

CHAPTER - 1

INTRODUCTION

1.1 General Introduction

Nanoscience primarily deals with synthesis, characterisation and exploration of nanostructured materials. These materials are characterised by at least one dimension in the nanometer range. A nanometer (nm) is one billionth of a meter or 10^{-9} m. One nanometer is approximately the length equivalent to 10 hydrogen or 5 silicon atoms aligned in a line. The processing, structure and properties of materials with grain size in the tens to several hundreds of nanometer range are research areas of considerable interest over the past decades. New materials with outstanding electrical, optical, magnetic and mechanical properties are rapidly being developed for use in Information technology, Bioengineering, Energy and Environmental applications [1-5].

On nanoscale, some physical and chemical properties can differ significantly from those of the bulk structured materials of the same compositions. For example, the theoretical strength of nanomaterials can be reached or “quantum effects” may appear. The crystals in the nanometer scale have a low melting point and reduced lattice constants, since the number of surface atoms or ions becomes a significant fraction of the total number of atoms or ions and “the surface energy” plays a significant role in the thermal stability. Therefore, many material properties must now be revisited in light of the fact that a considerable increase in surface-to-volume ratio is associated with the reduction in material size to the nanoscale often having a prominent effect on material performance. Historically, fundamental material properties such as elastic modulus have been characterised in bulk specimens using macroscopic and more recently microscopic techniques. However, as nanofabrication

advances continue, these bulk properties are no longer sufficient to predict performance when devices are fabricated with small critical dimensions [3,4].

Nanotechnology can be defined as the design, characterisation, production and applications of structures, devices and systems by controlling shape and size at the nanometer scale [1, 2]. One of the most important aspects of this field is the preparation and development of nanomaterials. There have been a variety of techniques used for preparing different types of nanomaterials.

1.2 Classification of Nanomaterials

A reduction in the spatial dimension or confinement of particles or quasiparticles in a particular crystallographic direction within a structure generally leads to changes in physical properties of the system in that direction. Hence, one classification of nanostructured materials and systems essentially depends on the number of dimensions which lie within the nanometre range [1].

1) Zero-dimensional nanostructures also named as nanoparticles (NPs), include single crystal, polycrystalline and amorphous particles with all possible morphologies such as spheres, cubes and platelets. In general, the characteristic dimension of the particles is one hundred nanometers or below. Some other terminologies are zero-dimensional nanostructures: If the NPs are single crystalline, they are often referred to as nanocrystals. When the characteristic dimension of the NPs is sufficiently small and quantum effects are observed, quantum dots are the common term used to describe such NPs.

2) One-dimensional (1D) nanostructures have been called by a variety of names including: whiskers, fibres or fibrils, nanowires and nanorods. In many cases, nanotubes and nanocables are also considered one-dimensional structures. Although, whiskers and nanorods are in general considered to have smaller length to thickness

ratio (aspect ratio) than fibres and nanowires, the definition is a little arbitrary.

3) Systems confined in one dimension or quasi-2D systems, include discs or platelets, ultrathin films on a surface and multilayered materials; the films themselves could be amorphous, single-crystalline or nanocrystalline. Table 1.1 gives the examples of nanostructured systems which fall into each of the three categories described above.

Table 1.1 Examples of reduced-dimensionality systems [1]

Confined system	Example
Zero dimensional material (or) 3D confinement	<ol style="list-style-type: none"> 1. Fullerenes 2. Colloidal particles 3. Nanoporous silicon 4. Activated carbons 5. Semiconductor quantum dots 6. Quasi-crystals
One dimensional material (or) 2D confinement	<ol style="list-style-type: none"> 1. Carbon nanotubes and nanofilaments 2. Metal and magnetic nanowires 3. Oxide and carbide nanorods 4. Semiconductor quantum wires
Two dimensional material (or) 1D confinement	<ol style="list-style-type: none"> 1. Semiconductor quantum wells and superlattices 2. Magnetic multilayers and spin valve structures 3. Langmuir–Blodgett films 4. Silicon inversion layers in field effect transistors

1.3 Properties of Nanomaterials

Nanomaterials are of great interest because at this scale unique optical, magnetic, electrical and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine and other scientific fields.

Nanocrystalline materials represent a state of matter in the transition region between bulk solid and single molecule. As a consequence, their physical and chemical properties gradually change from solid state to molecular behaviour with decreasing particle size. One could describe these differences in a simplified way, as arising from the fact that the material having the nanoscale present: (1) dimensions comparable to characteristic length such as the limiting size of magnetic domains and (2) broken translational symmetry which results in sites with reduced co-ordination number with broken exchange bonds and frustration. The absence of translation symmetry brings about several important consequences to the physical properties of these systems. Three aspects of the effect of symmetry breaking are:

(1) The relation of the physical properties of the samples to their dimensionality (samples with quasi-zero dimension (0D), one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D))

(2) The change in coordination of the atoms at the interface and

(3) The effect of the increase in the proportion of surface (or interface) atoms in nanoscopic samples. Table 1.2 gives the values of increasing the surface to volume ratio for the cubic nanoscopic clusters [1,2].

