction processes.

Thus, these processes do not occur by active manipulation at the nanometer level. The underlying phenomena, though molecular in nature, are random and cannot be controlled macroscopically. The dream of nanotechnology is to assemble and build devices using building blocks of nanodimensions – the building blocks are akin to bricks. Of course, the commercialised technology can end up being hybrid! This dream has arisen out of a talk [1] given by the well-known physicist Richard Feynman, which was titled "There's Plenty of Room at the Bottom". Feynman said that physical laws do not prohibit synthesis of even chemical compounds by placing atoms at the proper location, and so it became a challenge to at least synthesize devices at a slightly larger scale. This approach is normally referred to as 'bottom-up' as opposed to the methods of the conventional semiconductor industry, also known as 'top-down'. These names are evocative of the starting points.

Building Blocks

There are not many building blocks that one can imagine. There are *nanoparticles*, *nanotubes* and *nanorods*. Nanoparticles and nanorods are synthesized from materials with a wide variety of properties, such as, metals, oxides and semiconductors. *Nanoballs* can also be made and are hollow, as opposed to nano-spherical particles. Fullerenes, which are closed structures made of carbon atoms, are an example of nanoballs. The most famous one is the Buckminster fullerene, which comprises of 60 carbon atoms and its structure resembles a football. Nanotubes or *nanowires* are the next building blocks. The most famous one is also made of carbon, known as carbon nanotube (CNT),which looks like a tube made by rolling a graphite sheet. The structures of 'wires' and 'rods' are more differentiated than just spheres and balls.

Chemists have shown great ingenuity and have synthesized nanostructured materials with a wide variety of chemical compositions, which implies a wide range of properties that can be imparted to materials and, thus, offers tremendous flexibility. Undoubtedly, this ability to 'tune' properties is one of the reasons fuelling the growth of nano S&T. Nanomaterials have special properties that offer scope for developing new technologies.

Special Properties and Applications

Nanomaterials offer special properties compared to the same material in bulk or at macroscopic scale. Novel applications arise because of some special characteristics imparted by the nanodimensions, because of: (i) large ratio of surface area to volume, (ii) large fraction of surface atoms to that in its bulk, (iii) smallness of size, and (iv) size dependent properties. Reasons for some special properties are still not understood.

Large Surface Area

The effect of a large ratio of surface area to volume is well-known to chemical engineers who are generally concerned with heterogeneous catalysis, multiphase reactions and transfer processes. It is easy to see that nanomaterials will make good catalysts. One disadvantage for using nanomaterials as catalysts is their instability, especially at high temperatures. However, they are finding applications in fuel cells, solar cells, and batteries, where temperatures are not high. An example of use in multiphase reactions is the

application of nanosized $CaCO_3$ particles, which are additives to automotive lubricants. They are referred to as "over-based lubricants". These particles, because of their large surface area, are able to neutralise the acids liberated due to incomplete combustion. The large surface area improves the bond between nanomaterials and any bulk material in which they are incorporated. Thus, nanomaterials are good reinforcement compounds and fillers. Some of the applications in building industry are in construction materials, insulation materials, flame retardants, coatings etc. Some of the applications in machines and other manufacturing sectors involve improvement in the mechanical properties of metals and alloys, ceramics, improvement in surface properties like protection against wear, etc. Automotive industry utilises nanomaterials as fillers, catalysts for exhaust etc. Textile industry uses nanomaterials for alteration of surface properties and to impart flame retardancy. Use of CNT as reinforcement for clothing in defence applications is another example. Sports industry also uses them to make anti-fogging glasses, improved tennis balls etc. The large surface area also makes transport processes more efficient and, hence, for a given amount incorporated, sensors made of nanomaterials can be sensitive even at low concentrations.

Functionalisation is a concept that has been very effectively used in applications. In view of the large surface area, nanomaterials possess high surface energy. As a result, a large variety of compounds can be adsorbed strongly onto their surface. The most well-known example is that of thiols, which can chemisorb onto gold. The adsorbent can be chemically synthesized in such a way that one end of the molecule forms the adsorbent group (e.g. thiol for gold particles) while the other end can have a different affinity (e.g. an antibody to recognise invading cells). Nanomaterials to which adsorbents are bound are referred to as "functionalised nanomaterials" since the adsorption imparts functionality (e.g., recognition of invading cells, in the given example) to nanomaterials (e.g. gold nanoparticles, in the given example). Functionalisation of nanomaterials offers extra potential for application. It is easy to see that effectiveness of all the applications mentioned above can be enhanced by this procedure. Medical diagnostics has been a major beneficiary of the concept of functionalisation. For example, to detect the presence of a genetic sequence in a sample of DNA, gold particles are functionalised with one strand of a fragment of DNA complementary to the sequence to be detected. The particles are loaded into a solution containing a sample of DNA. If the genetic sequence is present in the DNA, it binds to the functionalised gold particles. The gold particles aggregate into a large mass and their colour changes, which can form the basis for diagnostics.

