

Synthesis and Fabrications of Nanomaterials

- ❖ Scaling the *particle size down to nanometer dimensions provides exciting challenges and opportunities* for chemists, physicists, biologists, and materials scientists.
- ❖ On the *nanometer scale, many material properties*, which are usually regarded as being intrinsic for bulk material, *become extremely sensitive to its dimensions*.
- ❖ In other words, *besides composition, size and shape/morphology control became a new way of tuning the properties* of nanostructured materials.
- ❖ Knowledge of *nanomaterial synthesis, nano-structured thin film deposition, and nanopatterning techniques is fundamental for the development of nanotechnology enabled applications*.
- ❖ One of the *major challenges in nanoscale science begins with the synthesis* of new nanomaterials with desired *composition, monodispersed sizes, uniform morphologies*, and comprehensive and *functionalized surfaces*.
- ❖ Let us see a few simple examples. One example is *a magnetic nanoparticle that is used to store a single bit of information by defining the direction of its magnetization*.
- ✓ If one wants to do this, using nanoparticles with diameters *smaller than about 6 nm at ambient temperature, simple elemental nanoparticles made*, for example, *of pure Fe will not work because thermal vibrations will instantly change their direction of magnetization*.

- To produce a particle that doesn't lose its "memory" without cooling to very low temperatures, each one has to be made with more than one material and formed either as a uniform alloy or as a core-shell particle (see Fig. 0.3a)—that is, a kind of nanoscale chocolate peanut with a core consisting of one material surrounded by a shell of a different substance.
- As stated above, these have to be assembled in vast numbers into some sort of ordered array (the big unsolved problem with this technology) to produce a useful device, but each particle has within it the capacity to store a data bit. When this technology succeeds, it would represent a storage density about 1000 times greater than existing hard disks on computers. For example, the bottom image in Fig. 0.3a shows an array of core-shell nanoparticles used to store the word "nanotechnology" in ASCII code. The storage density represented would allow about two million books or a large library to be written in an area the size of a postage stamp.

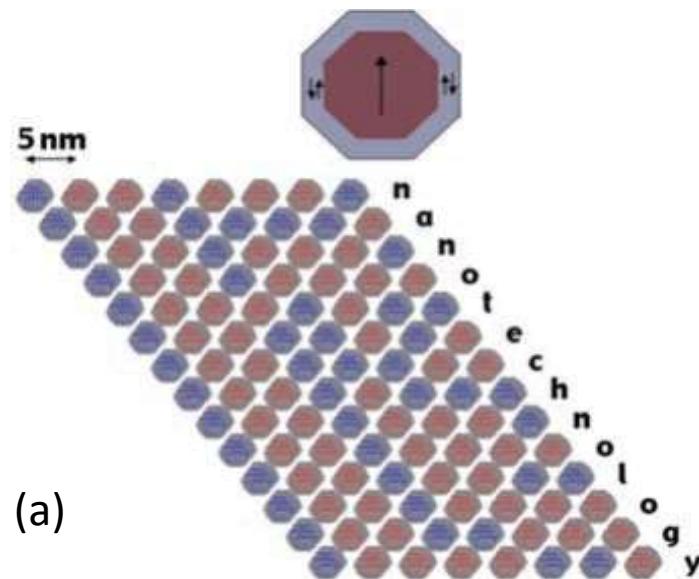
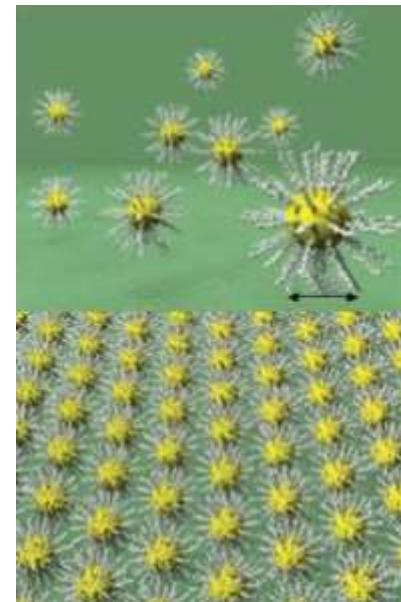


Fig. 0.3 (a) (Top): A "core-shell" magnetic nanoparticle consisting of a ferromagnetic metal core (e.g., iron or cobalt) surrounded by an antiferromagnetic shell, e.g., cobalt-oxide or manganese) that is specialized to record a single bit of information encoded by the direction of the core magnetization.

The bottom picture shows an array storing the word 'nanotechnology' in ASCII format with blue representing down magnetization or '0' and red representing up magnetization or '1'. Writing at this density would enable the storage of about two million books (a large University library) on an area the size of a postage stamp.

- An example of a more sophisticated “***functionalized***” nanoparticle, shown in Fig. 0.3b, is a *gold nanoparticle about 2 nm across with attached molecules called thiols*.
- ✓ ***If wires could be attached to this nanoparticle, it could be made to act like a transistor by a process called Coulomb blockade.***
- ✓ It turns out that the ***thiols, of which there are many types, can act as wires if they come together in the right way.***
- ✓ A ***slight change in the bonding produces a change in the resistance of the link or makes it capacitive (insulating).***
- In other words, ***an entire circuit network consisting of transistors, capacitors, and resistors can be produced by placing an array of thiol-coated nanoparticles in the correct positions.***
 This, of course, is the unsolved problem but is a tantalizing one
 because ***the density of components in such an array means that about 1000 nanoparticle transistors could be placed in the space occupied by a single silicon-based transistor on a Pentium IV chip.***

Fig. 0.3 (b) Gold nanoparticles with attached thiol molecules. Each nanoparticle can behave as a transistor and the thiols can bond onto other thiol-coated gold nanoparticles via electrically resistive or capacitive links to build circuits with a component density 1000 times greater than existing devices. Reproduced with the permission of Dr. Mark Everard.



- Continuing the trend toward complexity of individual nanoparticles, Fig. 0.3c shows a combination of the types in Figs. 0.3a and 0.3b consisting of **a magnetic core-shell particle, with controlled properties, coated with a second shell of gold that facilitates its attachment to complex biological molecules**—for example, drugs, proteins, or antibodies.
 - The magnetic core of the particle can be utilized to steer the attached molecule to specific areas of the body by external fields for targeted drug delivery.
 - Alternatively, the attached biological molecule could be used to target specific cells (e.g., tumor cells) that could then be heated and killed by a weak external radio-frequency field that is harmless to healthy tissue.
- ✓ For heating purpose, Au nanoshell or magnetic core or both can be used.

Fig. 0.3 (c) A core-shell magnetic nanoparticle (as in Fig. 0.3 (a)) with a second shell of gold that makes it easy to attach biological molecules such as proteins or antibodies, or drugs. The magnetic core of the particle can be utilized to steer the attached molecule to specific areas of the body by external fields for targeted drug delivery. Alternatively, the attached biological molecule could be used to target specific cells (e.g., tumor cells) that could then be heated and killed by a weak external radio-frequency magnetic field that is harmless to healthy tissue.



- ❖ No one can fail to be impressed by the huge increases in performance and density of components/memory elements in devices made by the electronics and magnetic recording industries in the last few decades. The above two examples illustrate, however, that there is still a long way to go.
- ❖ As a rough guide to where we are with evolutionary nanotechnology, the functional nanoparticles shown in Fig. 0.3 can be routinely manufactured, but their use in technologies such as those described above awaits the solution to enormously difficult technological problems such as controlling their self-assembly into arrays, etc.

➤ **In principle, all the methods for synthesizing nano entities can be divided into two basic groups:** Top-down and Bottom-up (Fig. 24.75).

- ✓ The first is to take a macroscale (or microscale) object and carve out nanoscale patterns; methods of this sort are called top-down approaches. Physical interactions are used in **top-down fabrication approaches**, such as photolithography, electron-beam (e-beam) lithography, and soft lithography; photolithography is used to fabricate very large-scale integrated circuits having feature dimensions on the 100 nm scale.
- ✓ The second technique is to build larger objects by controlling the arrangement of their smaller-scale components, and methods of this sort are called **bottom-up approaches**. The bottom-up approach to nanoscale fabrication is emphasized in this text because it focuses on the chemical interactions of atoms and molecules, and their controlled arrangement, using chemistry, into larger functional structures. *The two basic approaches most widely used to prepare nano-materials using bottom-up methods are solution and vapor-phase methods.*

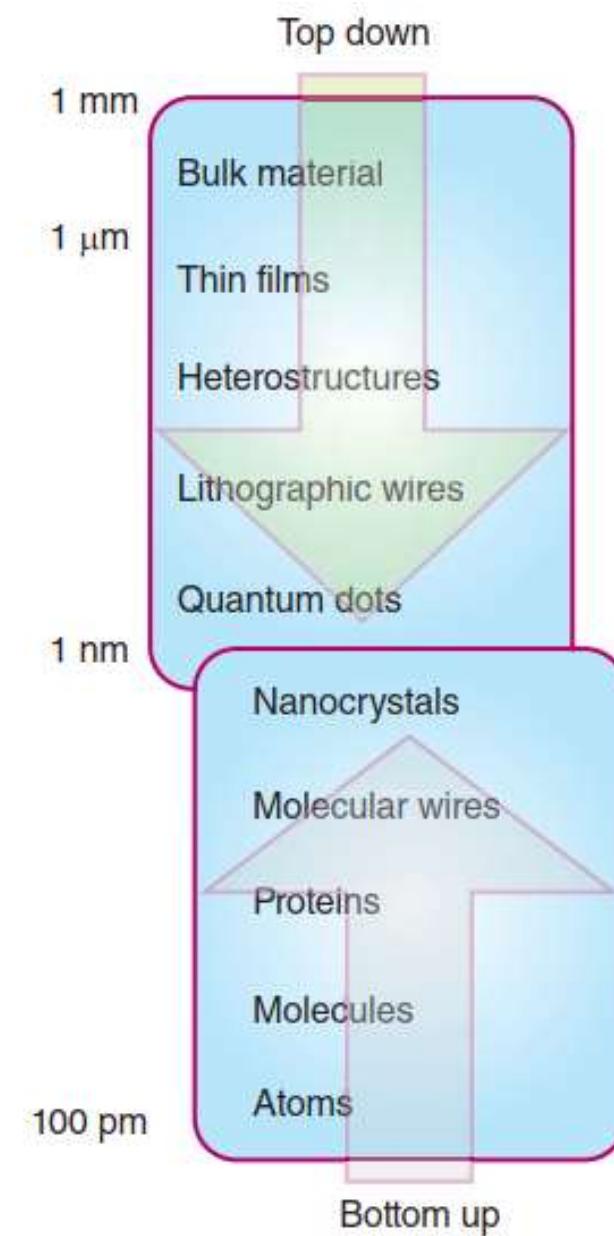


Figure 24.75 The two techniques for making nanoscale structures. The **top-down** technique starts with larger objects that are whittled down into nanoscale objects; the **bottom-up** technique starts with smaller objects that are combined into nanoscale objects.

- The approach from the “bottom” largely pertains to chemical methods of preparation of nanosize particles starting from atoms and molecules, whereas the approach from the “top” is typical of mechanical/physical methods that use various dispersion and aggregation procedures.

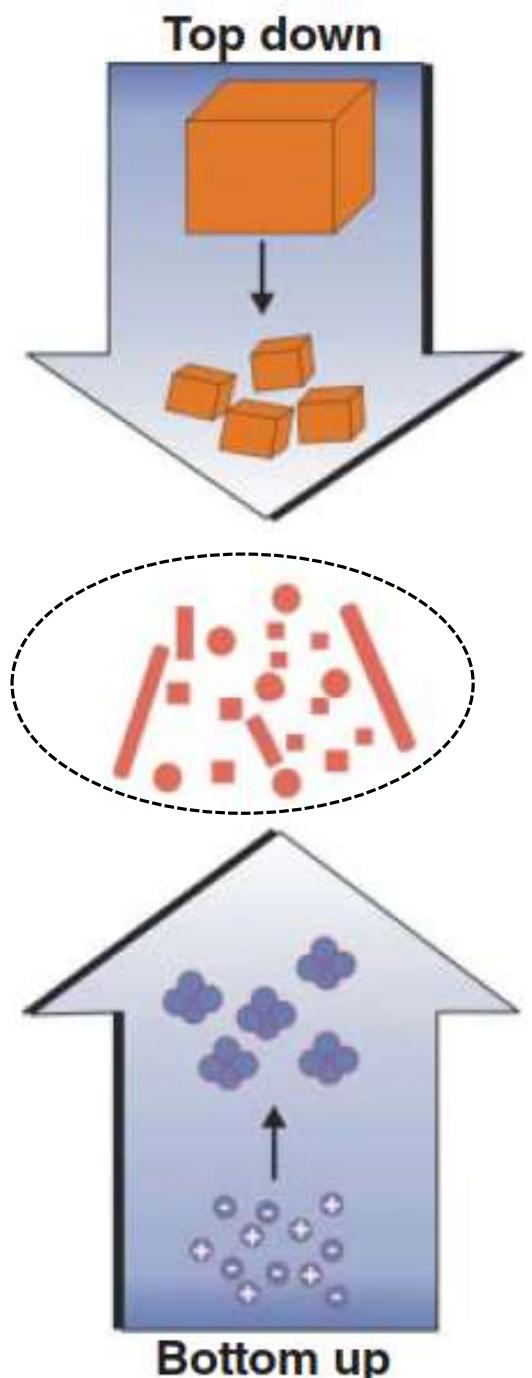
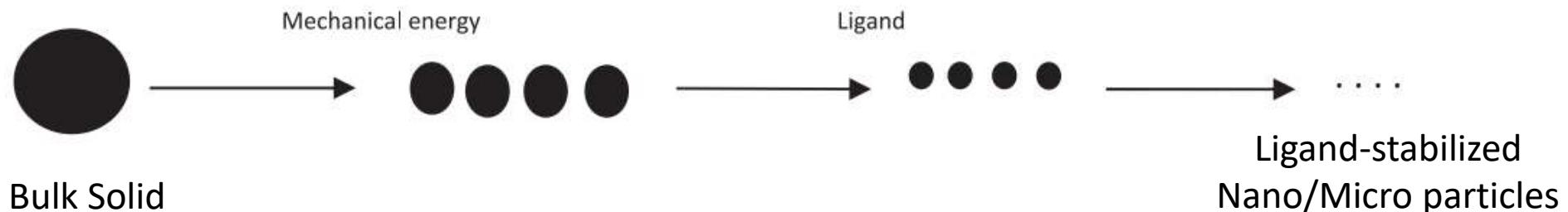
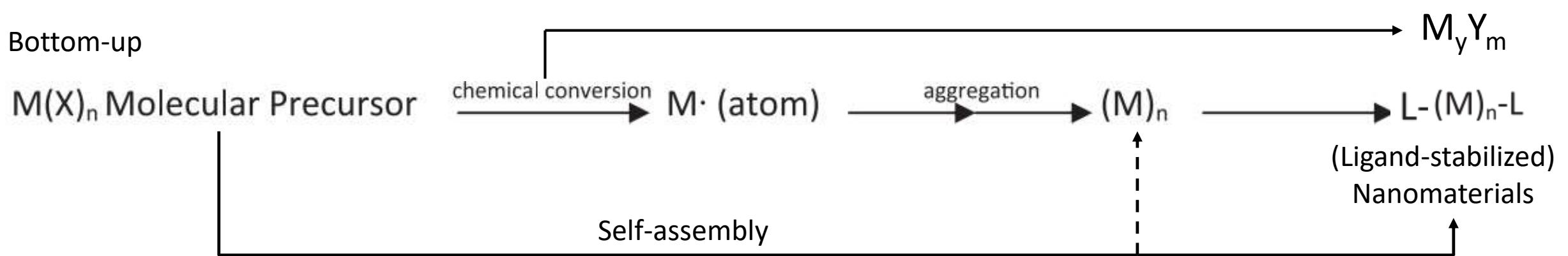


Figure 2.1 “Top-down” and “bottom-up” approaches for the synthesis of nanomaterials.

Top-down



Bottom-up



SCHEME 2.1 Representation of top-down method (grinding/pulverizing bulk solids) and bottom-up method (creating a reactive atomic or molecular precursor that aggregates/assemble to clusters and eventually nanoscale particles or materials).

- The top-down method that involves ***grinding and pulverizing*** have, however, ***limits*** because, *as particle size decreases, chemical reactivity increases*. This eventually *leads to the back reaction of particles, necking, and coalescence*. Thus, consider the extreme of water droplets. These droplets never spontaneously split apart but do spontaneously coalesce to form larger droplets. The same is true of metal droplets as well as solid particles.
- *Because of these increased surface energies and reactivities, grinding and pulverization are not good methods for reaching below about 50 nm, and certainly not good for attaining monodispersity (all particles the same size).*
- The most satisfactory results are for solids with very high lattice energies, such as magnesium oxide and other ceramics. *The least satisfactory results are for low melting, low lattice energy solids, such as zinc metal or magnesium metal.*
- A modification that helps stabilize small particles as they form, is adding an active surface ligand, called a ***chemo-modified grinding***. But even this approach has not proven to be very successful, at least for exacting studies.
- Nonetheless, if large amounts of nanomaterials are needed, and there are no requirements for monodispersity or ligand stabilization, grinding/pulverization of bulk solids is a viable synthetic method.

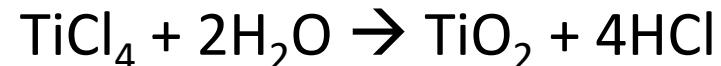
- The “bottom-up” methods of synthesis yield more control in nanoscale synthesis, but usually are more expensive than “top-down.”
 - Bottom-up means building nanoparticles from their constituent fundamental building blocks, such as atoms or reactive small molecules.
 - So, in bottom-up synthesis, there is a need for a molecular precursor that can be suddenly changed to a fundamental building block.
- ✓ For example, a soluble stable metal salt could be reduced to form metal atoms, which rapidly aggregate to nanoparticles.
- ✓ Another example is to hydrolyze a soluble metal alkoxide to an insoluble metal hydroxide, which rapidly aggregates to nanoparticles.
- Preparation of nanoparticles from atoms allows individual atoms to be considered as the lower limit of nanochemistry. Its upper boundary corresponds to atomic clusters, whose properties no longer undergo qualitative changes with an increase in the number of constituent atoms, thus resembling the properties of compact metals.
 - The number of atoms that define the upper boundary is unique for every element in the Periodic Table.

- It is also of paramount importance that the structures of equal-size nanoparticles can differ if they were obtained by using different approaches.
 - As a rule, dispersion of compact materials into nanosize particles retains the original structure in resulting nanoparticles.
 - In particles formed by aggregation of atoms, the positions of atoms can be different, which affects their electronic structure.
- ✓ For example, a particle measuring 2–4 nm can demonstrate a decrease in the lattice parameter.
- ✓ The above factor poses a problem of the necessity of analyzing the law of conservation of chemical composition at the nanolevel.

SYNTHESIS OF INORGANIC NANOPARTICLES

- In this section, our attention will be focused on the synthesis of inorganic nano-particles, which consist of semiconducting, magnetic and noble metal constituents.
- There are numerous methods for synthesizing nanoparticles. The type of method to be used depends strongly on the type of particle to be synthesized, the particle's functional medium, and the surface to which they will be attached.
- Many synthesis methods are conducted in liquid to form colloidal suspensions. The dimensions of these nanoparticles can be tailored, as can their surface functionalities. It is also possible to influence some level of control of their shape. This is achieved through tight control of the conditions and parameters during synthesis.
- Solution-based processing routes used for the *synthesis of nanoparticles include precipitation of solids from a supersaturated solution, homogeneous liquid phase chemical reduction and ultrasonic decomposition of chemical precursors*. These processes are attractive due to their simplicity, versatility and availability of low-cost precursors. Inorganic salt compounds used in the wet chemical synthesis routes are more versatile and economical than alkoxides employed in the sol–gel process.