Table 1.2 Proportion of number of surface atoms in cubic nanoscopic clusters [2]

No. of atoms on each side	No. of surface atoms	Total No. of atoms	Ratio of surface atoms to total No. of atoms
5	98	125	78.5
10	488	1000	48.8
100	58,800	1×10^6	5.9
1000	6×10^6	1×10^9	0.6

1.4 Nanoparticles

In recent years, NPs have been the center of attention of researchers in the field as the transition from microparticles to NPs was seen to lead to immense changes in the physical and chemical properties of a material. Nanoparticles are a quasi-zero-dimensional (0D) nano-object in which all characteristic linear dimensions are of the same order of magnitude (not more than 100 nm). Because of this very small size scale, NPs possess an immense surface area per unit volume, i.e., a huge number of atoms are located on the surface and near surface layers and they have the ability to exhibit quantum effects. Importantly, the resulting unique properties of NPs cannot be anticipated from a simple extrapolation of the properties of bulk materials. Nanoparticles exist with great chemical diversity in the form of metals, metal alloys, metal oxides, multi-metallic oxides, other non-oxide compounds and organic based materials (such as, polymers, carbon and organometallic compounds) [2].

Initially, researchers studied single NPs because such particles have much better properties than the bulk particles. In the late 1980s, researchers found that heterogeneous, composites or sandwich colloidal semiconductor particles have better efficiency than their corresponding single particles, in some cases they even develop

some new properties [3-5]. More recently, during the early 1990s, researchers synthesised concentric multilayer semiconductor NPs with the view to improving the property of such semiconductor materials. Hence, subsequently the terminology “core-shell” was adopted [6-8]. Furthermore, there has been a gradual increase in research activity because of the tremendous demand for more and more advanced materials fuelled by the demands of modern technology. Simultaneously, the advancement of characterisation techniques has also greatly helped to establish the structures of these different core/shell nanostructures.

1.4.1 Importance of Core-Shell Nanoparticles (CSNPs)

Recently, core–shell nanoclusters have received considerable attention owing to their physical and chemical properties that are strongly dependent on the structure of the core, shell and interface. This structure dependence, opens possibility for tuning properties by controlling their chemical composition and relative size of the core and shell. The core–shell magnetic nanoclusters are of special interests since the heterogeneous nanostructures offer opportunities for developing devices and cluster assembled materials with new functions for magnetic recording, bio and medical applications. In fact, superparamagnetic NPs with suitable biocompatible coatings have important implications in biology, biotechnology and other biomedical disciplines [9-11].

1.4.2 Classes of Core-Shell Nanoparticles

Nanoparticles can be categorized based on single or multiple materials into simple and core-shell or composite NPs. In general, simple NPs are made from a single material whereas, as the name implies, composites and core-shell particles are composed of two or more materials. The core/shell type NPs can be broadly defined as comprising a core (inner material) and a shell (outer layer material). These can

consist of a wide range of different combinations in close interaction, including inorganic/inorganic, inorganic/organic, organic/inorganic and organic/organic materials. The choice of shell material of the CSNP is generally strongly dependent on the end application and use.

Different classes of CSNPs are shown schematically in Figure 1.1. Concentric spherical CSNPs are the most common (Figure 1.1a) where a simple spherical core particle is completely coated by a shell of a different material. Different shaped CSNPs have also given rise to immense research interest because of their different novel properties. Different shaped CSNPs are generally formed when a core is nonspherical as shown in Figure 1.1b. Multiple-core, core-shell particles are formed when a single shell material is coated onto many small core particles together as shown in Figure 1.1c. Concentric nanoshells of alternative coating of dielectric core and metal shell material onto each other (A/B/A type) are shown in Figure 1.1d. Here, the nanoscale dielectric spacer layers separate the concentric metallic layers. These types of particles are also known as multilayered metallodielectric nanostructures and are mainly important for their plasmonic properties [12-15]. It is also possible to synthesize a movable core particle within a uniformed hollow shell particle (Figure 1.1e) after a bilayer coating of the core material and just removing the first layer by using a suitable technique.