Large Fraction of Surface Atoms

A large fraction of the total number of atoms or molecules are present on the surface in a nanomaterial. A 1 nm cluster contains about 10 atoms, and 90% of them are on the surface. A 5 nm cluster contains about 2,000 atoms and 40% of them are on the surface. Thus, the surface energy per unit volume for nanoparticles is large compared to the same material in bulk state. It also leads to lowering of the melting point. One can imagine they can be compacted and sintered easily. It also means that the material can sublime, aggregate, and grow due to Ostwald ripening. This is the cause for the disadvantages mentioned earlier.

The large number of surface atoms also means that the properties determined by the electrons on the surface will be different. Thus, small metal clusters possess catalytic properties different from that of same material in bulk form.

Smallness of Size

The smallness of nanomaterials makes many barriers transparent to them, e.g. they can penetrate skin. This property can be utilised in cosmetic applications. Nanomaterials can also pass through intestinal cell walls, which makes them suitable for drug delivery. Once again, functionalisation of the surface of nanomaterials can be effectively used in these applications. Targetted drug delivery is possible through this route. Liposomes are a spherical capsule, referred to as a 'vesicle', whose wall comprises of a phospholipid and cholesterol bilayer membrane. When functionalised they are used for cancer therapy and treatment of inflammatory diseases. Another interesting idea is based on the use of functionalised magnetic nanoparticles as targetting can be achieved through magnetic properties. Yet another novel idea is based on synthesis of core-shell particles. The shell can be functionalised to lock onto a target and the core can be made to generate heat. After locking, the core can be used to deliver heat. Gold on silica particles [2] seems to have this potential where gold is functionalised to lock onto cancer cells and silica can be heated by near infrared radiation.

Another interesting application is creation of roughness at very small length scales, which is possible through nanomaterials. The small scale roughness alters the wetting properties of the surface. The rolling off of water droplets on the leaves of a lotus plant is due to the roughness on a small length scale. Thus, the alteration of wetting properties is referred to as the "lotus effect", which has been exploited to create self-cleaning fabrics.

Small size facilitates denser packing of particles. Thus, nanosized magnetic particles can increase the storage capacity of data memory devices since each of them can be used as a 'unit' for storage. Here, the idea of 'tuning' the properties arises naturally since size can be controlled through engineering the process of synthesis.

Size Dependent Properties

Some properties of nanomaterials depend upon their size. One such interesting property is the size dependent absorption of light of a certain frequency. The main cause for this is the onset of quantum effects when size of the material is small, usually, of the order of a few nanometers. Nanoparticles are, thus, also called *quantum dots*. It was discovered that when light is directed at the interface of a metal nanoparticle and a non-conducting medium, resonance develops between the incident wave and mobile electrons of the metal. This propagates along the surface of the metal [2] and it is called a *surface plasmon*. The resonance depends upon the size of the nanoparticles. Hence, absorption and scattering of the resonant frequencies of the incident light depend on the size. The suspension of nanoparticles will show the colour of the scattered light in reflection. But in the transmitted light, the scattered frequency will be missing and the sample will show a different colour.

Another quantum effect is the development of discrete energy levels [3]. Let us take metals as an example. Bulk metal has many delocalised electrons and, consequently, the

energy levels they can occupy nearly form a continuum. The confinement of a few metal atoms to a small size creates discretely spaced energy levels for electrons, which can be explained as: The depth to which electromagnetic waves penetrate is comparable to the size of the particle. As a result, the incident wave is able to create collective oscillation of the conduction electrons. Resonance and, hence, absorption is set up when the frequency of this oscillation matches that of the incident wave. It can be seen that the frequency of absorption will be a function of size. Thus, suspensions of nanoparticles of same material but different sizes will absorb light at different frequencies. This property is exploited in medical diagnostics, as explained earlier.

Yet another quantum effect is the tunable frequencies of absorption in semiconductors [3, 4]. Here, separation of the distance between a pair of hole and excited electron created (referred to as *exciton*), unlike in bulk materials, is restricted to the size of the particle. This causes size dependent discrete energy levels, leading to absorption of electromagnetic waves of a particular frequency. All these effects can be 'tuned' by altering the size and chemical composition of the particle.