- A typical example is the formation of ***nanocrystalline titania powders*** via hydrolysis of TiCl_4 at lower temperatures:



- ✓ Once the solution becomes saturated, crystallization of titania takes place either through homogeneous or heterogeneous nucleation. In the latter case, crystal seeds are added to the solutions to promote the crystallization of titania nanoparticles.
- One of the ***greatest challenges faced in nanoparticles synthesis is the instability of the nanoparticles and their tendency to easily aggregate or precipitate. These effects are avoided through the use of stabilizing (capping) agents that adhere to the surface of the nanoparticle.***
- ✓ Generally, these ***stabilizing agents can manipulate the solubility, growth and surface charge of the particles.*** As a result, they keep the particles separated and suspended in the liquid environment during their synthesis.

SYNTHESIS OF INORGANIC NANOPARTICLES: Semi-conductor Nano-particles

- Semiconductor nanoparticles and nanocrystals (often called quantum dots or Q-dots, if their dimensions are less than ~10 nm) exhibit optical, thermal, mechanical and electrical properties that are strongly dependent on the dimensions of the particle.
- Their unique properties arise from their ability to confine the conduction band electrons, valence band holes, vibrations and other particle activities in all three spatial directions.
- When the dimensions of these nanoparticles are in the order of a few nano-meters they possess discrete, quantized, molecular-like energy spectrums caused by ***quantum confinement effects***. Their energy spectrum can be engineered by manipulating their dimensions, shapes, and other related properties.
- There are many methods for the synthesis of semiconductor nanoparticles.
 - Generally, they are based on initiating and stopping the growth of nanoparticles in either a gaseous or liquid environment with a high degree of control.
 - Low-cost routes capable of mass-producing nanoparticles of desired dimensions are generally performed via colloidal synthesis.

- The use of ***reverse micelles*** as nano-scale reaction vessels is one the most common methods in colloidal synthesis. After coming into contact, reverse micelles exchange their contents. This process has been used to make nanosized materials via either the chemical reduction of metal ions or co-precipitation reactions.
 - An example is the synthesis of the CdS nanoparticle. CdS has a direct band-gap of 2.42 eV and is widely studied for applications in both photoresistive and photovoltaic devices.
 - In this process, reverse micelles containing two different precursors are prepared: one with metal salts and the other with a sulphide source (such as Na_2S). The solutions are mixed and nanoparticles are formed as the different micelles exchange their contents. After the formation of these nano-particles, thiol molecules can be employed to stabilize them as they bond to the surface.
 - Other nanoparticles such as CdSe, PbS, TiO_2 , etc. can also be obtained using different colloidal synthesis processes.
- Other synthesis methods include electro-deposition, formation in gas phase and pyrolysis, to name a few.

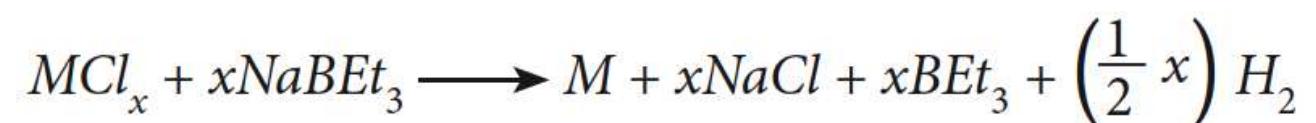
SYNTHESIS OF INORGANIC NANOPARTICLES: Magnetic Nanoparticles

- Amorphous and nano-crystalline soft and hard magnetic (whether they are non-permanent or permanent) materials have many applications including transformers, inductive devices and sensors, etc.
- Additionally, the development of uniform magnetic nanoparticles is typically an important issue in ultrahigh-density magnetic storage devices and sensors.
- *Magnetic alloys are materials such as cobalt and Iron.*
- *Magnetic type oxides* are materials such as magnetite (Fe_3O_4), cobalt ferrites, nickel ferrites, zinc ferrites (MFe_2O_4 - with M to be metals such as Co, Ni, Zn) and the mixed nickel and cobalt ferrites.
- It is known that the magnetic anisotropy of nanoparticles within an exchange length dictates the magnetic softness/hardness of such materials.
- The magnetic exchange length is typically measured in nano-meters or tens of nano-meters which highlights the underlying importance of the nano-metric dimensions in the properties of magnetic systems.
- Several synthetic approaches of magnetic nanoparticles include ***thermal and sonochemical decomposition of organometallic precursors, high-temperature reduction of metal salts, and reduction inside reverse micelles*** to name a few.

SYNTHESIS OF INORGANIC NANOPARTICLES: Metallic Nanoparticles

- There has been an enormous amount of research carried out into synthesizing metallic nanoparticles especially noble metals such as gold and platinum.
- The reason for such widespread efforts is the novel use of noble metal nanoparticles in a wide variety of applications, such as medicine, electronics and optics. In sensors, nanoparticles of this type can be put to use as catalysts, biomaterial tags, optical resonators and many other functional devices.
- Due to their inert nature, noble metals are generally not hazardous to living tissue and hence they are becoming attractive in biosensing and biotechnology.
- They exhibit properties that are markedly different from those of their bulk counterparts, are very stable, and their size can be easily controlled via the synthesis approach chosen.
- Colloidal gold nanoparticles are among the most stable metal nanoparticles and have many fascinating properties. For example, their size and quantum confinement effects cause them to absorb and scatter light several orders of magnitude greater than other materials.

- Salt reduction is one of the most commonly adopted methods to generate the metal colloid particles.
- ✓ The process involves the dissolution of metal salts in aqueous or non-aqueous environments followed by the reduction of metal cations to the zero-valent state.
- ✓ The nature of the metal salts determines the kind of reducing agent to be applied.
- ✓ To produce transition metal nanoparticles, group 6 metal chlorides such as CrCl_3 , MoCl_3 and WCl_4 are reduced with NaBET_3 in *toluene solution* at room temperature to form metal colloids of high yield.
- ✓ A typical reaction for forming metal powders is given as:



where $x = 3$ for $\text{M} = \text{Cr}$ and Mo ; $x = 4$ for $\text{M} = \text{W}$.

- ✓ However, the reduction of the chromium, molybdenum and tungsten halides with either LiBET_3H or NaBET_3 in *tetrahydrofuran (THF) solution generates the corresponding metal carbides (M_2C) rather than the metals.*

- One of the conventional methods for the synthesis of gold nanoparticles is the reduction of gold(III) derivatives. In 1951, **Turkevitch** and coworkers suggested the use of citrate for reducing HAuCl_4 in aqueous conditions to synthesize gold nanoparticles with dimensions of approximately 20 nm.
- Later **Frens** and coworkers showed that gold nanoparticles of predetermined dimensions (between 16 and 147 nm) could be ***obtained by controlling the ratio between the reducing and stabilizing agents (the trisodium citrate-to-gold ratio).***
- This method still remains very popular and is especially useful for applications where the surface of the gold particles is functionalized or capped with ligands.
- As an example, Fig. 4.1 shows the preparation of sodium 3-mercaptopropionate-stabilised gold nanoparticles, where citrate salt and amphiphilic surfactant molecules were simultaneously added.

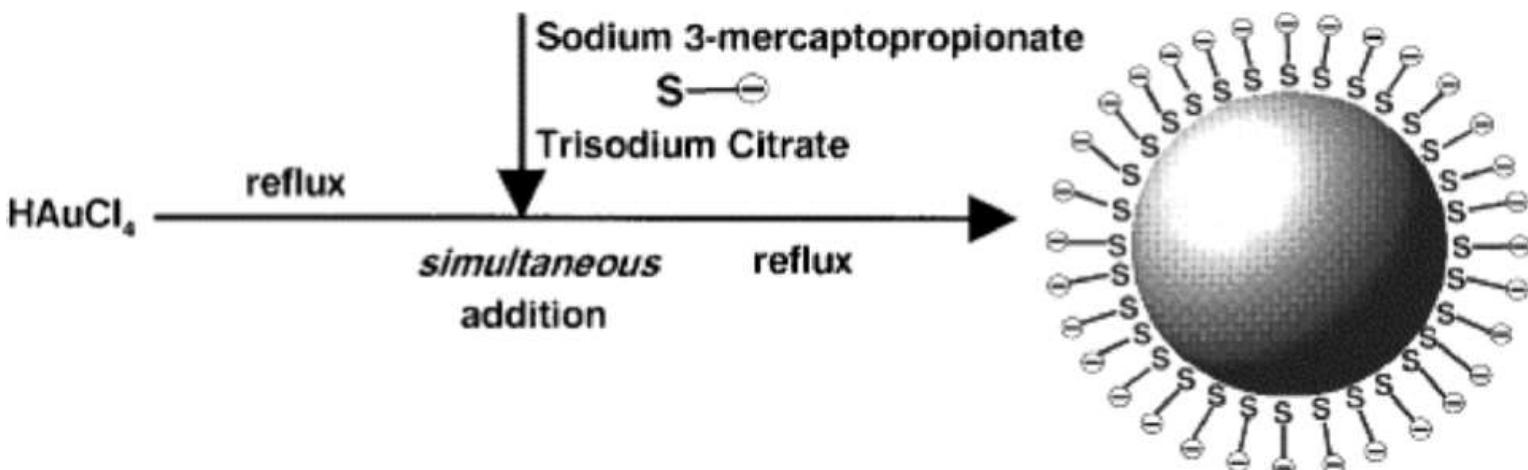


Fig. 4.1 The procedure for preparing anionic mercapto-ligand-stabilized gold nanoparticles in aqueous media. Reprinted with permission from Elsevier publications.

- Reductive synthesis of metal nano-particles is by no means limited to gold, as many noble metals can be synthesized similarly.
- Chemical reduction is used most extensively for synthesis of metal nanoparticles in the liquid phase, including aqueous and nonaqueous media.
- The wide application of this method stems from its simplicity and availability.
- As a rule, ***metal compounds*** are represented by their ***salts***, while ***aluminohydrides, borohydrides, hypophosphites, formaldehyde, and salts of oxalic and tartaric acids serve as the reducing agents***.
- ✓ As an example, we consider the synthesis of gold particles. Three solutions are prepared: (a) chloroauric acid in water, (b) sodium carbonate in water, and (c) hypophosphite in diethyl ether. Then, their mixture is heated for an hour up to 70 °C. As a result, gold particles of 2–5 nm diameters are obtained.
- ✓ The major drawback of this method is the large amount of admixtures contained in a colloid system of gold nanoparticles formed, which can be lowered by using hydrogen as the reductant.

- In the general case, the behavior of a metal particle in solution is determined by the potential difference $\Delta E = E - E_{\text{redox}}$, where *E* is the equilibrium redox potential of the particle and E_{redox} is the corresponding solution potential.
- Particles grow when $\Delta E > 0$ and dissolve when $\Delta E < 0$.
- For $\Delta E = 0$, an unstable equilibrium is established.
- The situation is complicated by the fact that *the redox potential of a metal particle depends on the number of atoms*.
- In this respect, *the chemical reduction occurs in systems thermodynamically and is kinetically unstable*.
- *Chemical reduction is a multifactor process. It depends on the choice of a redox pair and concentrations of its components as well as on the temperature, pH of the medium, and diffusion and sorption characteristics.*

- ❖ *Reagents most frequently used as the reducers of metal ions are tetrahydroborates of alkali metals (MBH_4), which operate in acidic, neutral, and alkaline aqueous media.*
- ✓ *Alkali-metal tetraborates can reduce most cations of transition and heavy metals*, which is explained by the high redox potential of MBH_4 (1.24 V in alkaline medium) as compared with the standard potentials of many metal ions, which lie in the interval $-0.5 \leq -E \leq -1.0$ V.
- ✓ Reduction of metal ions was shown to involve the formation of complexes with bridge bonds $\text{M}\cdots\text{H}\cdots\text{B}$, which favors the subsequent hydrogen-atom transfer with the break of the bridge bond, followed by a redox process with the breakage of a $\text{B}-\text{H}$ bond to give BH_3 .
- ✓ The obtained borane undergoes hydrolysis and catalytic decomposition on the surface of metal particles.
- ❖ Syntheses of metal nanoparticles in liquid media involved using *hydrazine hypo-phosphite* and its derivatives and also various organic substances as the reductants.
- ❖ Recently, the processes in which *a reducer simultaneously performs the function of a stabilizer* became widely used. Among such compounds are numerous *N–S-containing surfactants, thiols, salts of nitrates, and polymers containing functional groups*.

Spherical silver nanoparticles measuring 3.3–4.8 nm were synthesized by the reduction of silver nitrate by sodium borohydride in the presence of tetraammonium disulfide.

Dibromidebis[(trimethyl ammoniumdecanoylamino)ethyl] disulfide was used as the stabilizer. Particles show intense light absorption in the wavelength region of 400 nm, which corresponds to the silver plasmon peak and points to the metallic nature of particles.

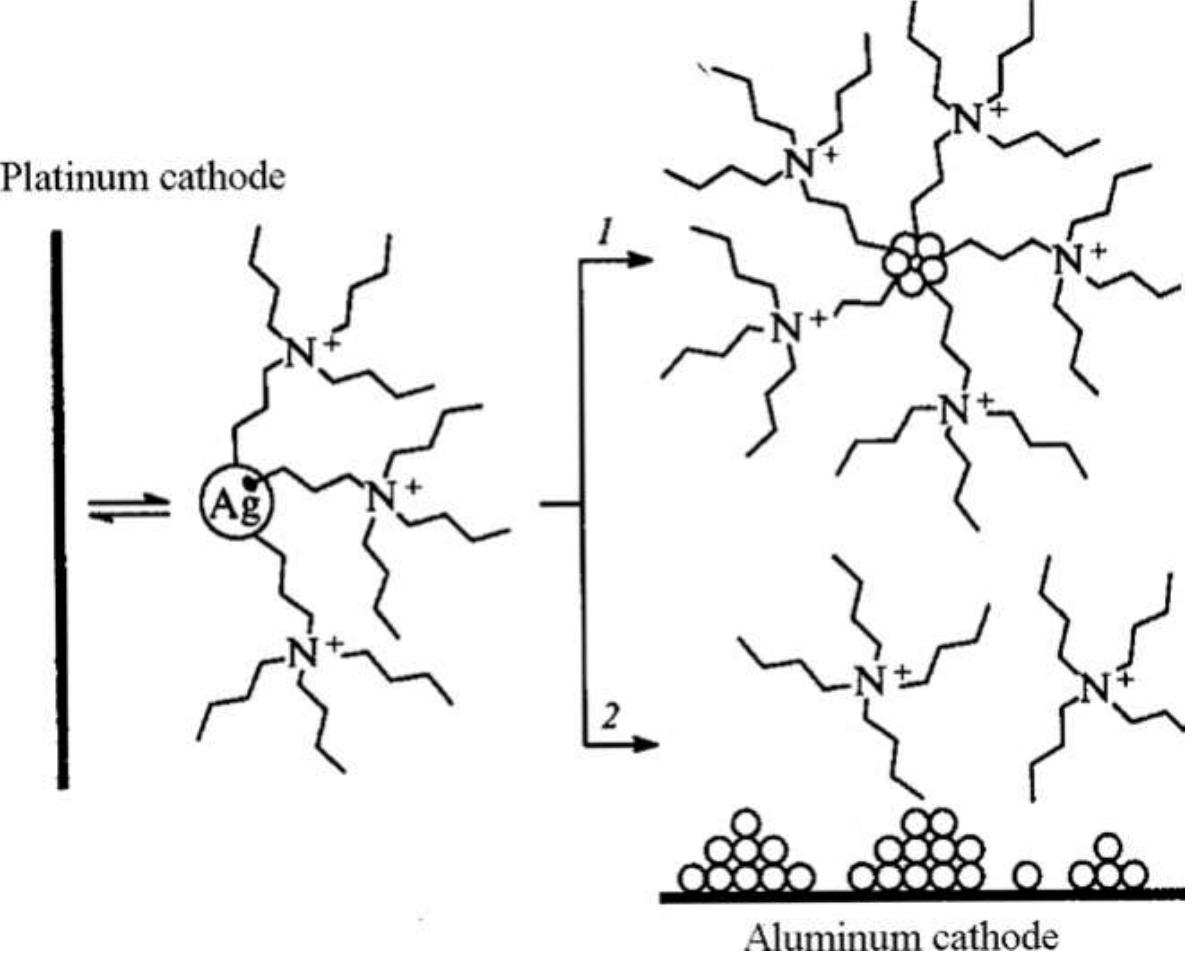
- ✓ By studying the effect of the medium on the stability of particles, it was found that the latter are ***aggregated in the presence of sulfuric and hydrochloric acids***.
- ✓ The stability of silver particles also depended on the pH of the medium: in aqueous media with pH 5–9, the particles remained stable for a week. An increase or a decrease in the pH resulted in fast aggregation and deposition of silver particles. The effect of the latter factor on the stability of gold particles was less pronounced.
- ✓ Particles of controlled sizes (1–2 nm) were obtained by using an amphiphilic polymer poly(octadecylsiloxane) as the matrix.

- Hybrid materials based on polyelectrolyte gels with oppositely charged surface-active substances (surfactants) were used as nanostructured media for the reduction of various platinum salts with sodium borohydride and hydrazine. *It was shown that the reduction with sodium borohydride mainly yields small platinum particles with radii of ca. 2–3 nm, while the reduction with hydrazine produces particles measuring ca. 40 nm.*
- Monodispersed particles of amorphous selenium were prepared in ethylene glycol via the reduction of selenious acid with hydrazine.
- A synthesis of stable nanoparticles (average size of 1–2 nm) of platinum, rhodium, and ruthenium in organic media as a result of heating colloidal solutions of corresponding metal hydroxides in ethylene glycol was described.
- In another experiment, nanostructured $\text{Fe}_{50}\text{Ni}_{50}$ alloy has been synthesized by ultra-rapid autocatalytic chemical reduction of the corresponding transition metal ions in alkaline aqueous solution with hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) at 353 K. The alloy powder is composed of spherical particles with 96 nm mean size diameter.

- Metal nanoparticles can also be generated via **ultrasonic and thermal decomposition** of metal salts or chemical precursors.
- Recently, ultrasonic waves were employed to stimulate the chemical reactions of inorganic salts. Sonication of argon-saturated aqueous solutions of NaAuCl and PdCl₂ results in the formation of noble metal AuPd alloy nanoparticles.
- Power ultrasonic waves can stimulate certain novel chemical processes due to the formation of ***localized hot spots in the liquid of extremely high temperatures ($\sim 3000\text{ K}$) and high pressures ($\sim 1000\text{ atm}$)***. The main event in the ***process is the nucleation, growth and collapse of cavitation bubbles formed in the liquid***. The cooling achieved during the cavitation collapse is estimated to be greater than $2 \times 10^9\text{ K}$. This process is commonly referred to as the ***sonochemical method***.
- Transition metal nanoparticles can be produced via sonication of their respective chemical precursors***. For example, Ni(CO)₄ has been sonicated under argon atmosphere to obtain *amorphous nickel*. *Nanostructured α -Fe (bcc iron) is usually synthesized either via sonication or thermal decomposition of Fe(CO)₅ solution*.
- One disadvantage of the sonication process is the difficulty in controlling the resulting particle size and distribution due to the agglomeration of particles into a porous coral-like microstructure.