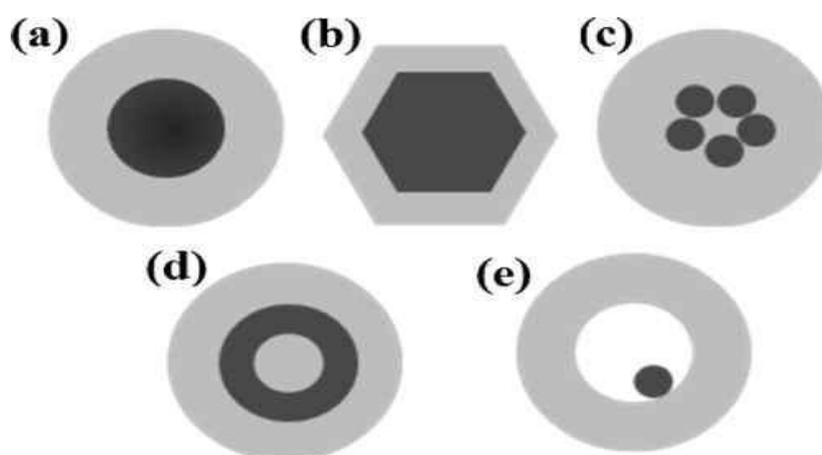


Figure 1.1 Different core-shell nanoparticles: (a) spherical, (b) hexagonal, (c) multiple small core materials coated by single shell material, (d) core-multi-shell nanoparticles and (e) movable core within hollow shell material

1.4.2.1 Core and multi-Shell Nanoparticles

The core-multi-shell NPs are a type of CSNPs, it contains a single core with a concentric shell layer and they have several exciting applications. The efficiency of a core-shell semiconductor particle can be enhanced in terms of increased quantum yield and reduced response time by selective coating of the core material with higher band gap shell materials. Great advances have been made in this area as a result of the invention of core-multi-shell devices to replace the normal core/shell materials. This is especially true for the quantum-dot/quantum-well combinations (CdS/HgS/CdS, CdS/CdSe/CdS, etc.). In these systems, the electrons and holes are confined within a low band gap first shell layer, resulting of these materials have excellent photoluminescence properties [16]. $\text{TiO}_2@ZrO_2@Y_2O_3:\text{Eu}^{3+}$ composite particles with a core–multi-shell structure were synthesised through the combination of a layer-by-layer (LBL) self-assembly method and a sol–gel process. The presence of a ZrO_2 layer on the TiO_2 core can effectively prevent the reaction between the

TiO₂ core and Y₂O₃ shell. The Eu³⁺ ion in the Y₂O₃:Eu³⁺ shell shows its characteristic red emission (611 nm, ⁵D₀→⁷F₂) and the photoluminescence intensity of the phosphor with the core-multi-shell structure was obviously greater than that of the core-shell TiO₂@Y₂O₃:Eu³⁺ phosphor [17]. Fleige *et al.* [18] described the novel pH-responsive dendritic core-multi-shell (CMS) nanocarriers with monomethyl polyethylene glycol (mPEG1000), obtained by introducing an aromatic imine linker between the shell and the core. At a pH of 5 and lower, the used imine linker was rapidly released guest molecules of the anticancer drug doxorubicin evaluated by NMR studies. The CMS nanocarriers were loaded with the anticancer drug doxorubicin (DOX) and their transport capacities were determined using UV-Vis spectroscopy. They found that the DOX was transported in a unimolecular fashion. After cellular uptake, the DOX-loaded pH-responsive nanocarriers showed higher toxicities than the stable CMS nanocarriers. This is due to a more efficient DOX release caused by the cleavage of the pH-labile imine bond at lower pH within the intracellular compartments.

Recently, the skin penetration efficiency of 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (PCA) spin label within the carrier systems of polymer based core-multi-shell (CMS) NPs have been analysed by Haag *et al.* [19] using electron paramagnetic resonance (EPR) spectroscopic techniques. CMS NPs made up of small polyglycerol core which is surrounded by a lipophilic inner shell and a hydrophilic outer shell. Due to the nanoscale effect of CMS, the skin penetration efficiency of PCA carried CMS were enhanced 2.5 fold compared to bare PCA solution. This offers possibilities for improved photodynamic therapy.

1.4.2.2 Hollow Core-Shell Nanoparticles

Hollow CSNPs have recently received considerable attention. This is due to their diverse application of drug encapsulates, as transducers and dielectrics for

electronics and as capsules for energy storage [20-23]. Varieties of chemical and physicochemical approaches such as hydrothermal method, spray pyrolyzing and template free syntheses have been developed to produce hollow NPs [24-26]. An effective approach of template-free alcoholysis is employed to prepare hollow core-shell SnO_2/C NP aggregates as anode materials for Li-ion batteries [27]. For instance, Eisenberg *et al.* [28] reported pioneering studies of hollow structures by self-assembly of PS-*b*-PAA amphiphilic diblock copolymers. Hollow particles with a hollow cavity have also been prepared by self-assembly of diblock copolymers with driving forces of covalent and hydrogen bonding [29].