Unexplained Properties

It has been observed that silver and gold nanoparticles are more effective disinfectants than in the bulk form, but the cause for this is not clear. This has led to the development of antibacterials, water purifiers, food and drink packaging materials etc. Professor Pradeep of Indian Institute of Technology (IIT) Madras, Chennai has developed a device for water purification using silver nanoparticles. Perhaps, anti-odour devices have a similar basis.

Innovative Applications Under Development

A few selected science-based applications that still require considerable development, but are directly relevant to chemical engineers, are presented below. They also illustrate the possibility of discovery of new and unexpected properties of nanomaterials.

Aligned CNTs

Recently, Holt et al. [5] described the preparation of a nanoporous membrane where pores are also aligned. They prepared aligned CNTs on a wafer and embedded them in silicon nitride. The length of the tubes was micron sized. By suitable etching process, the base on which the nanotubes were grown as well as the SiN on the top surface of CNTs was removed. Clearly, the product is a nanoporous membrane. This process resulted in a membrane with 10^{11} pores/cm^2 while the same measure for polymer membranes is 10^8. The membrane showed greater permeability, though the pore size is smaller. The cause for enhanced permeability is still not clear. They also showed good size selectivity for gaseous permeants. It is easy to see the potential of nanomaterials as size selective membranes. Such inventions will have special significance to separation processes.

Voltage Generation by Flow

Ghosh et al. [6] have reported a very interesting phenomena. They assembled a packed bed of CNTs and passed polar liquids, such as, water, methanol, aqueous solutions

glycerol, aqueous solutions of HCl etc., over it. It was discovered that due to the flow, even at a low velocity of 0.05 cm/s, a voltage developed across the ends of the bed. The same effect was discovered [7] even when gases like Argon, Oxygen, Nitrogen etc., were passed through the bed. The phenomena are not understood though several explanations have been offered. The results, however, show the potential to act as flow sensors and possibilities of power generation.

Thermal Properties of Nanofluids

Maxwell has derived an expression for predicting the thermal conductivity of suspensions of solids in fluids [8]. The thermal conductivity of the suspension is greater than that of pure fluid since solids, in general, are better conductors than fluids. Suspensions of nanomaterials in fluids are referred to as *nanofluids*. Recently, it was found that thermal conductivity of a fluid was enhanced by large factors, compared to that predicted by Maxwell's theory, even when the volume fraction of nanoparticles in nanofluids was very small [9]. The enhancements can be as large as 10% when the volume fraction of metal nanoparticles is as low as 0.0001. The enhancement is greater than predicted by Maxwell's theory by orders of magnitude. The effect was found for nanoparticles of oxides and also CNTs. The discrepancy between theory and observation is still unexplained. Further, the critical heat flux in boiling was also found to be enhanced by nanofluids. Removal of heat in microchannels has obvious applications in cooling of high density electronic circuits. Conventional cooling fluids have reached their maximum heat removal capacity. As nanofluids have greater conductivities, using them as cooling fluids has great potential. Research in this area is being conducted at the Mechanical Engineering Department of IIT Madras.

Core-shell Particles

Nanoparticles can be made in a special form. A nanoparticle can be coated with a shell of a different material, like gold on silica. These are referred to as *core-shell particles*. One can see many applications for this structure if the shell is porous. It can be a good catalyst material with reactants and products diffusing through the porous shell. An example is anode coated with porous carbon, which can be used to make a high surface area electrode in lithium batteries. The power density can be increased enormously in this manner. Research in this area is being planned in the Chemical Engineering Department of IIT Kanpur. Core-shell structure can prevent loss of core material and this can find applications when a noble metal is used as catalyst material.

Sensors

The large surface area of nanomaterials offers great scope for detection of pollutants etc., at small concentrations. However, a signal from a single nanoparticle will be too weak. One, therefore, needs to employ assemblies of nanoparticles. Members in a randomly packed bed will not be fully effective since they are screened. An ordered array is, obviously, the best arrangement for a device. Development of such an ordered array of nanoparticles to develop a gas sensor is being undertaken in the Chemical Engineering

Department of Indian Institute of Science (IISc), Bangalore. Preparing an ordered array has many more applications than just in sensors, e.g. in electronics. To form an ordered array, a mono-dispersed sample of nanoparticles is prepared. The nanoparticles are stabilised by suitable surface active agents. Through colloidal interactions of the surfactants the particles self-assemble into ordered arrangements. Order is achieved since the particles are mono-dispersed. The nanoparticles are also functionalised to make them sensitive to chemicals to be detected. Resistance of such an array changes when the chemical adsorbs and this can be used to detect its presence. These devices are known as *electronic 'nano-nose'*.