- Many metal nanoparticles can be synthesized by **electrochemical methods**.
 - ✓ For example, *silver* particles with sizes ranging from 2 to 7 nm were synthesized by **electrochemical dissolution** of a metal anode (silver plate) in an aprotic solution of tetrabutylammonium bromide in acetonitrile.
 - ✓ This process was shown to depend on ***characteristics such as the current density and the cathode nature***.
 - ✓ Thus, *at high current densities under nonequilibrium conditions, particles of irregular shapes can be formed*. With an increase in the current density from -1.35 to -6.90 mA/cm², the particle diameter decreased from 6 ± 0.7 to 1.7 ± 0.4 nm.
 - ✓ The reduction of silver ions stabilized by tetrabutylammonium bromide resulted in the formation of metal nanoparticles and their deposition on cathodes made of either platinum or aluminum.
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- Figure 2.2 illustrates this process.
 - ❖ On a platinum cathode, spherical silver nanoparticles were deposited.
 - ❖ The deposition on an aluminium cathode produced films.

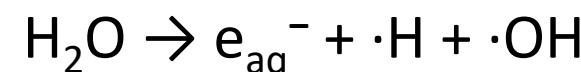
FIGURE 2.2 Illustration of competition of two processes: (1) *formation of silver particles on Pt cathode*, (2) *deposition of particles and film formation on Al cathode*.



- ✓ An analysis of optical spectra of nanoparticles in the course of their synthesis made it possible to conclude that this process involves an autocatalytic stage. Moreover, it was shown that the half-width of a peak corresponding to the surface plasmon of a particle depends linearly on $1/R$ (R is the particle radius) and the plasmon band shifts to lower frequencies with a decrease in the particle size.

- Metal nanoparticles have also been prepared by *photochemical and radiation-chemical reductions*. These methods involve the *generation of highly active strong reducers like electrons, radicals, and excited species*.
- **Photochemical (photolysis) and radiation-chemical (radiolysis) reductions differ in energy.**
Photosynthesis is characterized by energies below ~60 eV, whereas radiolysis uses energies of 10^3 – 10^4 eV.
- The main peculiarities of processes occurring under the action of high-energy radiation concern the nonequilibrium energy distributions of particles, the overlap of characteristic times of physical and chemical processes, which is of prime importance for chemical reactions of active species, and the presence of multichannel and nonsteady state processes in the reacting systems.
- *Photochemical and radiation-chemical reduction methods have advantages over the chemical reduction method.*
 - ✓ Owing to the absence of (or less) impurities formed when chemical reducers are used, the former methods produce nanoparticles of high purity.
 - ✓ Moreover, photochemical and radiation-chemical reductions make it possible to produce nanoparticles under solid-state conditions and at low temperatures.

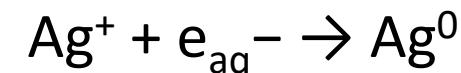
- ❖ **Photochemical reduction** in solution is employed most frequently for synthesizing particles of noble metals.
- ✓ Such particles were obtained from solutions of corresponding salts in water, alcohols, and organic solvents.
- ✓ In these media, under the action of light, the following active species are formed:



- ✓ By reacting with alcohols, a hydrogen atom and a hydroxyl radical produce an alcohol radical:



- ✓ A solvated electron interacts with, e.g., a silver atom, reducing the latter to metal:



- ✓ In the course of photoreduction, in the initial period of photolysis, the UV absorption spectrum reveals bands at 277 and 430 nm, which correspond to clusters and silver nanoparticles measuring 2–3 nm, respectively.
- ✓ With the increase in photolysis time, the absorption- band maximum can shift to both short and long wavelengths. The short-wave shift points to the decrease in the average size of silver particles, whereas the long-wave shift corresponds to the presence of aggregation processes.

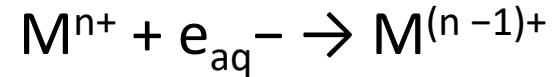
- ❖ **Photoreduction** gives rise to light-induced formation of not only nanoparticles of definite sizes but also of greater aggregates.
- ✓ The effect of light was studied by the example of gold particles in acetone, ethanol, and isopropanol.
- ✓ Illumination with a mercury lamp light led to broadening and disappearance of a band of gold surface plasmon at 523 nm. As a result, the band at 270 nm became more intense, and a new band appeared at 840 nm.
- ✓ The authors associated the shift of the plasmon band with the dipole–dipole interaction of particles in aggregates.
- ✓ Upon 20-h photolysis, complete precipitation of gold particles was observed.
- ✓ The aggregation rate was shown to depend on the nature of solvent and the light wavelength.
- ✓ The UV radiation effect is stronger as compared with that of visible light.
- ✓ The effect of light wavelength was associated with the strengthening of van der Waals forces and light-generated changes in the Coulomb interaction of surface charges.

❖ ***Light-stimulated*** aggregation of silver particles was studied.

- ✓ The aggregation mechanism was attributed to the appearance of light-generated particles with opposite charges.
- ✓ The appearance of such particles was caused by the exchange of electric charges formed as a result of photoemission.
- ✓ Such an exchange, being associated with the dependence of Fermi energy on the particle size, operates through a dispersed medium and results in leveling of potentials of different-size particles.
- ✓ The exchange gives rise to long-range electric forces, which favor the approach of particles to one another up to the distances at which van der Waals forces responsible for aggregation appear.
- ✓ Due to its availability and reproducibility, the radiation-chemical reduction for synthesizing nanoparticles progressively gains wide acceptance.
- ✓ In the liquid phase, the stages associated with spatial distribution of primary intermediate products play a key role in the production of metal nanoparticles.
- ✓ In contrast to photolysis, the distribution of radiolysis-generated intermediate particles is more uniform, which allows particles with narrower size distributions to be obtained.

The method of **pulsed radiolysis** made it possible to *synthesize active particles of metals in unusual oxidation degrees.*

➤ The reaction with a hydrated electron, which, that has a high reduction potential, proceeds as follows:



✓ The presence of a single electron in the outer orbital of an atom or a metal ion determines their high chemical reactivity.

✓ Lifetimes of such species in water run to several micro- or milliseconds.

✓ The optical properties of such metal particles are defined by their reduction potentials.

✓ For instance, in isoelectric series of metals with similar electronic configurations, the ionization potential increases with an increase in the metal-ion charge.

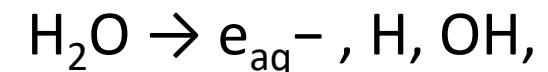
✓ Moreover, the wavelength corresponding to the maximum of light absorption shifts to the short-wavelength region.

✓ Whereas silver and gold atoms that are in the beginning of the period exhibit reductive properties, their isoelectron analogs in the end of the period, viz., trivalent tin and lead, are strong oxidants.

✓ Within the same subgroup, the potential of isocharged ions increase with the increase in the period number.

- ❑ In the course of radiation-chemical reduction, first, atoms and small metal clusters are formed, which is followed by their transformation into nanoparticles.
- ✓ For their stabilization, additives similar to those used in chemical reduction were introduced.
- ✓ The joint use of pulsed γ -radiolysis and spectrophotometry allowed studying the initial stages of the formation of the metal particles that represented the simplest type of charged clusters.
- ✓ Further interaction of clusters, the mechanism of which is still unclear, produced metal nanoparticles.
- ✓ Steady-state and pulsed radiolysis techniques allowed quite a number of nanoparticles of various metals to be obtained.

❖ For cobalt nanoparticles, the mechanism of formation, electron spectra, and reactions in aqueous media were studied. The **radiation-chemical reduction** of cobalt ions in aqueous solutions of $\text{Co}(\text{ClO}_4)_2$ and HCOONa produced spherical cobalt particles with diameters of 2–4 nm. As a stabilizer, sodium polyacrylate with a molecular mass of 2100 u was used. The radiolysis produced solvated electrons e_{aq}^- , hydroxyl radicals, hydrogen atoms, and CO_2^- radical ions:



- ✓ Hydrated electrons and radical ions CO_2^- reduced Co^{2+} ions to give cobalt nanoparticles with an absorption peak in the wavelength region of 200 nm.
- ✓ By using pulsed radiolysis, it was shown that these processes follow the autocatalytic mechanism.

- Radiation chemical reduction of Ni^{2+} ions in aqueous $\text{Ni}(\text{ClO}_4)_2$ solutions containing isopropanol, which was carried out in the presence of polyethylene, polyacrylate, and polyvinyl sulfate, produced metal sols formed by spherical particles with diameters of 2–4 nm.
- ✓ Nickel nanoparticles, which were easily oxidizable by O_2 and H_2O_2 , formed sufficiently stable nickel–silver nanosystems with silver ions.
- Spherical copper particles measuring 20–100 nm were obtained by γ -radiolysis of aqueous $\text{KCu}(\text{CN})_2$ solutions in the presence of either methanol or 2-propanol as the scavengers of hydroxyl radicals.
- The formation of silver particles during γ -radiolysis of silver nitrate solutions in water, ethanol, and 0.01 M $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$ was studied. The fractal dimensions of particle aggregates in these solutions were 1.81, 1.73, and 1.70, respectively.

TABLE 2.1 Core (gold) Diameter and Shell (Palladium) Thickness in Bimetallic Au–Pd Particles, nm¹¹²

| Au/Pd ratio | Experiment | | Calculations | |
|-------------|---------------|-----------------|---------------|-----------------|
| | Core diameter | Shell thickness | Core diameter | Shell thickness |
| 1:1 | 6.0 | 1.0 | 6.4 | 0.8 |
| 1:4 | 5.0 | 1.5 | 4.8 | 1.6 |

- ✓ As seen from the table, the sonochemical synthesis of bimetallic particles allows one to exercise control over sizes of cores and shells by changing the concentrations of Au^{3+} and Pd^{2+} .
- ✓ Bimetallic Au–Pd particles exhibited strong catalytic activity toward hydrogenation of pent-4-enic acid.

- ❑ The methods for synthesizing bimetallic and trimetallic metal nanoparticles with the core-shell structure, which employ radiolysis, were developed.
- ✓ Nanoparticles that consist of two or more different metals are of special interest in view of developing materials with new properties, because on the nano-level, one can obtain such intermetallic compounds and alloys that can never be formed as compact metals.
- ✓ Radiation reduction of salt solutions produced nanoparticles, which comprised two or three metals.
- ✓ Au–Hg particles were synthesized in two steps.
- ✓ First, gold particles measuring 46 nm were synthesized by radiation-chemical reduction. Then, $\text{Hg}(\text{ClO}_4)_2$ and isopropanol were added to the gold sol, which resulted in deposition of mercury ions on gold particles, after which mercury ions were reduced by free radicals formed during radiolysis.
- ✓ Palladium particles with 4 nm diameters and a narrow size distribution were obtained by the reduction of Na_2PdCl_4 salt in the presence of sodium citrate as a stabilizer.
- ✓ The addition of $\text{K}_2\text{Au}(\text{CN})_2$ to a sol of palladium particles in methanol and their γ -irradiation resulted in the reduction of gold ions.
- ✓ In the process, no separate Au gold particles were formed, and all gold was deposited on palladium particles to form an external layer.

- ✓ Moreover, a silver layer could also be deposited onto Pd–Au particles.
 - ✓ Synthesized particles consisted of palladium cores and two shells, namely gold and silver.
 - ✓ Such multiplayer clusters are of interest for studying femtosecond electronic processes.
- To obtain bimetallic gold–palladium nanoparticles, a **sonochemical method** was applied.
- ✓ The particles were synthesized from aqueous solutions of $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ and $\text{PdCl}_2 \cdot 2\text{NaCl} \cdot 3\text{H}_2\text{O}$ in the presence of sodium dodecylsulfate, which served as both stabilizer and reducer.
 - ✓ The synthesized bimetallic particles synthesized represented cores of gold atoms surrounded by shells of palladium atoms.
 - ✓ The dimensions of cores and shells for different gold-to-palladium ratios were measured by means of high-resolution electron microscopy. X-ray spectroscopy allowed determination of gold and palladium contents in the particles.
 - ✓ Given the density, mass, and initial ratios, it is possible to estimate the sizes of cores and shells. Table 2.1 compares experimental and calculated data.

➤ Templates can also be employed during the synthesis of nanoparticles. For instance, Fig. 4.2.24 shows the use of dendrimers as templates for the synthesis of platinum and other metals. The nanoparticles were prepared by sequestering metal ions within supramolecular organic assemblies, namely polyamidoamine (PAMAM) dendrimers, followed by chemical reduction to yield the corresponding metallic nanoparticles. The dendrimers served as both the template and stabilizer. The dimensions of such particles depend on the number of metal ions initially loaded into the dendrimer. By preloading a dendrimer nanotemplate with suitable metal ions and then chemically reducing this composite in-situ, a dendrimer-encapsulated metal nanocluster may be synthesized.

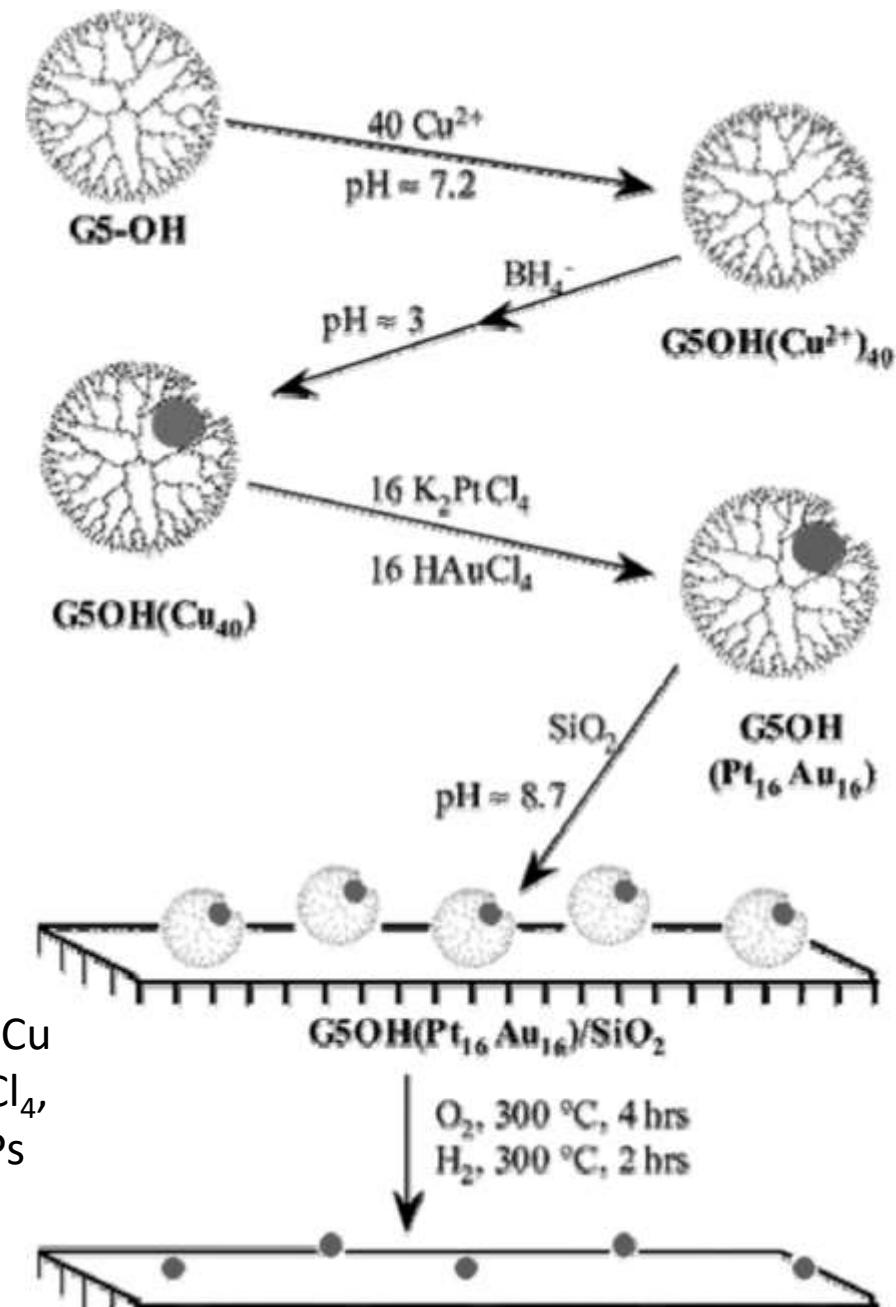


Fig. 4.2 Hydroxy-terminated generation 5 PAMAM dendrimers were used to prepare Cu nanoparticles (NPs). The Cu NPs were subsequently used to reduce K₂PtCl₄ and HAuCl₄, resulting in stabilized bimetallic Pt-Au NPs with a 1:1 stoichiometry. The stabilized NPs were adsorbed onto a silica substrate and thermally activated to remove the dendrimers. *Reprinted with permission from American Chemical Society publications.*

SYNTHESIS OF INORGANIC NAOMATERIALS: Sol-gel Synthesis of Metal Oxide Nanomaterials

- Sol-gel is a colloidal suspension that can be gelled to form a solid.
- Although in existence since the early 19th century, the sol-gel process gained popularity in the 1950s due to the work of Della and Rustrum Roy, who used the technique to prepare multi-component glasses. Since then, the process has been employed to fabricate films for a vast number of industries, with applications in optics, electronics and of course sensors.
- The sol-gel processing method has been in use for many years for producing **metal oxide** and **ceramic powders** with high purity and high homogeneity. Ebelman produced the first *silica gel* in 1846, and Cossa synthesized alumina gel in 1870. Since then, aerogels of zirconia, silazane, borate and other ceramics have been synthesized using the sol-gel technique.
- Using the sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms: ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, micro/nano-porous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials.
- The sol-gel route offers a degree of control of composition and structure at the molecular level.

- The ***process involves*** the generation of a colloidal suspension ('sol'), which is subsequently converted to viscous gel and solid material.
- In general, the sol-gel process involves the transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase.
- The precursors for synthesizing these colloids consist of metal or metalloid elements surrounded by reactive ligands.
- Metal alkoxides (an alkoxide is the conjugate base of an alcohol, and therefore has an organic group bonded to a negatively charged oxygen atom) are popular precursors because they react readily with water.
- The most widely used metal alkoxides are the alkoxy silanes such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS).
- However, other alkoxides such as aluminates, titanates, and borates are also commonly used in the sol-gel process.
- The precursor is subjected to a series of hydrolysis and polymerization reactions which lead to the formation of a new phase of colloidal suspension.

- During hydrolysis, the alkoxy group OR is replaced by hydroxo ligands (OH), i.e.,
- A series of standard sol-gel reactions for organometallic precursors is shown below:

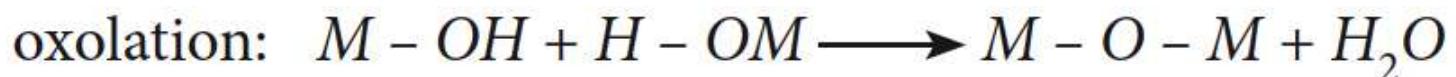


where M is the metal, and R is an alkyl group, $\text{C}_n\text{H}_{2n+1}$. Once the sol is cast into a mold, the colloidal particles condense into a new phase, gel, in which a solid macromolecule is immersed in a liquid phase (solvent).