The self assembly approach involves a careful selection of experimental parameters to control morphology such as copolymer composition, block length, ionic content, solvent and polymer concentration. Hollow Au@Pd and Au@Pt CSNPs are developed from galvanic displacement reaction have been reported [30]. Higher reduction potential of Au compared to Ag, Pd and Pt helps to produce hollow Au cores first, followed by Pd or Pt shell growth. Among the various approaches reported so far, template-directed synthesis is probably the most widely used method for the generation of hollow particles [31-33]. The process generally involves three steps as illustrated in Figure 1.2. Initially, surface modification of the template is carried out to capture shell ions during the subsequent nucleation process, avoiding self-nucleation and secondary-particles. Core-shell particles are prepared by uniform nucleation of shell material over the core using the surface modifier. The last step involves the removal of template cores by physical dissolution or chemical etching of the core-shell particles. In addition to the feasibility of fabrication, the template approach can also control the size and void space of the hollow particles precisely because of the known parameters about the selected template (size and surface

function) prior to grafting of a shell.

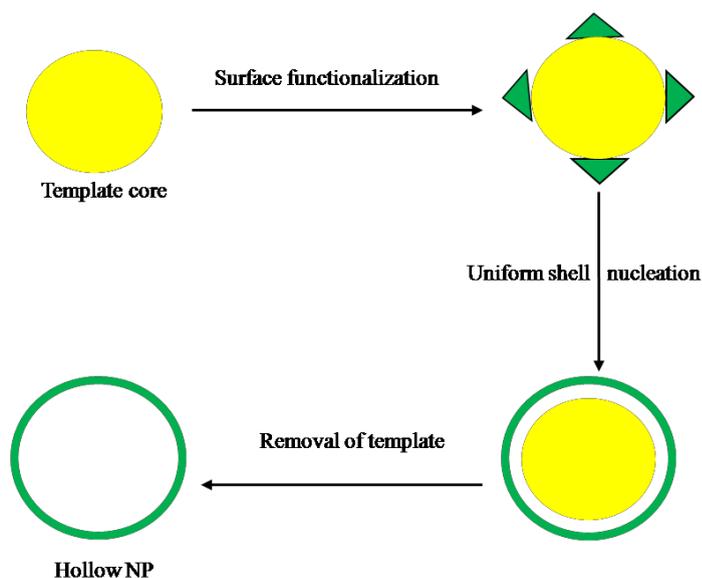


Figure 1.2 Synthesis of hollow CSNPs by a template approach

1.4.2.3 Different Shaped Core-Shell Nanoparticles

Other than the conventional spherical shaped CSNPs, different shaped CSNPs have proven equally important because of their potential applications. In the case of metallic NPs, the catalytic properties improvement observed for non-spherical shapes may be attributed to the exposure of different crystallographic facets. The change in catalytic activity and selectivity of the non-spherical NPs may be attributed to the introduction of a number of edges, corners and faces over the spherical particles. Recently, Narayan and El-Sayed [34] have reported that the tetrahedra shaped platinum NPs showed the better catalytic activity compared to the sphere and cube shaped NP for the electron-transfer reaction between hexacyanoferrate (III) ions and thiosulfate ions. The different shaped CSNPs available from the literature are summarized in Table 1.3.

Table 1.3 Different shapes of CSNPs with their synthesis method

Synthesis method	Type of core/shell	Core shape	Shell shape	Ref.
Control directional growth	Au/Cu ₂ O, Cu ₂ S/In ₂ S ₃	Octahedral, Spindle	Octahedral, Matchstick- like, and Pencil- like	35 36
Template assist route	SiO ₂ /TiO ₂	Movable sphere	Hollow sphere	37
Hydrothermal	Fe ₂ O ₃ /SnO ₂	Movable spindles	Nanococoons	38
Template assist route	Cu ₂ O/Au	Cubic	Cubic, flowery	39
Micro-emulsion polymerization	Fe ₃ O ₄ /PANI	Multi-core sphere	Sphere	40
Reverse micelles	CdS-SiO ₂	Multi-core	Sphere	41
Galvanic replacement route	Au/Pd	Hollow core	Spherical shell	42
Stober process	Au-Pt/SiO ₂	Multi-core	Sphere	43
Reverse micro-emulsion	CdTe/SiO ₂	Multi-core	Single shell	44
Instant direct-templating method	NiO/SiO ₂	Hexagonal	Hexagonal	45
Wet chemical solution route	SiO ₂ /Ni	Spherical	Flower	46
Reduction-transmetalation route	Au/Pt CdSe/CdS	Spherical, Hexagonal	Random structure	47
Precipitation	La _{2/3} Sr _{1/3} MnO ₃ /Au	Spherical	Sphere	48
Sol-gel method	Pt/CeO ₂	Spherical	Sphere	49
Nonorganic synthetic method	SiO ₂ /Zr _{0.5} Ti _{0.5} O ₂	Pomegranate- like Multicore	Nanosphere	50
Template-directed coating	Au/SiO ₂	Sphere	Hollow sphere	51
Controlled core- dissolution	Ag/Pd	Sphere	Hollow sphere	52
Polyol and galvanic displacement reaction	Pt/SiO ₂	Nanowire	Nanotube	53
Reduction by NaBH ₄		Single and multi-core	Mesoporous sphere	54