Many more applications that utilise the special properties of nanomaterials are being developed and the examples given here are a description of only a few.

Potential in Electronics

The big commercial applications of nanomaterials are likely to be in the areas of electronics and computers. At present, electronic circuits and elements in them, e.g. transistor gate, are assembled on silicon wafers using two basic steps. The first step is to make a drawing of the layout of the circuit and elements. The drawing is used to create an image on the wafer using ultraviolet (UV) light. In the second step, the image is used in a sequence of processes comprising of diffusion, doping, and etching to convert the image into the 'hardware'. This technology is classified by the minimum distance between two elements between adjacent devices, which are not directly connected. At present, it is about 90 nm. In the near future, it is expected to go down to 45 nm. However, there are limitations on further reduction in this dimension. One of them is that when the distance across devices, which are not connected directly, decreases to low values, current leaks between them. Another has to do with the fact that the devices are operated at constant electric field or potential gradient. Therefore, as the gap reduces, magnitudes of the potential differences and, hence, currents fall. Thus, current ceases to be continuous but becomes stochastic. This inherently increases noise levels. Due to these reasons, further miniaturisation is not possible to very low levels.

Nanotechnology seems to have the potential to offer an alternative way of making electronic circuits. The entire picture is not clear at the moment, though elements are coming into focus. Present architecture is based on three point connectivity: global two dimensional connectivity and independent access to as well as controllability of any point in the circuit. There are several investigators developing molecular wires, switches and gates. Assembling them into a circuit is still a very big challenge, which is yet to be overcome. One line of thinking is to build a nanogrid laid of, say, CNTs and place the devices at the junctions. This provides for two dimensional connectivity. Some investigators are trying to develop methods to access the junctions to provide three point connectivity. The difficulty arises due to the smallness of dimensions. Use of lasers and other such ideas are being investigated. Others are investigating ways to utilise the grid architecture itself in computing. If any of these succeed, nanoelectronics will become a reality and it is expected to replace the conventional methods of manufacture of electronics.

Manipulation of Nanomaterials

As mentioned earlier, one can 'place' nanodevices at chosen locations. A scanning tunneling microscope (STM) makes this possible. Apart from this, both STM and atomic force microscope (AFM) are very useful in investigating nanostructures.

Scanning Tunneling Microscope

Important tools of measurements and manipulation at the nanoscale are based on the tunneling effect. The STM was discovered by Binnig and Rohrer. They were awarded the Nobel prize for this discovery. Imagine a circuit in which a battery is connected to a light bulb. If one of the connecting wires is cut, the bulb goes off. Suppose the two ends of the connecting wires are brought closer to each other. When will the bulb come on, i.e., when will current flow? 'Classical' physics tells us that it happens only when the two ends touch each other, since the potential energy barrier for the electrons to cross over is infinitely high when the ends are not connected. Quantum mechanics predicts that bulb will come on when the two ends are very close but not necessarily touching each other. It is as if electrons flow, somehow bypassing the infinitely large potential energy barrier caused by lack of connectivity. A colourful description of this is to think that a tunnel has been bored through the barrier and electrons pass through it. That is why this effect is called *tunneling* and the current is known as *tunneling current*. The effect is observed by applying a voltage difference between a plane (it can be as large as mm in length) and a tip. Tunneling current decays exponentially with the gap between the plane and the tip. As a result, an atom at the "end of the tip", itself contributes to 90% of the tunneling current. Thus, the tips need not be made very sharp. Gaps as small as one-tenth of an Angstrom can be measured with STM. The STM scans a surface by moving the tip across it and observing gap between the tip and the surface while keeping the tunneling current constant. The topography of the surface can then be mapped to a very fine accuracy and roughness on atomic scale can be observed.

The AFM, a cousin of STM, can be used with non-conducting materials while STM can be used only with conducting materials. AFM also uses a tip, which is attracted to the plane above which it is placed through van der Waals forces and any other attractive forces. As these forces do not decay very rapidly with distance, many atoms contribute to the attractive forces. Hence, the tip has to be made very sharp, usually 30 nm in diameter or less. In the AFM, the tip is mounted on a very sensitive cantilever. This allows measurement of forces as small as 10^{-9} N by measuring the deflection of the cantilever. Suppose the cantilever is built such that the force is proportional to the distance between the tip and the surface. If, while scanning a surface with the tip, the deflection attained to keep force constant is measured, the topography of a surface can be mapped.