The factors that influence the hydrolysis reaction are:

- Nature of the alkyl group
- Nature of the solvent
- Concentration of each species in the solvent
- Temperature
- Water to alkoxide molar ratio
- Presence of acid or base catalysts

- Subsequent condensation eliminates either water or alcohol to produce metal oxide or hydroxide linkages. In this process, two mononuclear complexes of M, each comprising only one metal M, can react with one another to form a polynuclear complex consisting of two metal atoms.
- Condensation occurs only when at least one hydroxo ligand is bonded to the cation M and is designated as M-OH for simplicity. *Olation* and *oxolation* reactions lead to condensation. *Olation* is a reaction by which the hydroxo or ‘ol’ bridge (M–OH–M) is formed between two cations, while *oxolation* involves the formation of oxo bridges (M–O–M) between two metal cations:

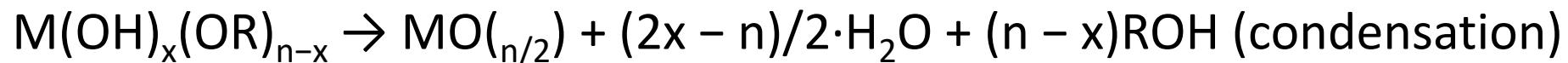
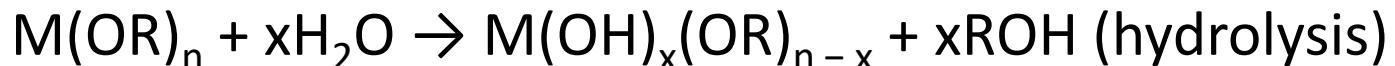


- The ‘ol’ or ‘oxo’ bridges between two metal atoms lead to the formation of condensed oxide or hydroxide species.

- Under acid conditions, three-dimensional solid phase networks consisting of extended linear M–O–M chain polymers are developed.
- Inorganic polymerization is believed to occur in three stages during acid-catalysed condensation:
 1. Polymerization of monomer units to form particles
 2. Growth of particles
 3. Linking of particles into chains, then solid networks that extend throughout the liquid medium, thickening it to a gel.
- In acid solution, the sol-to-gel transition allows the solid phase to be shaped into films, fibres and monoliths.
- ✓ For preparing coating films and fibres, the sol must exhibit spinnability.
- ✓ It appears that only solutions containing long-chained polymers are spinnable.
- ✓ Films are generally coated on the surface of the substrate via spin coating and dipping processes.
- ✓ Gel fibres are made by fibre drawing from the viscous alkoxide solution at or near room temperature.

- In contrast, on basic hydrolysis of metal alkoxides, a colloidal sol is generated. The gel is colloidal when the solid network is made of round sol particles.
- Removal of the solvents and appropriate drying are important steps to achieve gel densification.
- ✓ When a ***solvent is evaporated from the gel under atmospheric conditions***, capillary pressure due to the interfacial tension of the solvent places a high stress on the gel network. *This leads to considerable shrinkage and fracture of the gel during drying.* The resultant ***hard, glassy and porous product*** is called a ***xerogel***.
- ✓ When *the liquid within the gel is removed above its critical temperature and pressure (hypercritical) in an autoclave*, the capillary pressure can be eliminated. The product thus obtained is referred to as an ***aerogel***. An aerogel is generally amorphous and exhibits several unique properties such as high surface areas and porosities, and low densities and conductivities.
- ❖ In silica aerogels, particles of 1–100 nm are arranged in a highly cross-linked silica solid network.

- Different versions of the sol-gel synthesis were classified with chemical methods of fabrication of oxide and sulfide nanoparticles.
- The scheme of synthesis of nanooxides of metals is as follows:



- where M is a metal and R an alkyl group.
- The process was catalyzed by the changes in the pH initial solution.
- In acidic media, linear chains were formed, whereas in alkaline solutions, branched chains appeared.
- By substituting the corresponding sulfides $M(SR)_n$ for alkoxides of metals and treating them with hydrosulfide, nanoparticles of metal sulfides could be obtained.

- It is possible to produce thin films on a substrate with methods such as spin coating, dip-coating, and drop casting.
- With further drying and heat-treatment, the gel is converted into dense ceramic or glass.
- If the liquid in a wet *gel* is removed under a supercritical condition, a highly porous and extremely low-density material called an *aerogel* is obtained.
- The viscosity of a sol can be adjusted to a desired viscosity range to obtain ceramic fibers.
- Ultra-fine and uniform ceramic powders can also be formed by *precipitation, spray pyrolysis, and emulsion techniques*.
- After the formation of the sol-gel film, it is generally *annealed*. In order to prepare high quality thin films, it is of paramount importance to control the annealing parameters. Annealing is carried out in order to convert the organometallic film to a metal oxide in addition to enabling and controlling crystallization and grain growth. It also serves to remove organic compounds, which usually evaporate off the film at elevated temperatures.
- Furthermore, it promotes adhesion to the substrate.
- Unlike many other fabrication methods, which require starting materials to have the same composition as the final product, *sol-gel offers an economically feasible avenue to explore different ratios and combinations of the compounds*.

- Alkoxides of transition metals (e.g., titanium, zirconium) are highly reactive towards water. This implies that the ***rate of hydrolysis and condensation is very high, and thus it is difficult to form a stable sol of titania*** (TiO_2).
- ✓ Titania exists in three main crystallographic structures, namely, rutile, anatase and brookite. Among these, rutile is the only stable phase.
- ✓ Many acid catalysts such as nitric acid, hydrochloric acid and acetic acid have been added to lower the reaction rates. Apart from these acids, acetylacetone ($\text{C}_5\text{H}_8\text{O}_2$) can also moderate the reaction rate. It is added as a chelating agent to decrease the reactivity of titanium alkoxides and to form stable colloidal sols of ~ 5 nm.
- ✓ Under more controllable hydrolysis and condensation reactions, smaller particle sizes with more unique properties can be achieved. For example, TiO_2 aerogel nanocrystals can be obtained by supercritical evacuation of solvent from gels prepared through HCl-controlled hydrolysis condensation reactions of titanium isopropoxide in isopropanol. HCl catalyst favours the synthesis of titania powders with smaller grain size compared to acetylacetone catalyst under the same heat treatment conditions. Further, anatase crystallites are more stable if HCl is used as catalyst, while the pure rutile phase can be more easily obtained if acetylacetone is used as a catalyst.

Figures 3.7a and 3.7b show the TEM micrographs of nanocrystalline titania prepared by the sol-gel route with a precursor to water ratio of 1 and 4, respectively. Figures 3.7c and 3.7d indicate that the nanocrystallite titania does not significantly grow on calcination up to about 500°C.

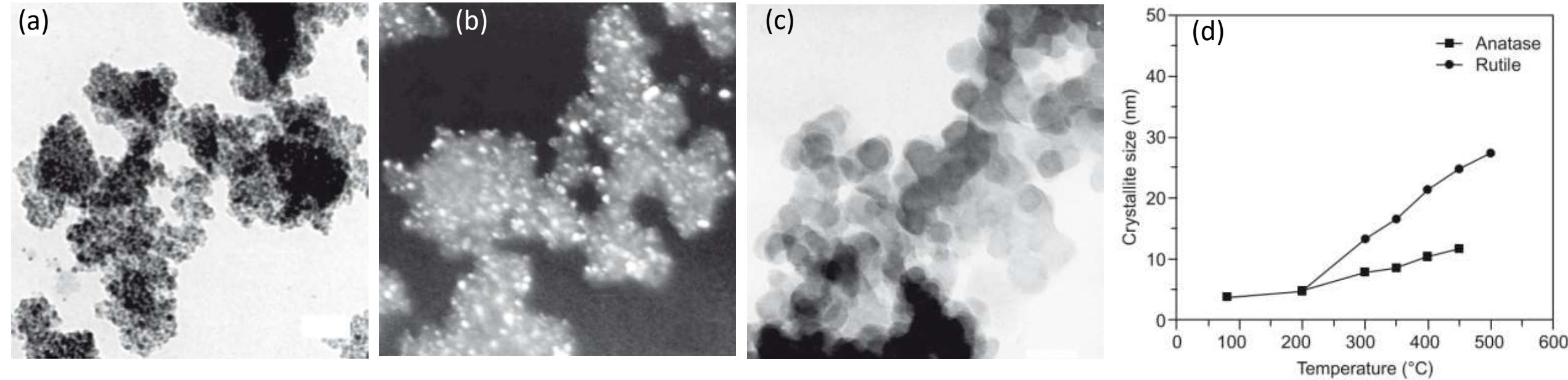


Fig. 3.7 TEM micrographs of nano titania (a) as-prepared (bright field image) with precursor to water ratio of 1, (b) as-prepared (dark field image) with precursor to water ratio of 4, (c) after calcination at 400°C for 2 h (bright field image) with precursor to water ratio of 4 and (d) Variation of the crystallite size of the anatase and rutile phases with calcination temperature with precursor to water ratio of 4. (Source: BS Murty, IIT Madras).

- According to the literature, various metal oxide nanocrystalline powders, e.g., SnO_2 , $\text{Ba}_2\text{Ti}_2\text{O}_5$, PbTiO_3 , $(\text{Pb}, \text{La})(\text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$, nanocomposite powders containing elemental particulates, e.g., nano- Ni/SiO_2 , $\text{Fe-Al}_2\text{O}_3$ and oxide nanocomposites, e.g., $\text{Fe}_2\text{O}_3-\text{SiO}_2$, NiO-SiO_2 , and $3\text{Al}_2\text{O}_3-2\text{SiO}_2$, have been synthesized using the sol-gel process.
- The sol-gel method can be employed to form nanostructured ***thin films*** for sensing applications and the grain size of these thin films can be engineered for the right application.
- ✓ As can be seen in Fig. 4.41, nanostructured In_2O_3 was prepared using ethanolic solutions of an indium isopropoxide ($\text{In}(\text{OC}_3\text{H}_7)_3$) precursor.
- ✓ The solutions were spin coated on sapphire substrates and annealed at 500°C for 1 h in air. This resulted in a well-developed polycrystalline and highly porous microstructure composed of approximately spherical grains with an average size of approximately 20 nm.

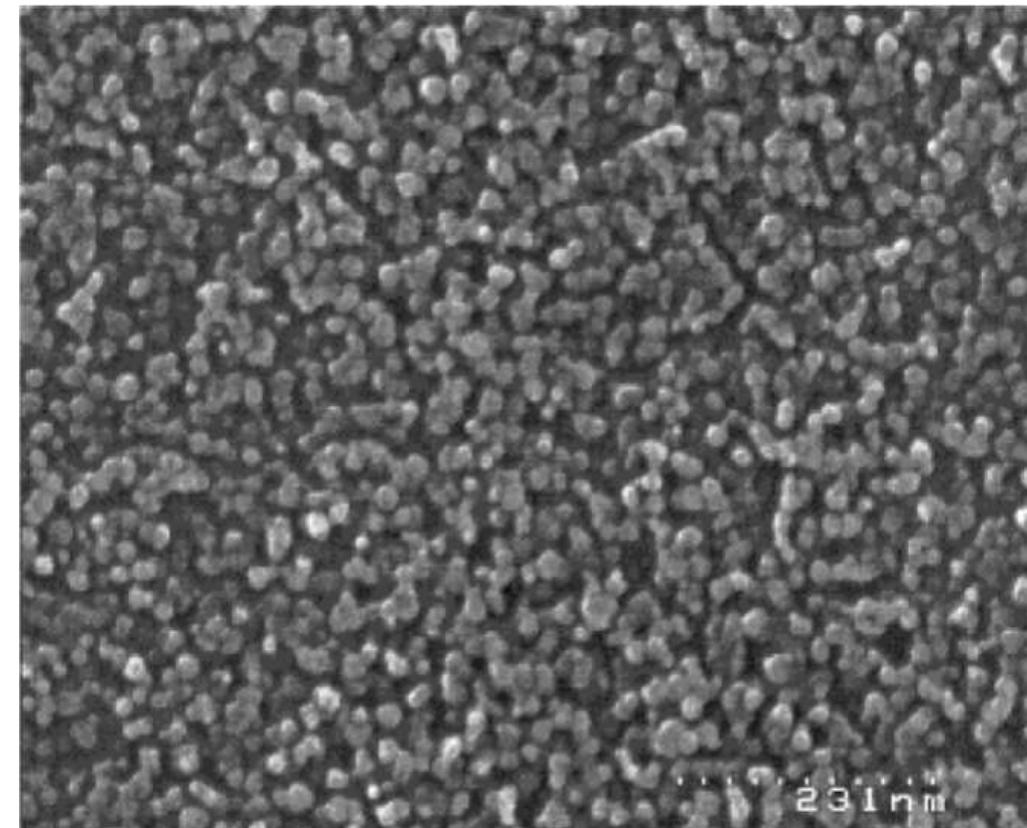


Fig. 4.41 SEM photomicrograph of an In_2O_3 film fabricated using the sol-gel method. Reprinted with the permission from the Elsevier publications.

- The anti-ferroelectric ceramics are promising candidates for new ceramic actuators because of their unique characteristics of big and isotropic strain changes under applied electric field, as well as shape memory effects.
- Nano-sized ceramics prepared by the sol–gel method are usually more homogeneous and reactive than those fabricated by conventional solid-state reactions since the mixing of the reagents occurs on a finer scale.
- The lower processing temperature is also helpful in minimising the PbO loss. One of the problems in lead-based complex perovskites is the evaporation of PbO at high temperatures, leading to undesirable phases. Sol–gel derived powders of single perovskite phase can be used to produce bulk ceramic samples after sintering at various temperatures.
- The sol–gel process has been useful for synthesizing only metal oxides as a result of the presence of metal–oxygen bonds in the alkoxide precursor, and the resulting gels are essentially metal hydroxides or oxides.
- This process has distinct advantages over other techniques for preparing metal oxide nanoparticles. These include the formation of high purity powders as a result of homogeneous mixing of the raw materials on the molecular level, and the large-scale industrial production of nanopowders.
- The disadvantage of the process is the high cost of alkoxide precursors.

- ❑ In some cases, the sol–gel route can also be used to prepare non-oxide ceramic powders such as β -SiC and ferroelectrics like $(\text{Pb}, \text{La})(\text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$ (PLZST).
- ✓ In the former case, heat treatment of the gel product at 1500°C in argon atmosphere resulted in 0.6 mm spherical agglomerates consisting primarily of particles of 40 nm in diameter.
- ✓ Recently, β -SiC nanopowders of 13–30 nm were synthesized by the chemical vapour reaction of the SiH_4 – C_2H_4 – H_2 system in the temperature range of 1423 K and 1673 K; the products were free from agglomeration.

- At present, new methods for synthesizing nanocrystalline oxide materials, which apply different compounds in ***subcritical and supercritical states***, are actively developed.
- Most widely used compounds are carbon dioxide and, recently, water.
- Nanoparticles of metal oxides were also obtained by changing their radius from the micron level to the nanolevel by dissolving them in electrolytes.
- A method of rapid expansion of supercritical solutions into a liquid solvent was extensively used for preparation of nanosize particles of metals, semiconductors, and their conjugates with biomolecules.
- This method was used for synthesizing particles of average diameter less than ~50 nm from CO₂-soluble polymers.
- Rapid expansion of supercritical solutions in liquids was used for production of the finely divided nonsteroidal antiphlogistic drugs Ibuprofen and Naproxen.
- The solution was rapidly expanded in water, poly(N-vinyl-2-pyrrolidone) with a molecular weight ~40,000 u, or sodium dodecylsulfate.
- In water, homogeneous particles of Ibuprofen (α -methyl-4-(2-methylpropyl)benzoacetic acid) formed a suspension in 15 min.
- In polyvinylpyrrolidone, Ibuprofen particles of an average diameter of 40 nm were stable for several days; in sodium dodecylsulfate, the particle size was 25 nm.

Hydrothermal Synthesis

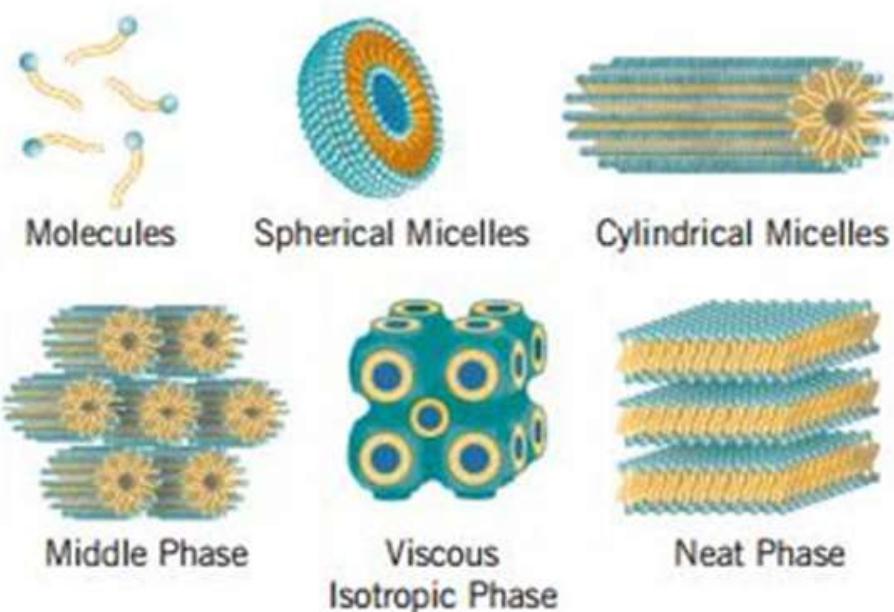
- Water at elevated temperatures plays an essential role in the precursor material transformation because the vapor pressure is much higher and the structure of water at elevated temperatures is different from that at room temperature. The properties of the reactants, including their solubility and reactivity, also change at high temperatures.
- The changes mentioned above provide more parameters to produce different high-quality nanoparticles and nanotubes, which are not possible at low temperatures.
- During the synthesis of nanocrystals, parameters such as water pressure, temperature, reaction time, and the respective precursor- product system can be tuned to maintain a high simultaneous nucleation rate and good size distribution.
- Different types of oxides and sulfides nanoparticles such as TiO_2 , LaCrO_3 , ZrO_2 , BaTiO_3 , SrTiO_3 , $\text{Y}_2\text{Si}_2\text{O}_7$, Sb_2S_3 , CrN , $\alpha\text{-SnS}_2$, PbS , Ni_2P , and SnS_2 nanotubes, Bi_2S_3 nanorods, and SiC nanowires have been successfully synthesized in this way.
- The solvent is not limited to water but also includes other polar or nonpolar solvents, such as benzene, and the process is more appropriately called **solvothermal synthesis** in different solvents.

Self-assembly

- ❖ There is a fundamental limitation with all the top-down assembling techniques that we have discussed. These techniques requires too much work to precise handling and keeping track of everything every time. We always take control where should things be and where they shouldn't.
- Self-assembly relies on the technique that you just mix the chemicals together and it's to the molecules themselves to sort it out to make a nanostructure. But a question arises, that is what would drive them to make these structures?
- The main driving force behind this technique is common to everything in this universe. No matter how big or small, ***everything attempts to lower the energy level that is associate with them***. When molecules are mixed together, they sort in such a way that their energy is at a minimum level. *In fact, self-assembly is the pathway nature has taken to build amazing nanostructures.* Mastering this technique would allow us to build everything from basic molecules.
- ✓ It's hypothesized that one day we will grow our own food, cloths, computers and just about everything we need in a molecular factory that we may have in our houses. Although seem strange and far stretched, this is theoretically possible.

Self-assembly

- The driving forces of self-assembly are forces like hydrogen and van der Waal forces which are much weaker than the covalent bonds that hold molecules together.
 - These weaker coulombic forces are found in many places from water to DNA molecules.
-
- ❖ There are other interactions such as [hydrophobic interactions](#) that allow hydrophobic materials to bind together in aqueous medium. The particles may not have a total charge, yet they bind together to reduce the surface area that expose to the aqueous surrounding.
 - ❖ Molecules also can be self-assembled into a reconstructed [nanostructure driven by favorable attraction between particular atoms and molecules](#) sometimes even making strong covalent bonds. The perfect example is assembly of fatty thiol molecules on a silver or gold surface.
 - ❖ Self assembly can also be [driven by templates](#). Molecular level templates such as spheres, tubes and bi-planes can be made with self-assembly of surfactant molecules that can be solidified with different means. These template shapes can be changed by varying concentration, pH, temperature, etc.