1.5 Synthesis of Nanomaterials

There are two approaches for the synthesis of nanomaterials and the fabrication of nanostructures. Top down approach refers to slicing or successive cutting of a bulk material to get nano sized particle. Bottom-up approach refers to the build up of a material from the bottom: atom by atom, molecule by molecule or cluster by cluster [1,2].

1.5.1 Top-Down Approach

Nanoparticles are created by these methods from breaking up the bulk materials. Attrition, milling is a typical top-down approach. The bigger particles or structures are broken into very small pieces to reach into nanoscale. So the biggest problem is the imperfection of the surface structure. It is the well known conventional methods to prepare NPs. The top-down technique such as lithography can cause significant crystallographic damage to processed patterns and additional defects may introduce during etching [55]. Lithography can be understood through the concepts of writing and replication. Writing involves designing a pattern on a negative and replication involves transferring the pattern on the negative to a functional material. Among the several types of lithography, Photolithography uses different kinds of electromagnetic radiation which is currently used to manufacture computer chips and other microelectronic devices. Photolithography, as currently used, is not an effective tool for fabricating structures with features below 100 nanometers. Electron-beam lithography is a technique that employs beams of electrons to write, can produce some nanostructures with high resolution. Soft lithographic techniques such as printing, moulding and embossing, involve the physical or chemical deformation of the functional material to yield the desired structure. While soft lithography can be used to construct less planar nanostructures, it may be less precise than other techniques.

This approach most likely introduces internal stress, in addition to surface defects and contaminations. In addition to the lithography, ball milling and physical vapour deposition (PVD) are also under the top-down synthesis method of nanomaterials.

1.5.1.1 Lithography

Nanolithography is one of the most established techniques for making nanostructured materials and patterns. This technique is based on depositing, etching or writing on a surface features with dimensions on the order of nanometers. Lithography can be performed using light (optical or photolithography), electrons (electron-beam lithography), ions (ion-beam lithography) or X-ray (X-ray lithography) depending on the desired minimum feature size of the outputs. Figure 1.3 illustrates the schematic diagram of thermal photolithography process [1,55].

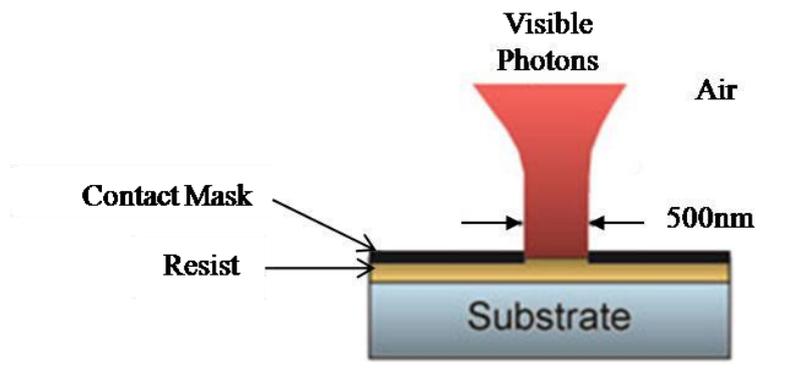


Figure 1.3 Schematic diagram of thermal photolithography process

Photolithography is the most common and widely used technique in applications requiring micron and submicron feature sizes, like electronic, integrated circuits manufacturing and microfluidic devices. With this technique, a design or pattern can be transferred at once on the surface of a device by exposure with light. Similarly, electron-beam, ion-beam and X-ray lithography use the exposure to beams of electrons, ions or X-ray for the design transfer. All the lithographic techniques involve multistep processes. As an example, here we describe the steps followed in the specific case of photolithography of a Si/SiO₂ substrate (Figure 1.4) and other

techniques follow a very similar process. The first step is to coat the surface of the desired substrate with a thin polymer layer of a positive or negative photoresist (Figure 1.4a) which is then covered by a predesigned, light-blocking mask and exposed to UV light (Figure 1.4b). After exposure, the cured photo-resist remains on the substrate as a protective coating and the uncured portions are removed by the developer (Figure 1.4c). This step is then followed by the etching of the substrate and the final removing of the photo resist (Figure 1.4d). The type of resist chosen allows having a direct duplication of the mask used (as in the case of positive resist) or inverse of it (negative resist) exactly like in the case of film photography developing.