Manipulation Using STM

It turns out that when the tip is brought close to an atom placed on a plate, and a voltage is applied, the atom is pulled away from the surface and it attaches itself to the tip. The tip can then be moved to a different location and the atom can be deposited back onto the plane by reversing the voltage. In this manner, atoms can be moved around and

'assembled' into patterns. Scientists at IBM have moved Xenon atoms on a metal surface to assemble their logo: IBM. Other beautiful images of complex objects assembled in this manner by IBM are available on their web site [10].

The assembled objects can be accessed by the same technique. A tip can be moved around on the plane to 'address' the atom and 'detect' its 'state'. If a device is made up of several tips, several atoms can be 'addressed' simultaneously. Such a device has been built by IBM and is evocatively called a 'millipede'. Its potential for reading stored data is obvious.

Synthetic Methods

The synthetic methods depend upon the product being made. Only a few typical ones are described as follows:

Nanoparticles

Nanoparticles have been made by dry as well as wet methods. Grinding is one of the dry methods and it is energy intensive. But there could be contamination from the grinding tools.

Vapourisation of material and condensation is another technique in which the material is vapourised by using electric arcs, lasers, ion beams etc. Alternatively, gas phase decomposition reactions of suitable precursors can also be used. When a large amount is vapourised, the vapour phase gets supersaturated, leading to nucleation. Provided the rate of nucleation is large and the material available is small, the particle size will be small. For example, metal clusters have been created in this manner.

Wet methods are based on solution chemistry. A suitable reaction is chosen to produce the material in solution. A very famous example is the reduction of tetracholoroauric acid by trisodium citrate to produce gold atoms in aqueous medium. Gold atoms nucleate and produce particles. Once again, if nucleation dominates growth, fine particles are produced. A variant of this method is the use of swollen micelles as reactors, where the reactants are 'micellised' by using a suitable surfactant. The micelles range from 10 nm upwards in size. When a suitable reaction is carried out, atoms are produced in the micelles. As the size of the micelles is small, the number of atoms contained in them is also small. By controlling the fusion of micelles, the rate of nucleation can be controlled and very small particles can be produced. A well-known example is the production of $CaCO_3$ nanoparticles by passing CO_2 into 'micellised' aqueous suspension of micron sized particles of $Ca(OH)_2$.

Two very good reviews are by Moser et al. [11] as well as Masala and Seshadri [12].

Fullerenes

Fullerenes are prepared from graphite. Typically, an arc is struck between two graphite electrodes placed in an evacuated chamber under Helium or Argon atmosphere. The soot produced contains fullerenes and it is collected on cooled surfaces, which can be extracted into an organic solvent and purified. A large fraction of the soot is C_{60} though higher fullerenes containing 70 or more carbon atoms are also produced.

Carbon Nanotubes

CNTs can be produced in several ways. Arcing between graphite electrodes in the presence of Helium produces a porous mass on the cathode. The porous mass contains multi-walled CNTs. Though this method is used, it is not very controllable. Catalytic chemical vapour deposition is the preferred method in which a substrate is prepared by depositing catalyst on it. The most commonly used catalysts are nickel, cobalt and iron. Then a carbonaceous gas is leaked into the reactor. Typically, these are acetylene, ethylene etc. Synthesis occurs at high temperatures of the order of 700°C. Other gases such as hydrogen are also passed, but their role is still not clear. Single walled CNTs are successfully produced using a catalyst. A most important development has been the technique to grow aligned CNTs. Here, a catalyst is deposited on a substrate in a regular array and the CNTs grow from the catalyst. There is useful literature available not only on CNTs but also on other carbonaceous nanomaterials [13].

Modelling of Nanoparticle Formation

Activity in this area has been increasing, since control of particle size in various synthetic methods is important. A few models, in the development of which the author has been involved, have been briefly described.

Overbased Calcium Carbonate

Nanoparticles of $CaCO_3$ are produced industrially by the following process described by Roman et al. [14]. A suspension of micron-sized lime particles in an organic medium is prepared. A very minor part of lime is used to make surfactant by a neutralisation reaction. Water is produced in the neutralisation reaction and solubilises a very small part of $Ca(OH)_2$ to form a saturated solution. The surfactant and the saturated solution form reverse micelles. Carbon dioxide is bubbled into this suspension. The end product of this process is a suspension of nanoparticles of $CaCO_3$ stabilised by the surfactant.