Different phases of self-assembled surfactents

- ✓ hydrophobic interactions that allow hydrophobic materials to bind together in aqueous medium

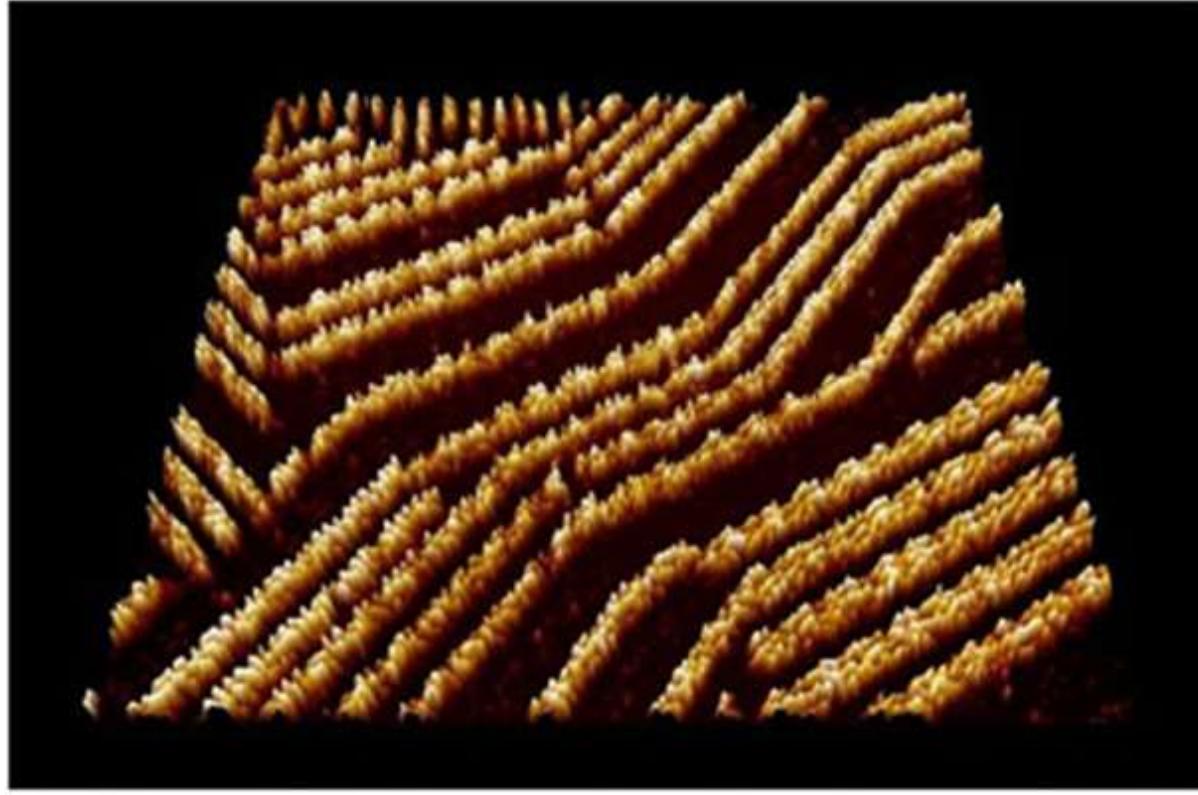
Self-assembly

- Self-assembly is a nanofabrication technique that involves aggregation of colloidal nanoparticles into the final desired structure.
- This aggregation can be either spontaneous (entropic) and due to the thermodynamic minima (energy minimization) energy minimization constraints, or chemical and due to the complementary binding of organic molecules and supramolecules (molecular self-assembly).
- Molecular self-assembly is one of the most important techniques used in biology for the development of complex functional structures.
- Since these techniques require that the target structures be thermodynamically stable, they tend to produce structures that are relatively defect-free and self-healing.
- Self-assembly is by no means limited to molecules or the nano-domain and can be carried out on just about any scale, making it a powerful bottom-up assembly and manufacturing method (multi-scale ordering).
- Another attractive feature of this technique relates to the possibility of combining the self-assembly properties of organic molecules with the electronic, magnetic and photonic properties of inorganic components.

- The central theme behind the self-assembly process is spontaneous (physical) or chemical aggregation of colloidal nano-particles.
- Spontaneous self-assembly exploits the tendency of mono-dispersed nano- or submicro-colloidal spheres to organise into a face-centred cubic (FCC) lattice.
- The force driving this process is the desire of the system to achieve a thermodynamically stable state (minimum free energy).
- In addition to spontaneous thermal self-assembly, gravitational, convective and electro-hydrodynamic forces can also be used to induce aggregation into complex 3D structures.
- Chemical self-assembly requires the attachment of a single molecular organic layer (self-assembled monolayer, or SAM) to the colloidal particles (organic or inorganic) and subsequent self-assembly of these components into a complex structure using molecular recognition and binding.

Physical self-assembly

- This method is driven by entropy that relies on the spontaneous organisation of colloidal particles into a relatively stable structure through non-covalent interactions.
- ✓ For example, Fig. 3.8 shows quinacridone molecules adsorbed on a graphite surface. The organic semiconductor molecules self-assemble into nanochains via hydrogen bonds. Natural assembly of on-chip silicon photonic band gap crystals, which are capable of reflecting the light arriving from any direction in a certain wavelength range, are also examples of this process. In this method, a thin layer of silica colloidal spheres is assembled on a silicon substrate. This is achieved by placing a silicon wafer vertically in a vial containing an ethanolic suspension of silica spheres. A temperature gradient across the vial aids the flow of silica spheres. Once such a template is prepared, LPCVD can be used to fill the interstitial spaces with Si, so that the high refractive index of silicon provides the necessary band gap.



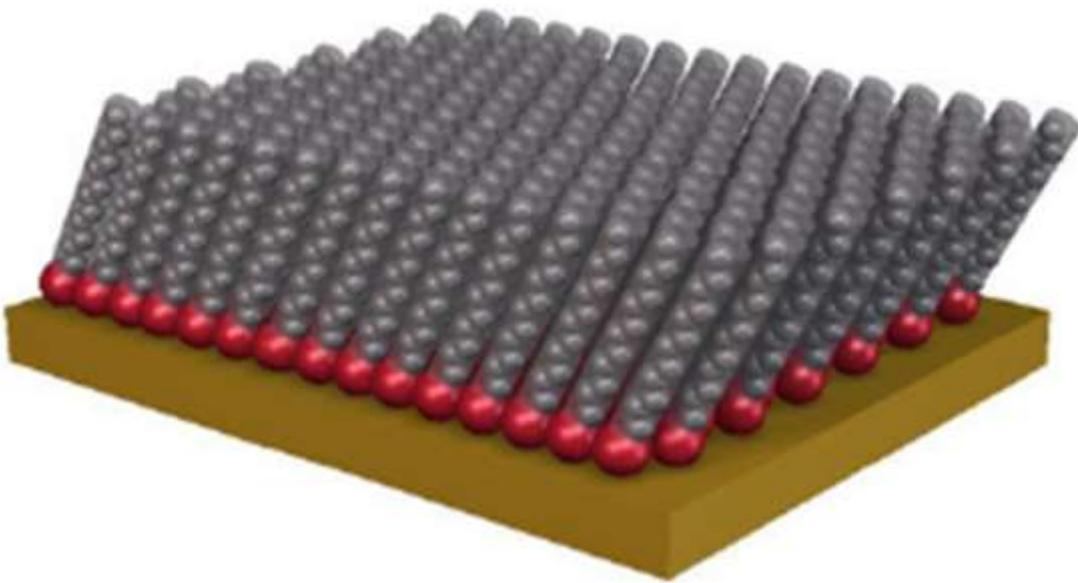
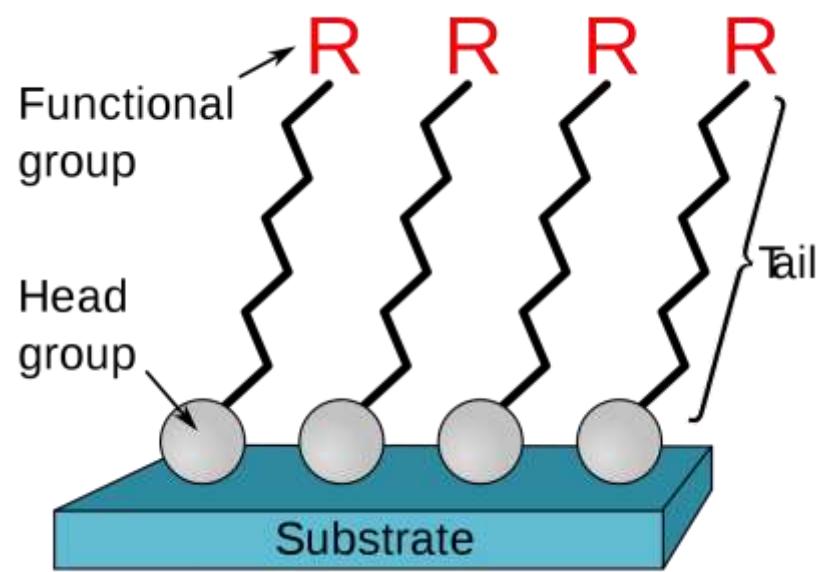
Self assembly of a organic semiconductor molecules
on Graphite

Fig. 3.8 Scanning tunnelling microscope image of quinacridone (organic semiconductor) molecules adsorbed on a graphite surface.
The organic semiconductor molecules self-assembled into nanochains via hydrogen bonds.
(Source: http://commons.wikimedia.org/wiki/File:Selfassembly_Organic_Semiconductor_Trixler_LMU.jpg).).

- ❑ One can also deposit colloidal particles in a patterned substrate (template-assisted self-assembly, TASAs).
- ✓ This method is based on the principle that when an aqueous dispersion of colloidal particles is allowed to de-wet from a solid surface that is already patterned, the colloidal particles are trapped by the recessed regions and assemble into aggregates of shapes and sizes determined by the geometric confinement provided by the template.
- ✓ The patterned arrays of templates can be fabricated using conventional contact mode photolithography, which gives control over the shape and dimensions of the templates, thereby allowing the assembly of complex structures from colloidal particles. This method can be used to fabricate a variety of polygonal and polyhedral aggregates that are difficult to generate.

Chemical self-assembly

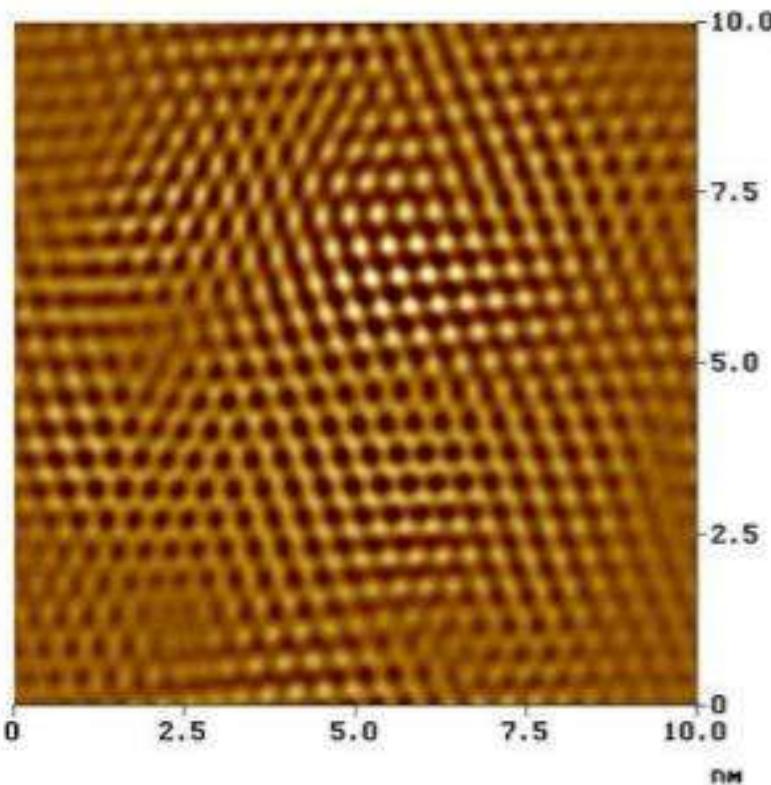
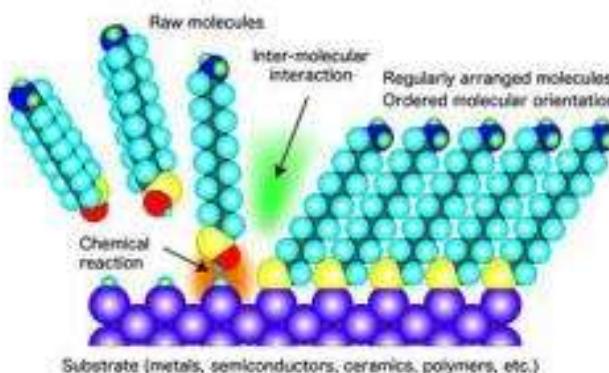
- Organic and supramolecular molecules play a critical role in colloidal particle self-assembly.
- In self-assembled monolayers (SAM), robust organic molecules are chemically adsorbed onto solid substrates.
- Most often, they have a hydrophilic (polar) head that can be bonded to various solid surfaces and a long, hydrophobic (non-polar) tail that extends outward.
- SAMs are formed by the immersion of a substrate in a dilute solution of the molecule in an organic solvent.
- The resulting film is a dense organization of molecules arranged to expose the end group.
- The durability of a SAM is highly dependent on the effectiveness of the anchoring to the surface of the substrate.
- SAMs have been widely studied, because the end group can be functionalised to form precisely arranged molecular arrays for various applications ranging from simple, ultra-thin insulators and lubricants to complex biological sensors.
- Chemical self-assembly uses organic or supramolecular SAMs as the binding and recognition sites for fabricating complex 3D structures from colloidal nanoparticles.



Self Assembled Monolayers (SAMs)



Alkane thiol on gold surface –
above schematic diagram –
AFM image of oriented thiols



Most commonly used organic monolayers include:

- Organosilicon compounds on glass and native surface oxide layer of silicon
- Alkanethiols, dialkyl disulfides and dialkyl sulfides on gold
- Fatty acids on alumina and other metal oxides
- DNA

Octadecyltrichlorosilane (OTS) is the most common organosilane used in the formation of SAMs, mainly because it is simple, readily available and forms good, dense layers.

- ✓ Alkyltrichlorosilane monolayers can be prepared on clean silicon wafers with a surface of SiO_2 (with almost $5 \times 10^{14} \text{ SiOH groups/cm}^2$).
- ✓ Since the silicon chloride bond is susceptible to hydrolysis, a limited amount of water has to be present in the system in order to obtain good quality monolayers.
- ✓ Monolayers made of methyl- and vinyl-terminated alkylsilanes are autophobic to the hydrocarbon solution and hence emerge uniformly dry from the solution, whereas monolayers made of ester-terminated alkylsilanes emerge wet from the solution used in their formation.
- ✓ The disadvantage of this method is that if the alkyltrichlorosilane in the solvent adhering to the substrate is exposed to water, a cloudy film is deposited on the surface due to the formation of a gel of polymeric siloxane.

- ❑ Another important organic SAM system is the alkanethiols $X(CH_2)_nSH$, where X is the end group) on gold.
- ✓ A major advantage of using gold as the substrate material is that it does not have a stable oxide and can thus be handled in ambient conditions.
- ✓ When a fresh, clean, hydrophilic gold substrate is immersed (several minutes to several hours) in a dilute solution (10^{-3} M) of the organic sulphur compound (alkanethiols) in an inorganic solvent, a close-packed, oriented monolayer can be obtained.
- ✓ Sulphur is used as the head group, because of its strong interaction with gold substrate (44 kcal/mol), resulting in the formation of a close-packed, ordered monolayer.
- ✓ The end group of alkanethiol can be modified to render hydrophobic or hydrophilic properties to the adsorbed layer.

- ❑ Another method for depositing alkanethiol SAM is soft lithography. This technique is based on inking a PDMS stamp with alkanethiol and its subsequent transfer to planar and non-planar substrates. Alkanethiol functionalised surfaces (planar, non-planar, spherical) can also be used to self-assemble a variety of intricate 3D structures.
- ❑ Carboxylic acid derivatives self-assemble on surfaces (e.g., glass, Al_2O_3 and Ag_2O) through an acid–base reaction, giving rise to monolayers of fatty acids.
 - ✓ The time required for the formation of a complete monolayer increases with decreased concentration.
 - ✓ A higher concentration of carboxylic acid is required to form a monolayer on gold compared to Al_2O_3 .
 - ✓ This is due to differences in the affinity of the COOH groups (more affinity to Al_2O_3 and glass than gold) and also the surface concentration of the salt forming oxides in the two substrates.
 - ✓ In the case of amorphous metal oxide surfaces, the chemisorption of alcanoic acids is not unique.
 - ✓ For example, on Ag_2O the oxygen atoms bind to the substrate in a nearly symmetrical manner, resulting in ordered monolayers with a chain tilt angle from the surface normally of 15 to 25°. But on CuO and Al_2O_3 , the oxygen atoms bind themselves symmetrically and the chain tilt angle is close to 0°. The structure of the monolayers is thus a balance of the various interactions taking place in the polymer chains.

- Deoxyribonucleic acid (DNA), the framework on which all life is built, can be used to self-assemble nanomaterials into useful macroscopic aggregates that display a number of desired physical properties.
 - ✓ DNA has a double-helix structure with two strands coiled around each other.
 - ✓ When the two strands are uncoiled, singular strands of nucleotides are left.
 - ✓ These nucleotides consist of a sugar (pentose ring), a phosphate (PO_4) and a nitrogenous base.
 - ✓ The order and architecture of these components are essential for the proper structure of a nucleotide.
 - ✓ There are typically four nucleotides found in DNA: adenine (A), guanine (G), cytosine (C) and thymine (T).
 - ✓ A key property of the DNA structure is that the described nucleotides bind specifically to another nucleotide when arranged in the two-strand double helix (A to T and C to G).
 - ✓ This specific bonding capability can be used to assemble nanophase materials and nanostructures.
 - ✓ For example, nucleotide functionalised nano-gold particles have been assembled into complex 3D structures by attaching DNA strands to the gold via an enabler or linker.

- ✓ In a separate work, DNA was used to assemble nanoparticles into macroscopic materials. This method uses alkane dithiol as the linker molecule to connect the DNA template to the nanoparticle. The thiol groups covalently attach themselves to the colloidal particles, leading to aggregate structures.

Three-dimensional DNA origami: DNA Box

Rothemund's origami demonstrated arbitrary flat 2D nanostructures. Andersen et al. extended this technique to construct hollow containers (box) with walls of flat 2D origami. A cube like hollow box with a hinged lid that can be opened and closed by a DNA strand as a key was constructed and imaged (see figure 26).