The technical limits of photolithography are related to the wavelength of light used which also determines the smallest feature sizes achievable. A limitation is dictated by the lens characteristics: if the used wavelength is made too small, the lens simply absorbs the light in its entirety and do not allow curing of the photoresist. This implies that photolithography cannot reach the superfine sizes of some other technologies, such as electron beam lithography, as the wavelength of typical light, even UV lasers, is somewhat limited. Small-wavelength UV light (deep UV techniques) can now be employed to obtain finer nanostructures. A technology that allows for fabrication of much smaller nanostructures than photolithography is that of electron beam (e-beam) lithography. The use of an electron beam to draw a pattern nanometer by nanometer and expose an e-beam resist layer (usually made of a polymer) allows achieving incredibly small sizes (on the order of 20 nm). Even though this technique is much more expensive and time consuming than photolithography, the e-beam exposure is carried out line-by-line or dot-by-dot, unlike the photolithography by which the whole area of, e.g., 12-in. diameter Si wafer can be exposed all at once [1,2,55].

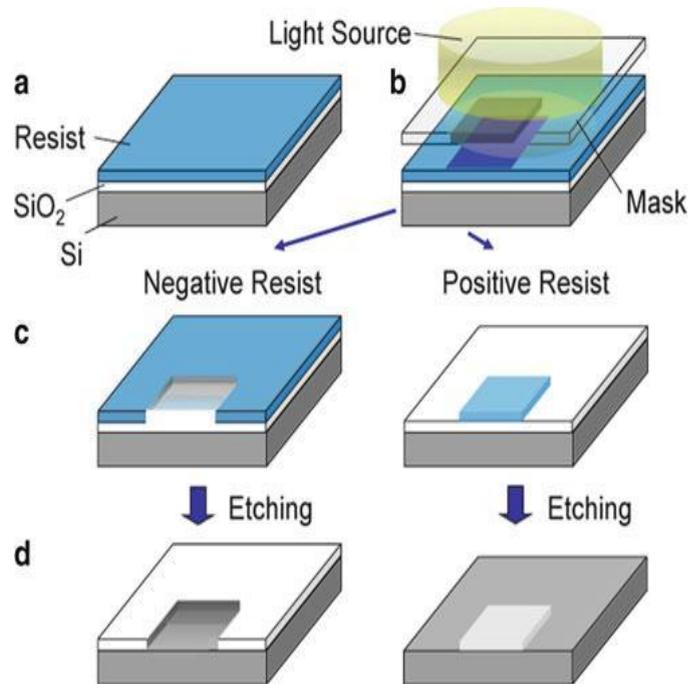


Figure 1.4 Photolithography steps of surface patterning [55]

1.5.1.2 Mechanical Milling Methods

Mechano-chemical synthesis or ball milling is a highly non-equilibrium top-down approach to synthesizing NPs. Nanoparticles are produced by grinding molecular precursors in a vial with grinding balls. There are two main advantages to mechanical milling. First is the ability to produce large quantities of product in a fairly short timeframe. The second is the ease at which the methods can be operated. These factors have contributed to making the technique fit for industrial applications. Also the generated thermal energy from the milling can facilitate chemical reactions including redox and formation reactions. The repeated deformation, welding and fracturing that occur in ball milling lead to an intimate mixing of the components in the atomic level. Compared to other methods, synthesis of metal based nanocomposites by ball milling offer advantages such as more uniform reinforcement

particle distribution and finer particle size, leading to stronger and more heat-resistant materials. Figure 1.5 shows the schematic diagram of the ball milling process.