The following mechanism was proposed by Bandyopadhyaya et al. [15] for the formation of nanoparticles. Carbon dioxide neutralises the hydroxide producing carbonate in the micelles, and this occurs fairly quickly. As the solubility of $CaCO_3$ is very low, the micelles become supersaturated, causing nucleation. Even the presence of a single molecule is sufficient to cause supersaturation in small micelles. The micelles also collide, fuse and exchange contents. Thus, nucleation does not occur in all micelles, since nuclei can grow by absorbing the carbonate formed in micelles. This growth process consumes supersaturation and prevents nucleation in some micelles. The main feature of modelling is to describe the competition between nucleation as well as growth, and to predict the fraction of micelles in which nucleation occurs. This process forms the first stage. In the second and slow stage, the micelles containing particles of $CaCO_3$ collide with particles of lime and solubilise the lime. Carbon dioxide enters these and by reaction with the hydroxide, produces more carbonate. As this process is slow, supersaturation is never built to high enough levels to cause nucleation and all product formed goes towards growth of $CaCO_3$ particles. The surfactant adsorbs on the nano-sized calcium carbonate particles and stabilises them.

It must be fairly clear that the process described is typical of any reactive precipitation process with which many chemical engineers are familiar. The new element comes from the presence of micelles, which act as reactors that coalesce and break up. Chemical reactor engineering concepts have been used in developing a model for this process. Here, a simplified version is described to focus on the main issues. Consider the first stage, and assume that the formation of $CaCO_3$ is completed very quickly. The initial condition in the reactor corresponds to supersaturated micelles, which are denoted by O. Some of these nucleate. Let N denote the micelles containing a nucleus. In chemical reaction engineering methodology, this can be described as a reaction with a rate coefficient k_n

$$O \xrightarrow{k_n} N$$
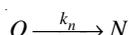
The micelles containing a nucleus collide and fuse with O to produce growth of the nucleus into a particle. Let the micelles containing a particle be denoted by P. The growth process can be represented by

$$O + N \xrightarrow{k_g} P$$
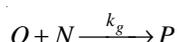
where the rate coefficient k_g represents the process of collision and transfer of carbonate onto the nucleus. P also can 'react' with O to produce a micelle containing a further grown particle. This can be represented as

$$O + P \xrightarrow{k_g} P$$
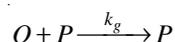
The similarity between these steps and polymerisation followed by initiation is striking. The steps described above form a series-parallel system of reactions occurring in a batch reactor, which can be modelled using the concepts of chemical reaction engineering. Complications arise since the rate coefficients are size dependent and since each micelle may not contain the same number of product and/or reactant molecules. Bandyopadhyaya et al. [15] developed a realistic model that accounts for the same. The predictions for the model of the size of particles formed as a function of batch time are compared with observations in Fig. 1. It can be seen that the model is very successful in predicting the characteristics of the industrial product.
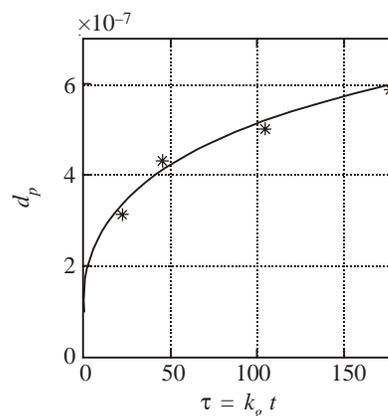

Fig. 1. Comparison of model predictions of size (cm) as a function of time with observations.

Citrate Gold Particles
Gold particles find application in diagnostics and are produced on a reasonably large scale. One of the common methods to produce them is to react auric chloride with tri

sodium citrate. This process has been pioneered by Professor Turkevich. A variant of this process, and a better one, is to add tannic acid, which is a stabiliser. Kumar et al. [16] analysed the process that uses only citrate using the conventional expertise of chemical engineers on kinetics and population balances. They proposed the following mechanism for the formation of nanoparticles. The initial step is the oxidation of citrate which yields dicarboxy acetone

$$({}^-OCCH_2)_2C(OH)CO^- \longrightarrow ({}^-OCCH_2)_2C{=}O + CO_2 + H^+ + 2e^- \tag{1}$$
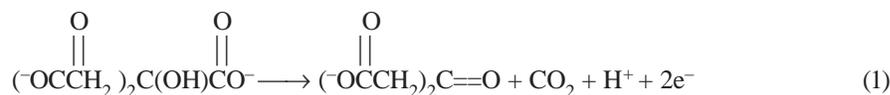
Auric state is reduced by the addition of electrons to the aurous state