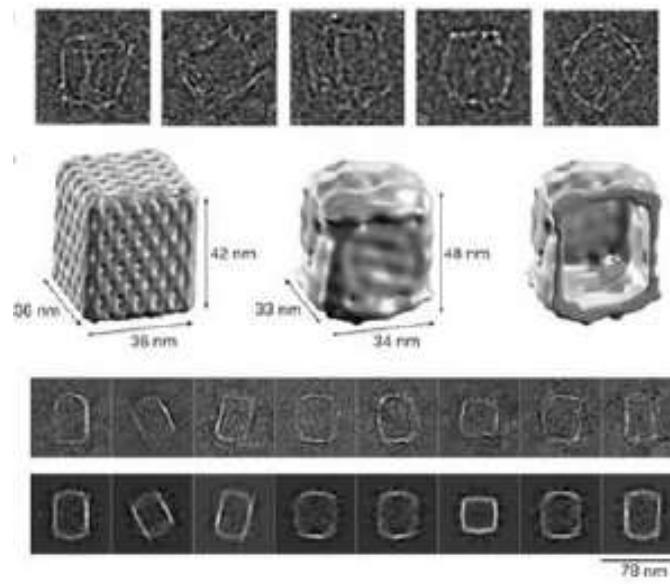
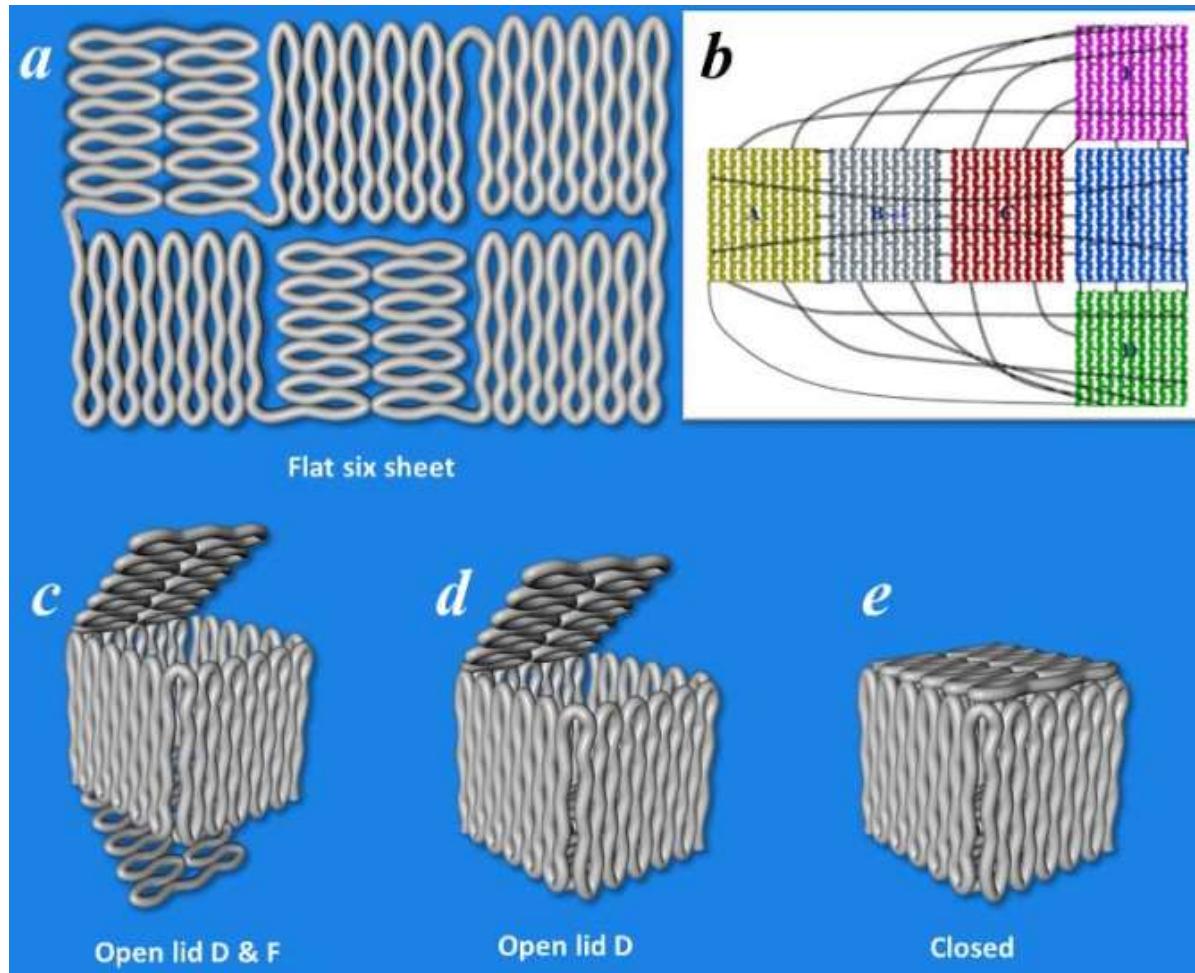
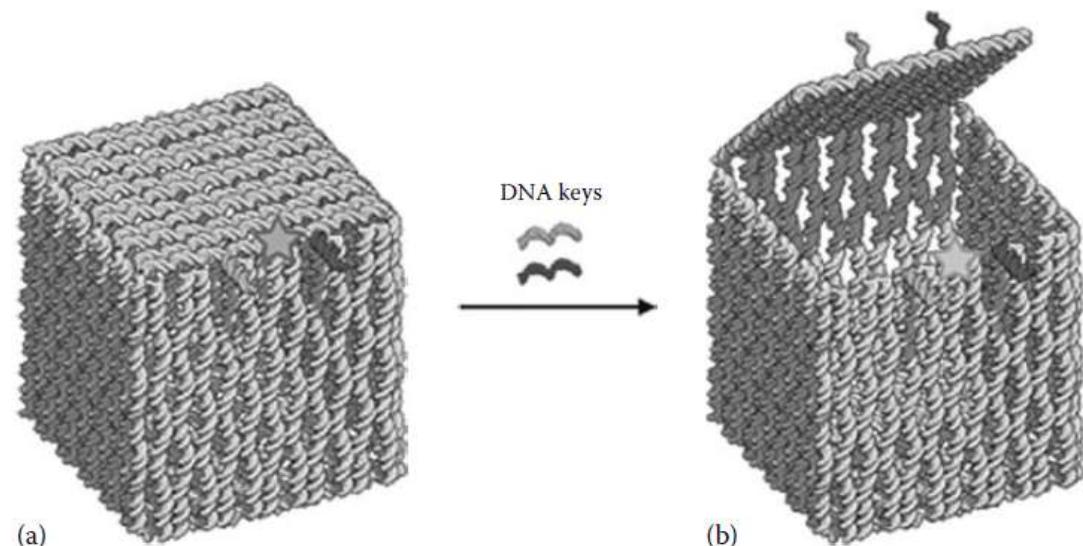


Figure 26: Left: 3D DNA box origami. (a) Six flat square-shaped origami domains which by their connection (black lines in (b)) will form a 3D DNA box origami; (c–e) DNA box origami in different states.

Top Right: Actual Images of DNA Box.

Mechanical motion can be created by release of a latch, as in the lid of the DNA box shown in Figure 1.8. As shown in panel a, the lid is initially held closed by two short duplex DNA “latches.” Each latch includes a toehold segment, so it can be unlocked by a complementary oligonucleotide via strand invasion. Addition of the two complementary oligos unlocks both latches, releasing the lid. Opening of the lid can be monitored either by AFM of individual boxes, or in bulk solution, by fluorescence resonance energy transfer (FRET) between a donor and a acceptor dye incorporated into staple strands on the rim of the box and on the lid of the box. A recent report describes the use of a “clamshell” filled with bioactive proteins, where the “shell” is held closed by DNA aptamers. The aptamers recognize and bind to specific cell types, causing the clamshell to open and releasing proteins that initiate programmed cell death.

Figure 1.8 Examples of reconfiguration of DNA origami structures. (a) Box with lid; the lid can be opened (b) by addition of an oligonucleotide “key.” FRET dyes on the rim of the box and the lid monitor whether the lid is open or closed. (Reprinted by permission from Macmillan Publishers Ltd. *Nature*, Andersen, E.S. et al., Self-assembly of a nanoscale DNA box with a controllable lid, 459, 73–76, Copyright 2009.)



Biosynthesis of Nanomaterials

- Living organisms, especially micro-organisms like Bacteria, Fungi, Algae, Actinomycetes, Yeast, and Virus etc. have a remarkable ability to form exquisite inorganic structures often in nanodimensions.
- This ability of living creatures has lured material scientists towards these biological systems to learn and improve the skills for the precise fabrication of nanomaterials at ambient conditions.
- There exist several examples in biological systems demonstrating not only the efficient synthesis of macroscopic materials like bones and teeth with precise positioning but also in making functional structures in mesoscopic and nanometer dimensions.
- Generally, synthesis of inorganic nanomaterials by microorganisms has been classified in two categories such as – ***biologically controlled*** synthesis and ***biologically induced*** synthesis.
- Biologically controlled synthesis of inorganic materials can often be considered as biominerization as it is known to occur naturally in few specific organisms.
- Biogenic nanomaterials commonly have attributes which distinguish them from their inorganic counterparts.
- The vast array of organisms are now known to synthesize inorganic materials, most of them are calcium carbonates, calcium phosphates, silicates, iron oxides and iron sulfides.

- ✓ During biologically controlled synthesis of inorganic materials, inorganic phases grow within or on organic matrix or vesicles inside the cell, allowing the organism to exert a strict control over the composition, grain size, habit, and intracellular or surface location of the produced minerals.
- ✓ Examples of such synthesis include silica biosynthesis in diatoms, sponges and radiolarians, calcareous structures in coccoliths, gypsum in S-layer bacteria and the nanocrystals of magnetite and greigite in magnetotactic bacteria. (Greigite is an iron sulfide mineral with the chemical formula $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{S}_4$. It is the sulfur equivalent of the iron oxide magnetite (Fe_3O_4). Like the related oxide magnetite, greigite is ferrimagnetic.)
- ☐ In Biologically induced synthesis of inorganic materials, organisms modify its ambient microenvironment and create conditions suitable for extracellular precipitation of minerals.
- ✓ Deliberate synthesis of inorganic nanoparticles is possible because of the specific resistant mechanism exerted by micro-organisms against the high metal ion concentration.
- ✓ At higher concentration of metal ions micro-organisms can cope with the toxic effect of metal ions by one of the defense mechanisms such as effluxing of metal ions by efflux pumps, alteration in the solubility of metal ions, alteration in redox state, extracellular complexation and extracellular precipitation of metal ions, etc.

➤ ***Nanoparticle Synthesis Using Plants***

- ✓ Recently, phytonanotechnology has provided new avenues for the synthesis of nanoparticles and is an ecofriendly, simple, rapid, stable, and cost-effective method.
 - ✓ Phytonanotechnology has advantages, including biocompatibility, scalability, and the medical applicability of synthesizing nanoparticles using the universal solvent, water, as a reducing medium.
 - ✓ Thus, plant-derived nanoparticles produced by readily available plant materials and the nontoxic nature have significant roles in metal salt reduction and, furthermore, act as capping and stabilizing agents for synthesized nanoparticles.
- ❖ Although, bottom-up approach would provide great flexibility and low material wastage, controlling matter in this scale with such a precision is still a challenging task.

Chemical and Physical vapor deposition

❖ Vapor deposition techniques are the most widely used bottom-up nanofabrication approach in nanotechnology research and industry alike.

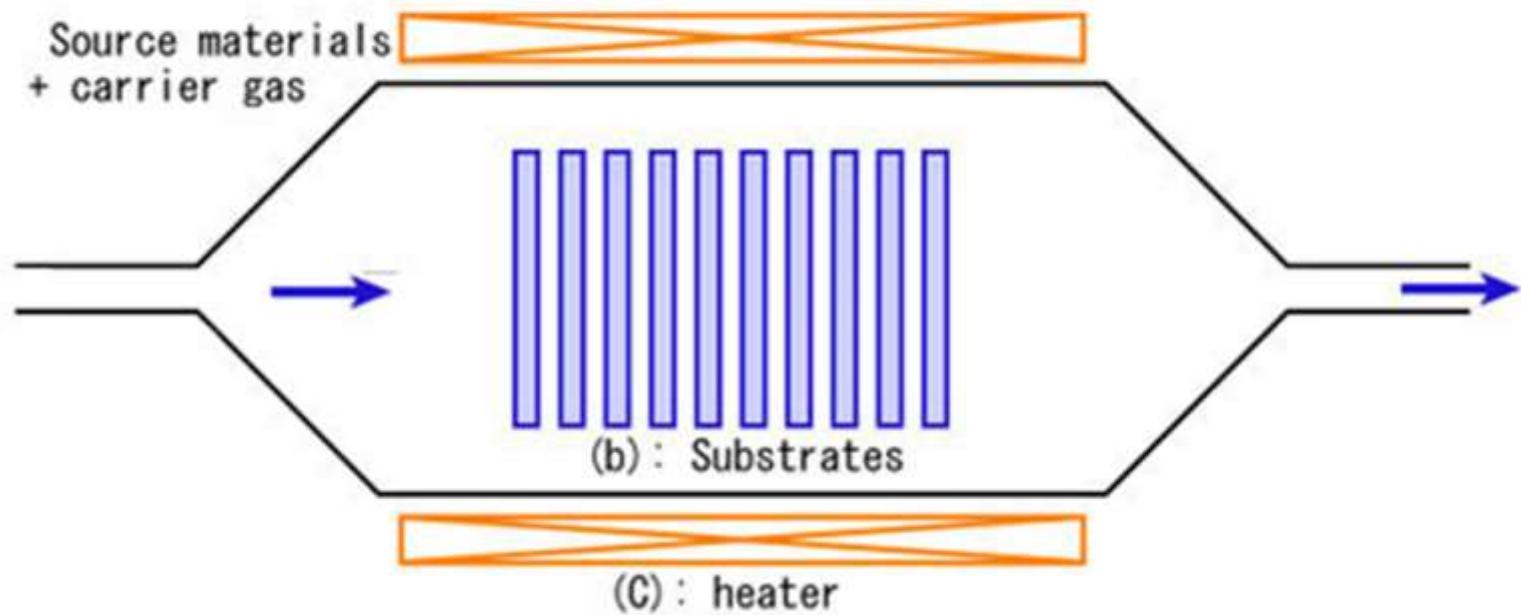
❖ **Physical vapor deposition (PVD)**, **chemical vapor deposition (CVD)**, and **sputtering** are the commonly used methods to form inorganic nanomaterials.

➤ **Chemical vapor deposition (CVD)** is a process where one or more gaseous adsorption species react or decompose on a hot surface to form stable solid products. *The main steps* that occur in the CVD process can be summarized as follows:

- ✓ 1. *Transport of reacting gaseous species to the surface*
- ✓ 2. *Adsorption of the species on the surface*
- ✓ 3. *Heterogeneous surface reaction catalyzed by the surface*
- ✓ 4. *Surface diffusion of the species to growth sites*
- ✓ 5. *Nucleation and growth of the particle and/or film*
- ✓ 6. *Desorption of gaseous reaction products and transportation of reaction products away from the surface*

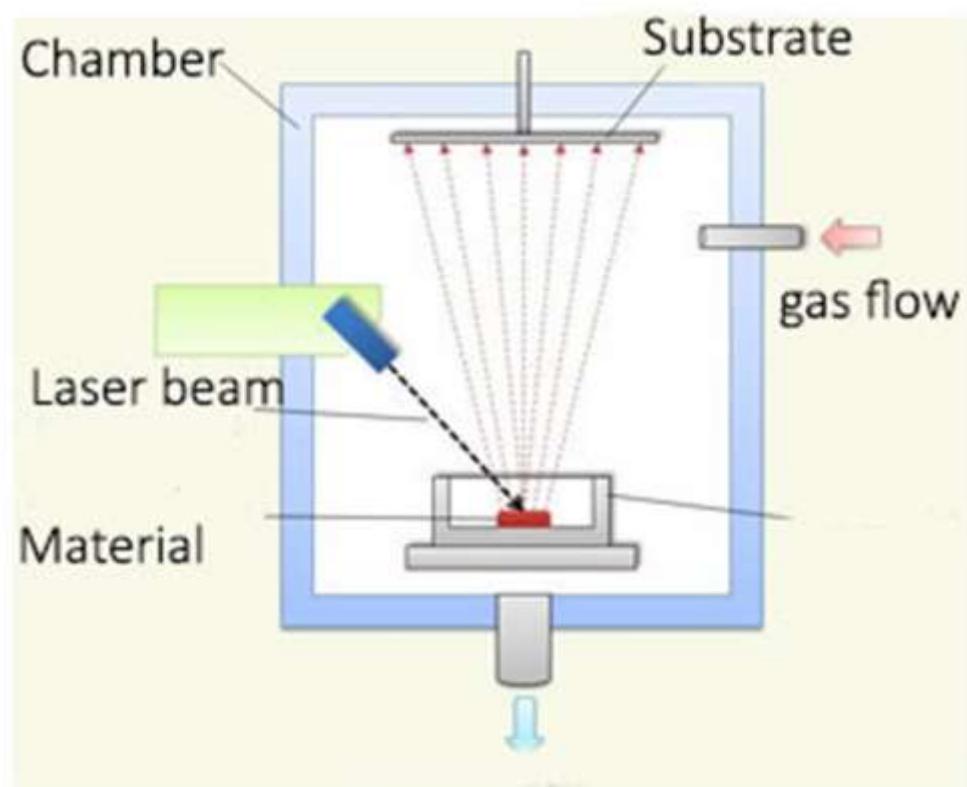
➤ The chemical reactions occur at the interface of the gas and the solid producing a thin sold film on the surface.

- CVD is a more complicated method than PVD for the formation of thin films and coatings.
- It exhibits several *distinct advantages*, such as the capability to produce ***highly pure and dense films or fine particles at reasonably high deposition rates***, and the capability of ***coating complex-shaped components uniformly*** due to its non-line-of-sight nature.
- A variety of *metallic, ceramic and semiconducting thin films* are being deposited by CVD.
- *Depending on the activation sources for the chemical reactions*, the deposition process can be categorized into *thermally activated, laser-assisted, and plasma-assisted CVD*.
- There are number of *CVD variants* developed for specific applications such as *spray assisted vapor deposition, aerosol assisted chemical vapor deposition, metalorganic chemical vapor deposition*, etc.
- This ***technique is quite versatile and can be used to apply wide range of materials onto a substrate***.
- This technique is widely used in semiconductor and ceramic industry.



Chemical vapor deposition process

- *The physical vapor deposition (PVD) involves vaporization of a material through heating, electron beam, ion beam, plasma or laser followed by solidification of the material back at the surface of the substrate that needed to be coated.*
- ✓ There are ***no chemical interactions*** occur in surface of the material.
- ✓ PVD is composed of three main steps: (1) formation of vapor phase by evaporation or sublimation of the material, (2) transporting the material from the source to the substrate, and (3) formation of the particle and/or film by nucleation and growth.
- ✓ PVD is usually carried out in high vacuum environment to enhance the effectiveness of the coating by reducing interactions with other atoms.
- ✓ Nanowire, nanorod, nanobelt, nanosheet, nanoribbon, nanotube, etc., have been synthesized using PVD.
- ✓ This technique also has found applications in metal coating, glass and semiconductor industry.
- ❖ ***In sputtering***, a discharge of nonreactive ions such as argon is created which fall on the target and break the surface atoms, which are collected on the surface to be coated.



Physical vapor deposition process

Dip-pen lithography

- Dip-pen lithography is a nanofabrication technique that is based on scanning probe microscopy technique.
- In contrast to the **scanning probe lithography**, which induce structural deformation into a substrate, **it uses an ink to write a pattern on a surface**.
- This is exactly similar to using a stylus that needed to be dipped in ink before writing, but at nanoscale.
- In **dip-pen nanolithography** (DPN), the tip of an AFM operated in air is ‘inked’ with a chemical of interest and brought into contact with a surface.
- The ink molecules flow from the tip onto the surface similar to a fountain pen.
- The water meniscus that naturally forms between the tip and the surface enables the diffusion and transport of the molecules, as shown in Fig. 3.24.
- Inking can be done by dipping the tip in a solution containing a small concentration of the molecules, followed by a drying step (e.g., blowing dry with compressed difluoroethane).
- There are instruments developed with more than 50,000 DPN tips in parallel to increase the fabrication throughput.
- Line widths down to 12 nm with spatial resolution of 5 nm have been demonstrated with this technique.