The mechanisms responsible for the formation of nanocrystalline structures by mechanical attrition of single phase powders, mechanical alloying of dissimilar powders and mechanical crystallisation of amorphous materials are briefly considered and as follows [56-58],

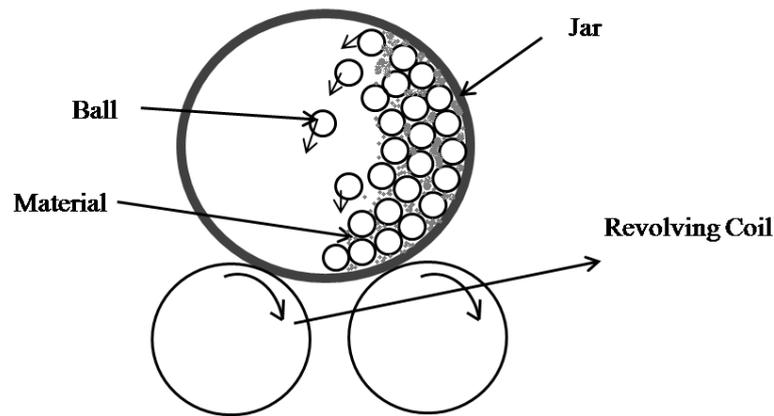


Figure 1.5 Schematic diagram of Ball milling process

Mechanical milling is typically achieved using high energy shaker, planetary ball or tumbler mills. The energy transferred to the powder from refractory or steel balls depends on the rotational (vibrational) speed, size and number of the balls, ratio of the ball to powder mass, the time of milling and the milling atmosphere. Nanoparticles are produced by the shear action during grinding. Milling in cryogenic liquids can greatly increase the brittleness of the powders influencing the fracture process. As with any process that produces fine particles, an adequate step to prevent oxidation is necessary. Hence, this process is very restrictive for the production of non-oxide materials since then it requires that the milling take place in an inert atmosphere and that the powder particles should be handled in an appropriate vacuum system or glove box. This method of synthesis is suitable for producing amorphous or

nanocrystalline alloy particles, elemental or compound powders. If the mechanical milling imparts sufficient energy to the constituent powders a homogeneous alloy can be formed. Based on the energy of the milling process and thermodynamic properties of the constituents, the alloy can be rendered amorphous by this processing.

This method, however, produces nanomaterials with high polydispersity, unusual cation distribution or vacancies and impurities. With the repeated fracture and re-welding of reagent powders, high defect densities are produced [56]. These issues are greatly influence the properties of the sample which can sometimes be less than the theoretical calculations, making reproducibility between batches near impossible [57]. Although, most ball milling synthesis methods involve grinding of dry powder precursors, the use of surfactants and solvent is becoming more common to improve homogeneity and eliminate impurity formation [58]. Impurities can also be introduced to the product from the reaction vial or milling balls. Finally, extensive milling times are often required to produce particles less than 20 nm.

1.5.1.3 Physical deposition

Physical deposition uses mechanical, electromechanical or thermodynamic means to produce a thin film of solid. Since most engineering materials are held together by relatively high energies and chemical reactions are not used to store these energies, commercial physical deposition systems tend to require a low-pressure vapour environment to function properly, most can be classified as physical vapour deposition (PVD).

Physical vapour deposition (PVD) is a collective set of processes used to deposit thin layers of material, typically in the range of few nanometers to several micrometers [59]. PVD processes are environmentally friendly vacuum deposition techniques consisting of three fundamental steps:

- Vapourization of the material from a solid source assisted by high temperature vacuum or gaseous plasma.
- Transportation of the vapour in vacuum or partial vacuum to the substrate surface.
- Condensation onto the substrate to generate thin films.

Different PVD technologies utilize the same three fundamental steps but differ in the methods used to generate and deposit material. The two most common PVD processes are thermal evaporation and sputtering. Thermal evaporation is a deposition technique that relies on vapourization of source material by heating the material using appropriate methods in vacuum. Sputtering is a plasma-assisted technique that creates a vapour from the source target through bombardment with accelerated gaseous ions (typically Argon). In both evaporation and sputtering, the resulting vapour phase is subsequently deposited onto the desired substrate through a condensation mechanism [60].

Deposited films can span a range of chemical compositions based on the source material. Further compositions are accessible through reactive deposition processes. The examples include co-deposition from multiple sources, reaction during the transportation stage by introducing a reactive gas (nitrogen, oxygen or simple hydrocarbon containing the desired reactant) and post-deposition modification through thermal or mechanical processing [61].

1.5.1.4 Laser Ablation

Laser ablation is a type of thermal evaporation method and is an efficient technique for nanomaterial fabrication because of less production of waste [62]. Laser ablation is the process of removing material from a solid (or liquid) surface by irradiating it with a laser beam. At low laser flux, the material is heated by the

absorbed laser energy and evaporates or sublimates. At high laser flux, the material is typically converted to plasma. When pulsed-laser radiation is focused on the surface of a solid target, it can be absorbed through various energy transfer mechanisms, leading to thermal and non-thermal heating, melting and finally ablation of the target. Laser ablation has shown itself as one of the most efficient physical methods for micro and nanofabrication due to the high resolution capability, low heat deposition in the target and high level of flexibility. On the other hand, the ablation of the target yields to an ejection of its constituents and to the formation of nanoclusters and nanostructures on the pulsed laser deposition (PLD) process. When the target is ablated in vacuum or in a residual gas, the nanoclusters can be deposited on a substrate placed at some distance from the target leading to the formation of a thin nanostructured film. The properties of synthesised nanostructures can be efficiently controlled by parameters of laser ablation (fluence, pulse duration, wavelength) and properties of the environment [61,62].