$$AuCl_3 + 2e^- \longrightarrow AuCl + 2Cl^- \tag{2}$$
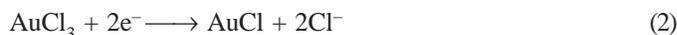
The final step is the disproportionation of aurous species to gold atoms

$$3\ AuCl \longrightarrow 2\ Au° + AuCl_3 \tag{3}$$

They proposed that the dicarboxy acetone formed plays the important role of an organiser in 'gathering' aurous species for the disproportionation step. The gold atoms produced nucleate and grow by disproportionation reaction occurring on their surface. Dicarboxy acetone also plays a crucial role in nucleation of gold atoms. Thus, both disproportionation and nucleation steps are hindered by decomposition of dicarboxy acetone. Stabilisation occurs in a complicated way in the citrate process. When citrate is in excess it can stabilise by adsorption, but in large excess it promotes coagulation through double layer compression. When citrate is in short supply, both auric and aurous salts can adsorb and provide partial stability.

The main challenge in modelling this process is the sensitive dependence of the particle size on the ratio of citrate to gold (Fig. 2). Thus, when this ratio increases by a factor of 5, from about 0.4 to about 2, the particle size decreases by a factor of 7, which
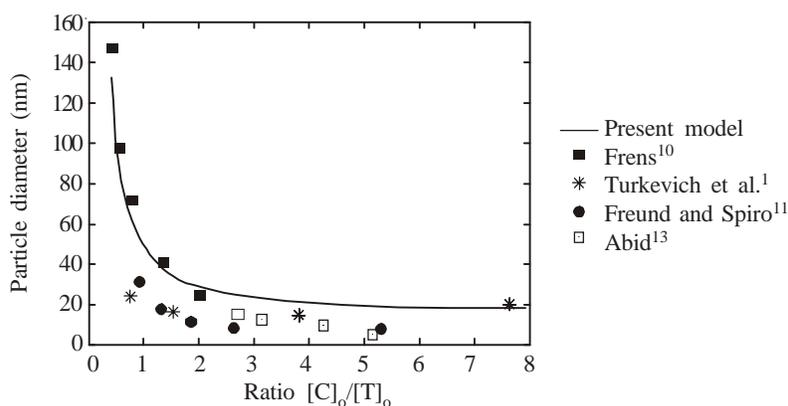

Fig. 2. Data on nanoparticles of citrate gold.

corresponds to a change of nearly three orders of magnitude in volume. Yet, when the ratio increases from about 2 to 7, there is very little change in the particle size. It is interesting to note that the data span observations over nearly 50 years! Kumar et al. [16] developed a quantitative model based on this description that could explain the sensitive dependence. Figure 2 shows the very good agreement between the observations and predictions of the model. Experiments were carried out by keeping concentration of gold salt fixed and by varying the concentration of citrate. Consider the situation when citrate is the limiting reactant. The concentration of dicarboxy acetone goes through a maximum due to its degradation and since rate of its formation by reaction with auric chloride decreases with time. The maximum concentration and, hence, the rate of nucleation can be expected to be proportional to the initial concentration of citrate. However, the amount of gold salt is constant. Hence, the particle size decreases as concentration of citrate is increased. When citrate is in stoichiometric excess, the maximum concentration of citrate and, hence, the rate of nucleation is determined by the initial concentration of gold salt. Since the latter is constant, the particle size becomes independent of the initial concentration of citrate. Thus, it was showed that, unlike the usual balance between nucleation and growth that determines the particle size, it is the balance between rate of nucleation and degradation of dicarboxy acetone that determines the particle size in this process.

Nucleation of Nanoparticles
In all the examples considered, it is seen that nucleation plays an important role in determining the particle size. The rate of nucleation is usually described by a classical theory involving two steps. The first step is the calculation of the critical size of a nucleus that grows. It is determined by making a balance between the surface energy required to form the nucleus and the decrease in the solute free energy when it is removed from the supersaturated solution. It turns out that the value of the final particle size predicted is very strongly dependent on the critical size. Calculation of critical size by using the classical theory produces odd results when applied to small systems. For example, it could result in predicting fraction of an atom or a molecule to be the critical size. This occurs since, as mentioned earlier, even one atom or a molecule can create supersaturation in a small micelle. Yet, it is unrealistic to speak of one atom as the size of a critical nucleus. Thus, an important issue is to model formation of a nucleus in small systems. Gopalarao [17] has been trying to resolve this issue through molecular simulations. The idea is to construct a micelle and introduce atoms into it. The atoms interact through various attractive forces between themselves and with water surrounding it.