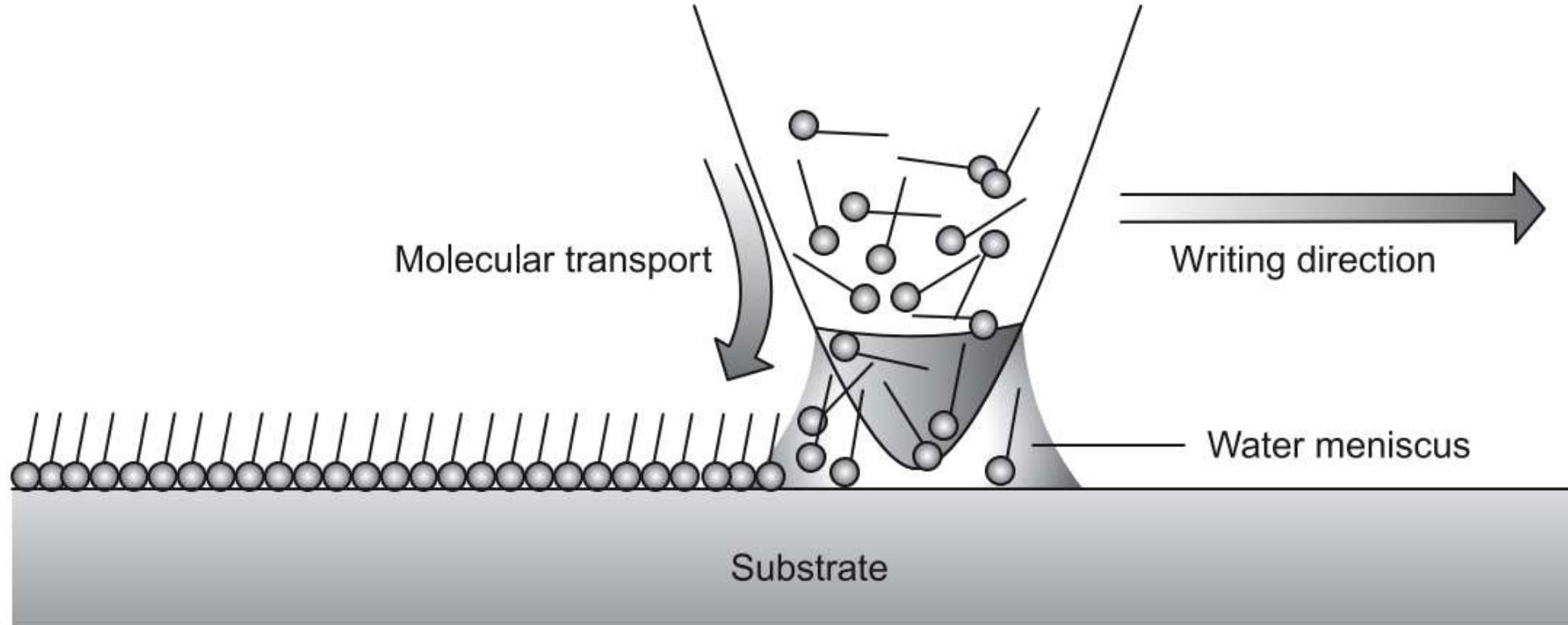


Fig. 3.24 Schematic representation of the working principle of dip-pen nanolithography.

- Species patterned with DPN include conducting polymers, gold, dendrimers, DNA, organic dyes, antibodies and alkanethiols.
- Alkanethiols have also been used as an organic monolayer mask to etch a gold layer, and subsequently etch the exposed silicon substrate.

TOP-DOWN METHODS

- Top-down nanoparticle preparation methods present interesting pathways to approach the nanoscale by starting with the bulk scale materials and then scaling them down to the nanometer level dimensions.
- These strategies involve physical breaking of the source material through high energy processes.
- In this page we will review some of the most frequently used top-down nanomaterial synthesis pathways that are used by scientists and industry alike.

Mechanical milling

- Mechanical milling is a top-down approach to prepare nanomaterials and has found great acceptability especially in industrial nanomaterial preparation environments due to its *simplicity, versatility of the process* (can be adapted to make many types of nanomaterials), *scalability of the process and for the low cost*.
- In this method, bulk material which is usually in the micro dimensions are grounded down to the nanoscale with strong mechanical shear forces applied by the milling technique.
- There are ***three types of attrition devices*** that are more frequently used than others.
- ✓ They are ***shaker mills, planetary ball mill, and attrition mill***.

- ❑ In the ***shaker mills***, as name suggests material to be milled is charged into a vial with “milling balls”, spherical balls that are made of hard material.
 - ✓ The sample is then securely attached to the shaker and energetically swung back and forth for several thousand cycles per minute.
 - ✓ During this shaking process, milling balls, collide on each other and with the vial wall.
 - ✓ The high shear and impact forces produced in the process grinds the solids down and mix it thoroughly.
- ❑ ***Planetary ball mills*** has gained its name from the movement of the vial in the device.
 - ✓ These vials are attached into a rotating disk that rotates around its axis and individual vials are also rotated in an axis of their own but in an opposite direction to the main rotating disk.
 - ✓ The whole system is rotated several thousand rpm and strong frictional and impact forces grinds the material down to smaller sizes.
 - ✓ Planetary ball mill is more popular among many as it can be used to grind several hundreds of material at a time.

- **Attrition mill** is a ball mill where grinding balls are loaded into a horizontal cylinder and rotated to perform the milling action.
 - ✓ However, in attrition mills the vertical drum is attached with series of carefully positioned impellers inside.
 - ✓ These impellers are fixed to have right angles to each other.
 - ✓ Unlike ball mill, attrition mill is rotated at high speeds with the inside impeller working.
 - ✓ This can produce very high shear and impact forces that are not possible to obtain with other mills.
-
- ❖ The **main problem** with this method is contamination of the nanomaterial with the milling balls and the container. High shear and impact forces generated inside can chip small surfaces from these surfaces and incorporated into the nanomaterial. This is the main reason, that at least in the labs, this method is slowly getting dismissed. Also, high shear forces applied in the milling process impart significant imperfections of surface and crystallographic structure of the material. The milling ball sizes, the milled material, duration of milling are typical control parameters of this process.

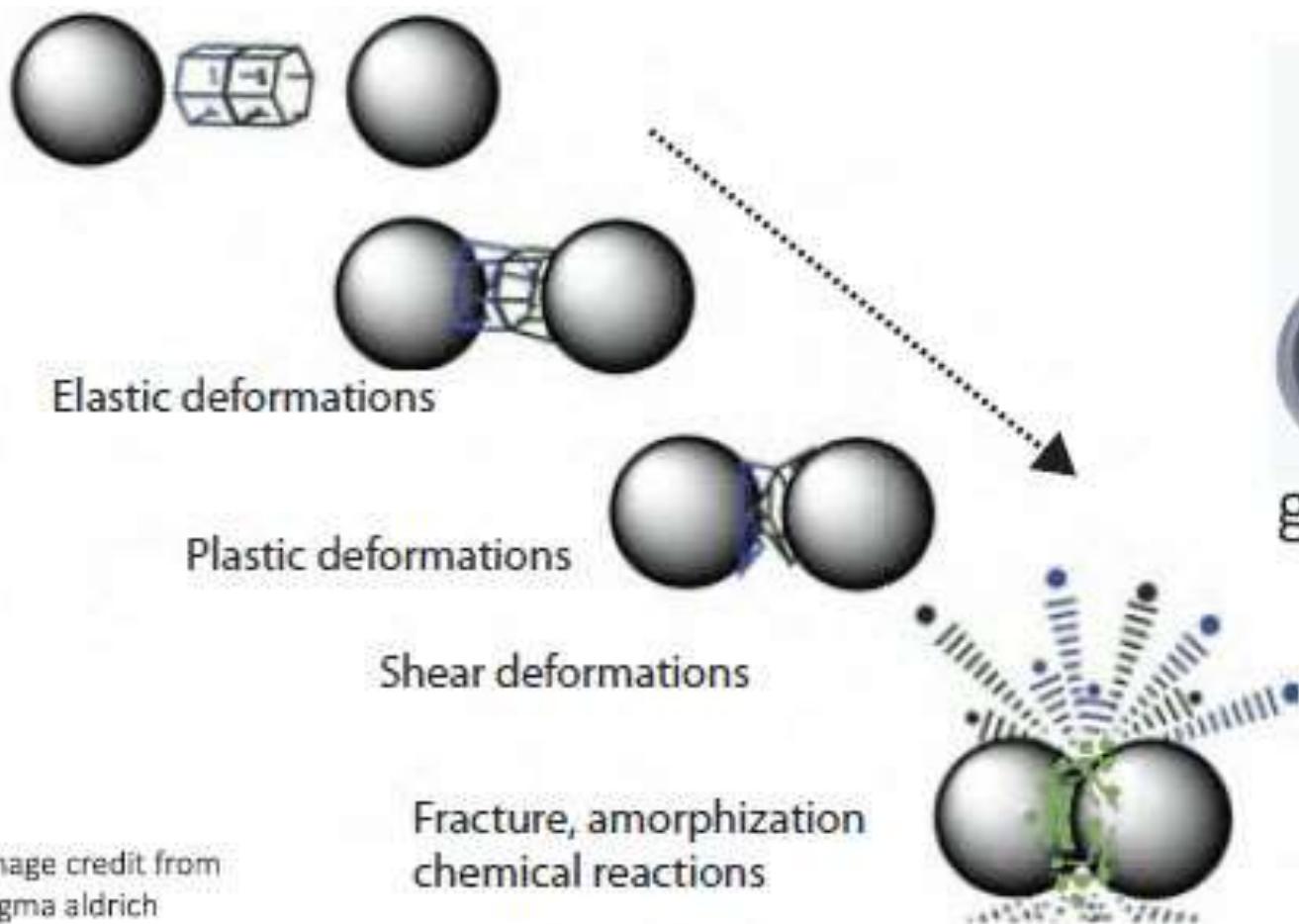
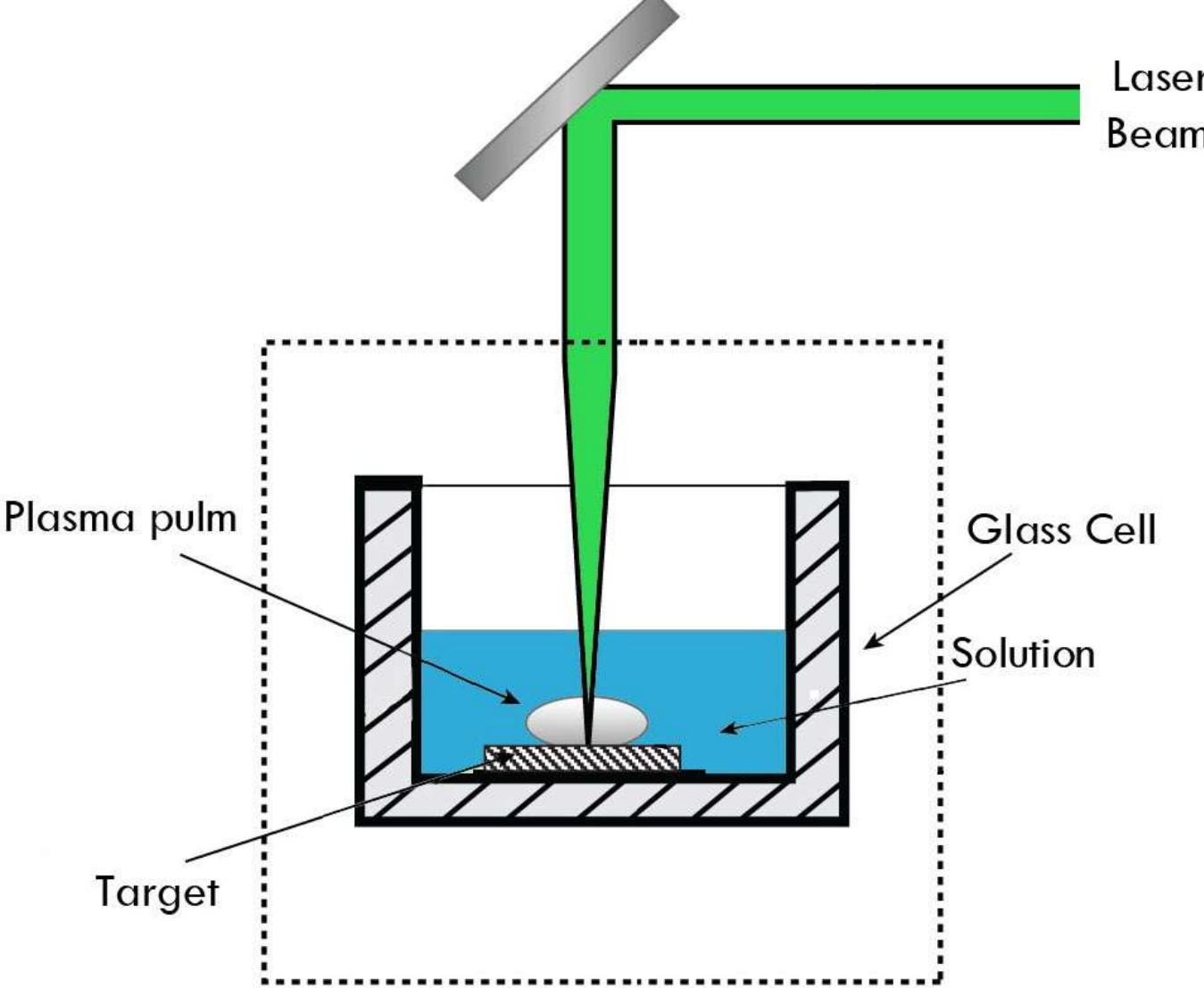


image credit from
Sigma aldrich

Laser ablation synthesis

- *This technique deals with generation of nanoparticles using a powerful laser beam.*
- It's a top-down process where *a high energy laser is focused on to a target in a solvent.*
- In this method, metal atom desorption occurs, when intense laser pulses are focused on a metal target.
- The *laser delivers, short pulses of energy which is enough to vaporize small spots of the metal target which condenses as nanoparticle in the solvent.*
- The typical setup consist of a pulsed laser, set of focusing optics and a container containing a metal target.
- The placement of the metal target is close to the focus of the laser.
- The container is filled with a solvent (e.g.: water, ethanol) in which the metal target is immersed.
- In a Laser ablation experiment, a bulk metal is immersed in a solvent containing surfactant.
- During the laser irradiation, the metal atoms will vaporize and are immediately solvated by the surfactant molecules to form nanoparticles in solution.

- The ***size and dispersion of the nanoparticles*** can be ***tuned*** by the ***pulse duration, wavelength*** and the ***intensity of the laser pulses***.
- Typically, the laser pulses are in extremely small-time scales such as femtoseconds ($1/1,000,000,000,000,000$ of a second), picoseconds ($1/1,000,000,000,000$ of a second) or nanosecond ($1/1,000,000,000$ of a second).
- Both visible and near infrared wavelength lasers are typical in laser ablation instruments.
- Use of short pulses in the process allows the ablation process to be carried out in number of different mediums, including very volatile solvents to highly reactive monomers.
- Since the action is primarily physical, this technology can be used on wide range of material and solvent possibilities.
- Another unique advantage of this method is the ability of making nanoparticles with very high purity. Since this method produce no by products or residual chemicals.
- Usually, this method is used to *generate noble metallic nanoparticles such as gold, silver and platinum*.
- However, it can seamlessly be extended to make other nanomaterials such as nanoparticles of *metal alloys: a unique advantage of this method*.

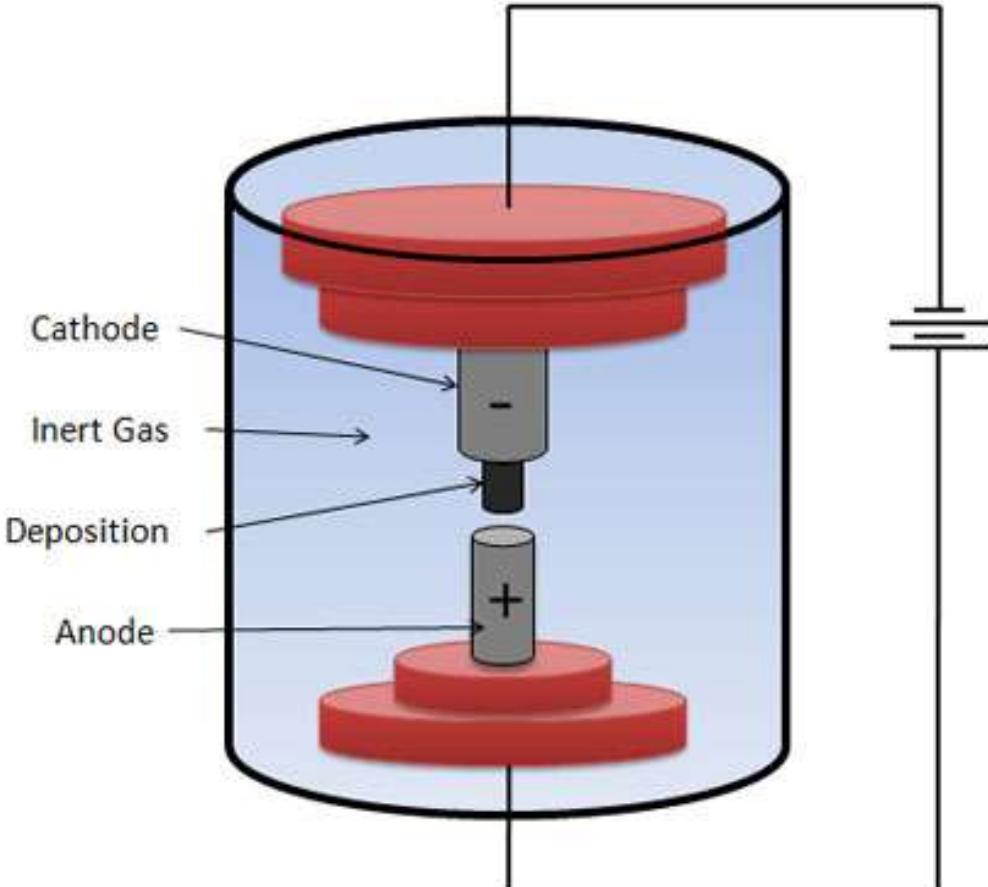


<https://youtu.be/kOy0yuWpUzU>

Arc discharge synthesis

- Arc discharge method presents another physical method of making nanomaterial.
- This can be classified as a top-down process as nanomaterials are produced from bulk materials due to ***arc assisted breakdown of the bulk material.***
- In the arc discharge process, *two electrodes are kept in proximity to each other in a solution and a high voltage is applied in between them.*
- Due to the ***high potential difference and the proximity, an electrical breakdown occurs in the medium, giving rise to arc discharge which produces an ongoing thermal plasma discharge.***
- The *local temperature of the ongoing plasma can reach several thousand of degrees Celsius, which effectively vaporized the electrode surfaces in the liquid medium.*
- ***Vaporized metal condenses in the solvent making nanoparticles.***
- Most of the metallic nanoparticles, nanostructures and metal oxide nanoparticles are produced in this way.
- The ***condensing solvent medium, voltage and current supplied to the electrode and electrode material are major parameters in determining the end product.***
- The extremely high temperature produced between the electrodes can also facilitate atomic assembly pathways that can create new nanostructures *that are different to the electrode materials.*

- Carbon nanotubes are produced this way in arc discharge synthesis.
- The discharge vaporized the surface of one of the carbon electrodes and forms a rod-shaped deposit on the other.
- This deposit is rich with mixture of single and multiwall carbon nanotubes.