Hopefully, aggregation would occur as concentration of the introduced atoms increases beyond a critical value and that should correspond to the size of a critical nucleus.

What Can Chemical Engineers Do?
Chemical engineers can contribute to this exciting area as follows:

Preparation of Nanomaterials
Today, the nanotechnology industry has about US$ 50 billion turnover. The major products

are nanoelectronics, nano-healthcare and textile applications. This is expected to grow. Clearly, larger scale production will be needed and chemical engineers can expect to play a role in this. Here, the issues involved are one of engineering structure into product and that of increase in the scale of production. As many of the properties of nanomaterials depend upon their size and structure, control of both is important.

Synthesis of nanoparticles by either wet or dry techniques has a lot to do with reactor design. Dry techniques are similar to combustion synthesis, on the one hand, and plasma reactors on the other. Energy efficiency and scale-up are important issues, with which chemical engineers are familiar. In the case of CNTs, many of the steps in the formation are still not understood and chemical engineers, with their considerable experience in interpretation of kinetic data, can play a role. Wet techniques involve liquid phase reactors. Chemical engineers with considerable knowledge of mixing and reactions can play a significant role in developing and designing reactors.

The basic processes in the formation of nanoparticles or CNTs are nucleation and growth. These are similar to processes like reactive crystallisation, aerosol formation etc., with which chemical engineers are familiar. Analysis of these processes from an engineering perspective would be a useful contribution that can be made only by chemical engineers.

Stabilisation of Nanomaterials

One of the main advantages of nanomaterials, namely, the large surface area per unit volume, also turns out to be a major disadvantage. The large surface energy promotes coagulation to minimise the free energy. Stabilising nanomaterials to increase shelf life is an important aspect. The basis of this is the same as that involved in emulsions foams and aerosols. Chemical engineers have been dealing with these issues in cosmetics and drug industries. The same knowledge can be applied in the case of nanomaterials as well. An example is stabilisation of gold nanoparticles. It was mentioned earlier that thiols adsorb strongly onto gold. Hence, long chain alkane thiols should stabilise gold particles by the steric repulsion between long alkane chains. Such stabilised particles are often referred to as molecularly (or monolayer) protected nanoparticles (MPNs).

Self Assembly Techniques

A lot of nanotechnology based on particles will depend upon assembling them in ordered structures. Success of this technique depends upon understanding the forces that play a role in the self-organisation in surfactant systems. Chemical engineers have contributed significantly in developing surfactant based products. Surfactant solutions form self-organised structures – micelles, bilayers, liquid crystals etc. – and chemical engineers can translate their experience with these materials in preparing structures of nanoparticles. Further processing of the structures involves many techniques of semiconductor technology in which chemical engineers have played an important role.

Nanobiology

Only applications in diagnostics have been discussed earlier. However, applications of nano S&T go well beyond that and chemical engineers can add value to them. Consider,

for instance, targetted drug delivery by using nanoparticles. The drug has to be given orally or injected through blood. First, the drug has to be loaded onto the nanoparticles. Then the nanoparticles have to diffuse through appropriate cell walls, travel through the body by convection, preferentially adsorb on to the target, desorb from the particle through some mechanism, and pass into the target. There may be some unwanted binding while it is convecting that may lead to inefficiency and adverse side reactions. All these processes can be described with an understanding of transport processes and reaction engineering.

Molecular Electronics

This is a new area, with which many chemical engineers are not familiar. In some ways, the situation is very similar to the early days of the semiconductor industry. Solid state physics has not been a familiar part of the conventional chemical engineering curriculum and, hence, entry of chemical engineers into semiconductor processing has been late and not penetrating enough. This, perhaps, is the time for chemical engineers to become familiar with the scientific developments taking place in the area of molecular electronics.

Conclusions

Nano S&T is growing due to increasing desire for miniaturisation and it is expected to have a large impact on the economy. It is acquiring importance since planned synthesis and ability to manoeuvre materials at the nanoscale have become possible in the last 20 years. It is also due to the special properties materials have when one of their dimensions is on a nanometer scale. These special properties arise mainly due to large ratio of surface area to volume, smallness of size, and size dependent properties. Many applications are already in commercial use and range from catalysis to diagnostics to sensors. The applications involve transport phenomena, adsorption, chemical reactions etc., with which chemical engineers are very familiar. Chemical engineers, therefore, are in a position to understand and analyse nanoscience, and contribute to developing new technologies. In quite a few areas, chemical engineers can definitely play a leadership role in years to come.

Acknowledgements

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