Arc discharge synthesis apparatus for CNT production

<https://youtu.be/yInS9hcYgSc>



TOP-DOWN METHODS: Nanofabrication techniques

- It's great to make elaborate nanomaterials in a beaker and nanostructures in a small glass plate and write and read about it.
- But real benefits of nanotechnology will be available to most if we can make them in a scalable, reliable and cost-effective means.
- This, however, demands lot of advances in technology in terms of precise manufacturing, material science and quality control.
- This is because the products that are going to be built-in the nanoscale cannot be seen without high-end equipment, cannot be worked by simple techniques and it's simply not possible to test each of them as thousands of them can sit on a single pinhead.
- Still, some great advances has been made in the field of nanofabrication, especially in the area of electronics.
- The Apple mobile phone 5S, has approximately ten times more processing power and 16 million times more memory power than the computer that landed us on the moon: Apollo Guidance Computer (AGC). The most amazing thing is it can fit in your palm (AGC is as big as an old CRT monitor) and it's only 399 US dollars, much smaller compared to estimated 150,000 USD to make one AGC. This is a perfect example of benefits that nanofabrication could bring us. We will be able make much faster, better performing devices in smaller packages and at much lower costs.

Apollo Guidance Computer (AGC)

Dimensions: 24 x 12.5 x 6.5 inches

Weight: 70 pounds

Processor speed: 1 MHz

Memory: 2,048 words (32,768 bits or roughly 4kB)

Display: Seven-segment numeric

Price: \$150,000 (est.)



Apple iPhone 5s

Dimensions: 4.87 inches x 2.31 inches

Weight: 3.95 ounces

Processor speed: 1.3GHz, dual-core

Memory: 64GB

Display: 4-inch diagonal Multi-Touch display, 136 x 640 pixel resolution at 326 ppi

Price: \$399

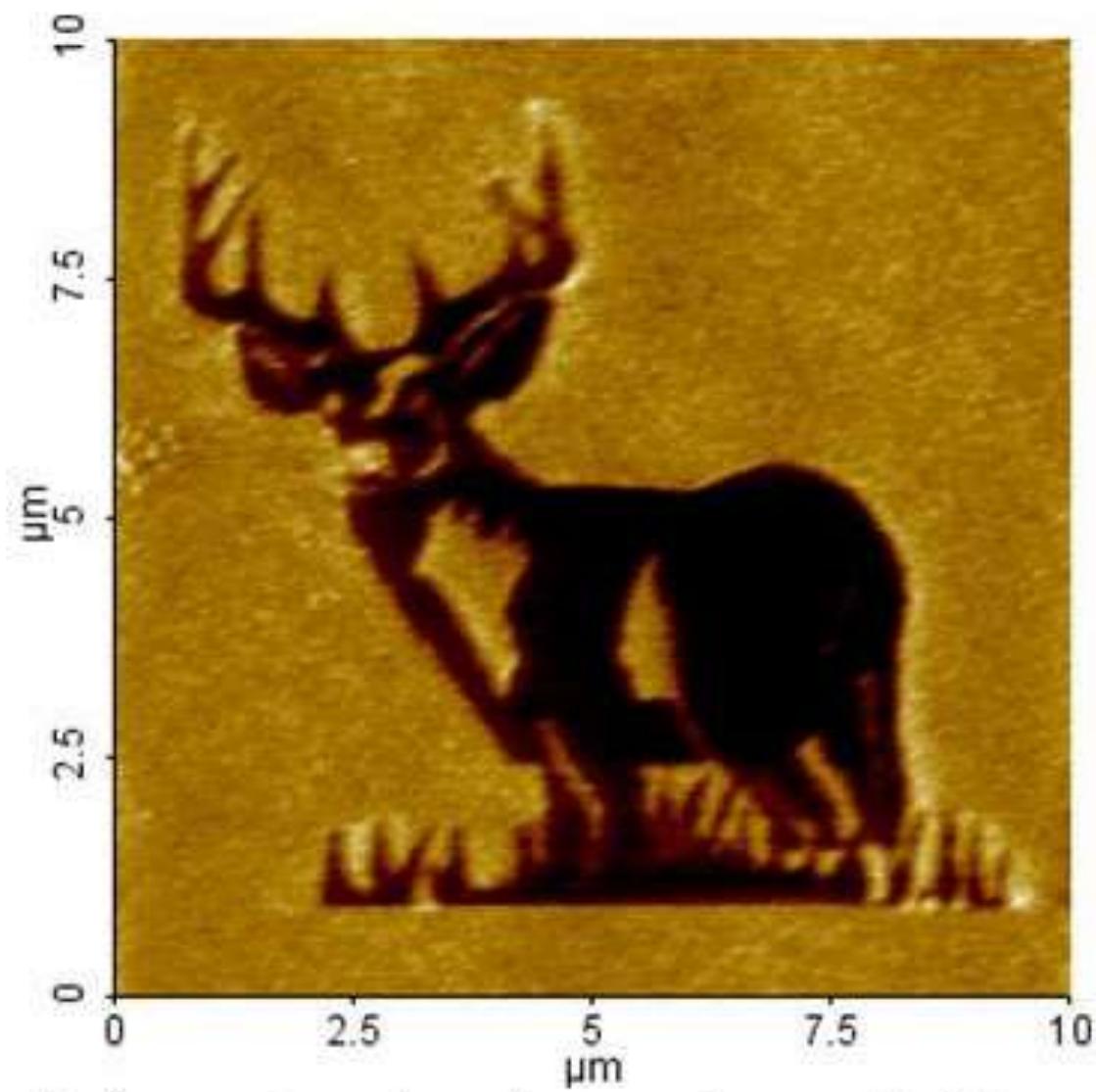


- Here we will look at few major Top-Down nanofabrication strategies that are frequently followed by nanotechnologists to create nanoscale structures.
- Top-down approaches are primarily used for surface patterning of micro/nanoscale features in a desired substrate.
- The well-developed patterning techniques include, *scanning probe lithography*, *soft lithography*, *focused beam lithography* and *nanoimprint lithography*.

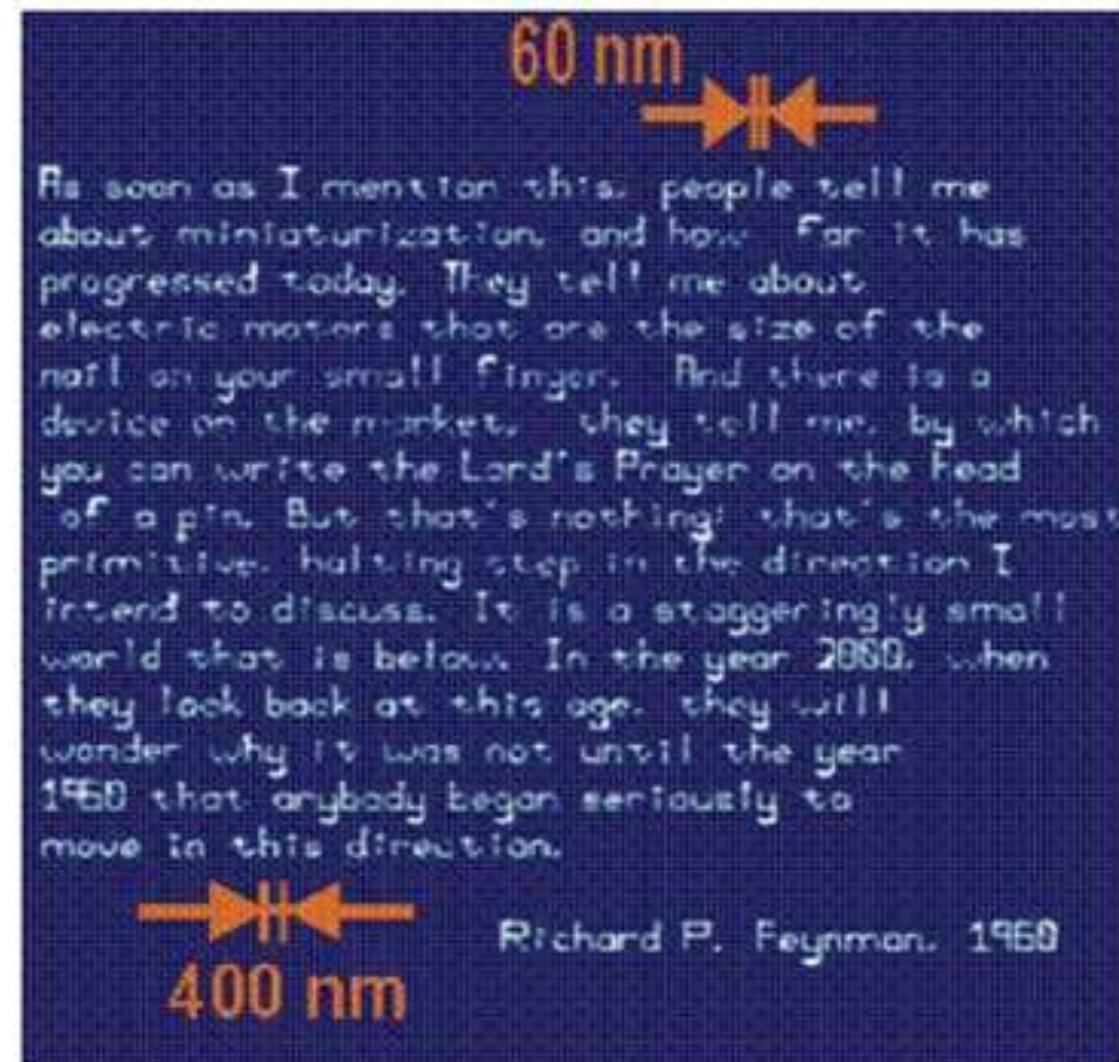
Scanning probe lithography

- Scanning probe microscopes (SPMs) provide a great way to probe into the nanoscale world.
- Similarly, one can use SPMs to manipulate things in the nanoscale too.
- SPMs or more specifically in atomic force microscopes (AFMs) physically make contact with the specimen during the scanning.
- Same strategy can be used to scratch, dimple or score a soft surface as the tip is dragged along the surface.
- They have been used to create wonderful creations and art at the nanoscale.
- Scanning tunneling microscopes (STMs) have been used by scientist to create atomic level manipulations either by pushing individual atoms or picking up the individual atoms through making a temporary bond between the tip and the atom and then place it at a desired location.

- Although, SPMs can be very precise and can manage matter at the smallest scale possible this technique suffer from limited scalability and slowness.
- Although, the rate of production can be increased with operating number of tips at a single time, its output cannot compete with the other techniques.
- Hence, this technique is appreciated as suitable to create works of art and wonderful structures, it may not be able to satisfy demand of the mass.



An image drawn by using scanning probe lithography



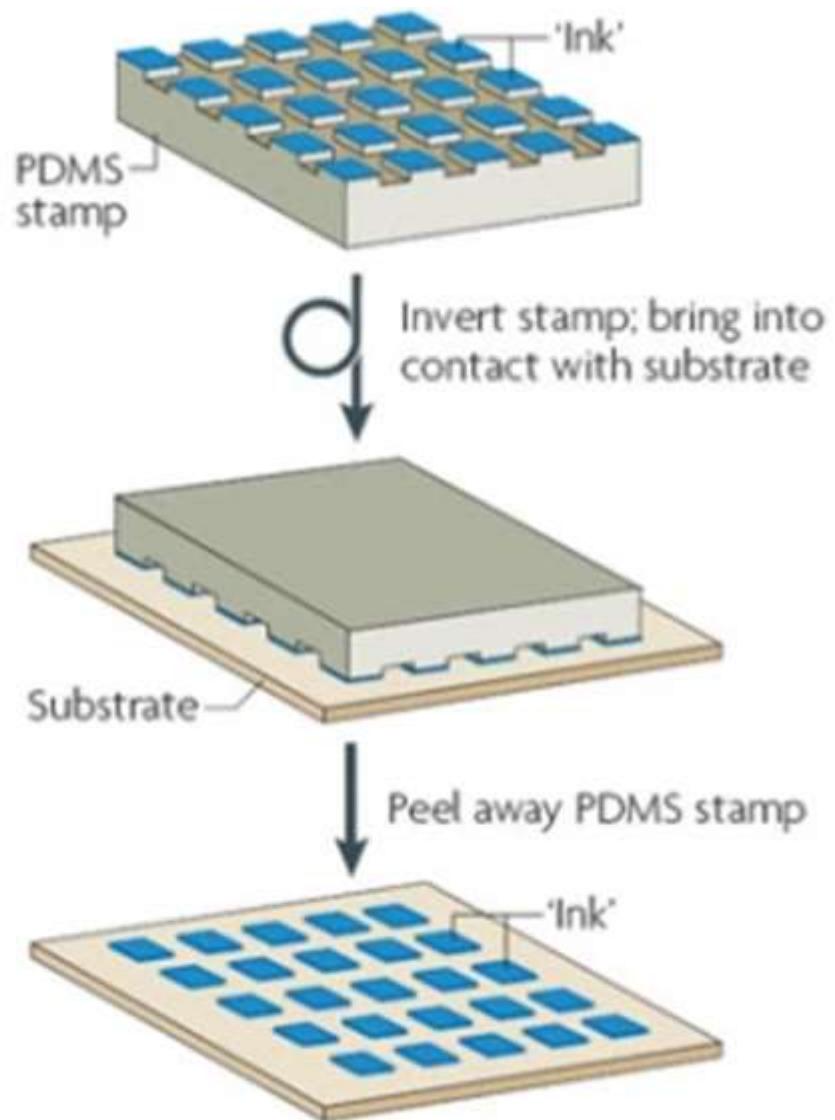
Feynmann's speech written in molecules on a gold surface

Focused beam lithography

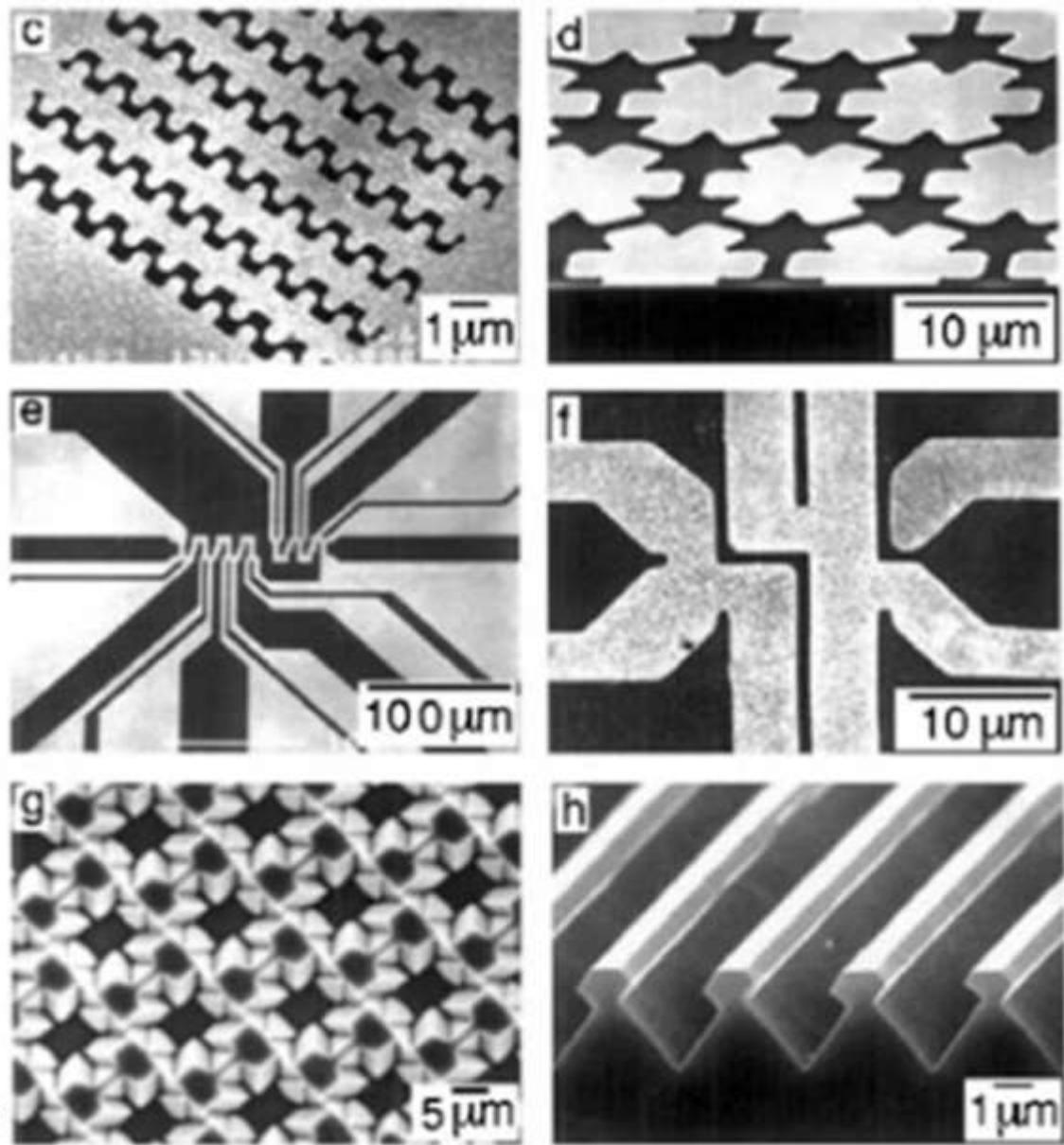
- As the name suggests, focused beam lithography take use of electron or ion beam focused onto a resist surface to generate patterns by exposing the surface followed by removing the resist through a chemical process.
- If electron beams are used, lithography can be used on an electron-sensitive resist film.
- ✓ Most widely use material for this is polymethylmethacrylate.
- ✓ Electron beam can induce very precise patterns to the resist surface in the scale of 3-4 nm if required.
- ✓ Electron beam lithography can be carried out in a modified electron microscope.
- Focused ion beam lithography uses an ion beam to induce high-resolution patterns in a resist.
- ✓ This technique has found applications in semiconductor industry for mask repairing and device modification.
- Unlike electron beam, ion beam has comparatively low backscattering and higher exposure sensitivity. It can also be used as a precise milling tool.

Soft lithography

- Soft lithography is the technique of transfer or fabricate a structure by stamps and molds made of elastomeric materials.
- The most widely used elastomeric material used in this technique is polydimethylsiloxane (PDMS) due to its favorable properties.
- This technique has found much interest due to its simplicity and low cost.
- In fact, it's possible to make submicron length scale dimensions with relative ease with ordinary chemical apparatus.
- The complete lithographic process consist of two main steps.
- ✓ First, precisely fabricated masks made by AFM, electron or ion beam lithography are used to transfer the pattern onto the elastomeric element or stamp.
- ✓ Then the elastomeric elements are used to pattern features back onto a desired surface using an ink or a polymer.
- ✓ Both molecular level and solid inks are used in the stamping.



Process of making a soft lithographic pattern and examples



Nanoimprint lithography

- Nanoimprint lithography (NIL) is widely used technique to imprint micro/nanoscale patterns with low cost, high throughput and high resolution.
- Unlike soft lithography, NIL uses a hard mold to create patterns on a resist through direct mechanical deformation and therefore achieve limitations set by light diffraction or beam scattering in conventional lithographic processes.
- The resolution of the NIL primarily limited by the resolution of the template feature.
- The masks can be made of a number of different substrates such as glass, silicone, polymers, etc.
- Nanoimprint lithography has found applications in organic light emitting diode fabrication and sensor fabrication.