The laser pulse with pulse duration ranging from 30 ns to a few femtoseconds is focused to an energy density of 1-10 J/cm² vaporizing a few hundred angstroms of surface material. The evaporated flux contains neutral atoms, positive and negative ions, electrons, molecules, molecular ions and free radicals of the target material in both their ground and excited states. These vapours absorb incoming radiation as a result of which the particle acquires the kinetic energy of 1-5 eV and move in the direction perpendicular to the target. The particles then deposit on a substrate generally heated to allow for crystalline film growth. Laser beam interaction is a complex phenomenon. Energy of the laser photon beam is absorbed by the solid surface leading to electronic excitation. Thermal conductivity of the target solid is too low to dissipate energy in the short period of the laser pulse, photon energy converted

into the thermal and chemical energy. As a result, temperature of the order of 3500 °C is reached in a small volume of the target leading to instantaneous evaporation, ionization and decomposition of the material. The moving front of such collection of particles constituting plasma called a plume. The plumes expand rapidly having high pressure and deposit on the substrate forming a nanoscale material [62,63].

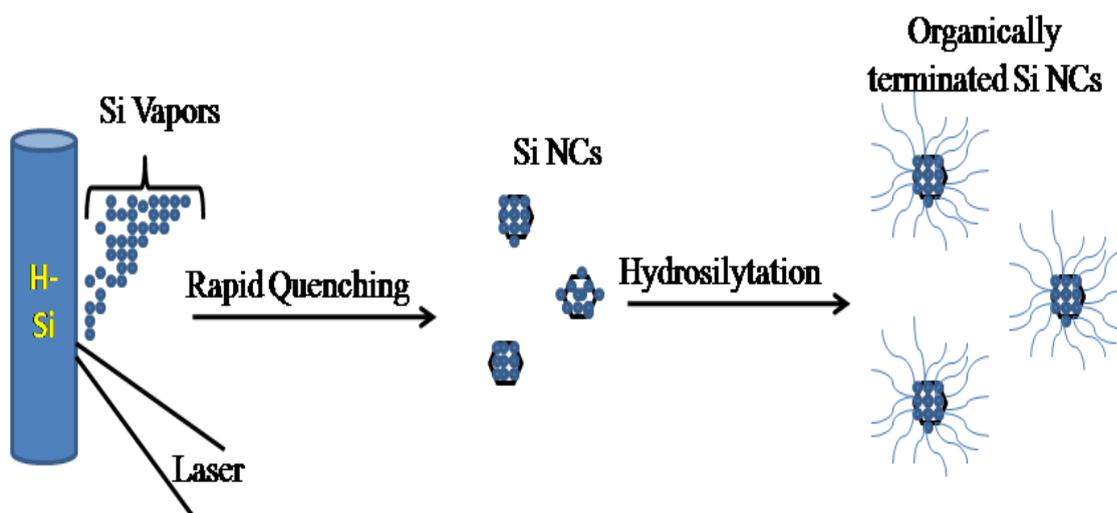


Figure 1.6 Schematic illustrations of the representative top-down approaches for the synthesis of free-standing silicon QDs by liquid laser ablation

The reactants used as a solvent for liquid laser ablation, surface passivated free-standing quantum dots (QDs) were prepared in one step. Instead of a two-step process which is a common method to produce organic-capped QDs is attractive because of automatic synthesis process. Figure 1.6 illustrates the one-step process of synthesizing free-standing silicon QDs. A hydrogen-terminated silicon substrate immersed in 1-alkene was ablated with a laser beam. The silicon vapours and clusters produced by laser ablation assemble immediately to reduce the surface free energy, yielding the formation of NCs. This facile route allows fabrication of colloidal silicon QDs in one step without waste. But, it has disadvantages such as low product yield and less flexibility in tuning of the emission due to a rapid reaction of 1-alkene preventing the growth of NCs [63].

1.5.1.5 Thermal Evaporation

Thermal evaporation is one of the simplest and most popular synthesis methods and it has been very successful and versatile in fabricating nanomaterials with various characteristics. The basic process of this method is sublimating source material(s) in powder form at high temperature and a subsequent deposition of the vapour in a certain temperature region to form desired nanostructures. Figure 1.7 represents the schematic diagram of thermal evaporation process set-up.

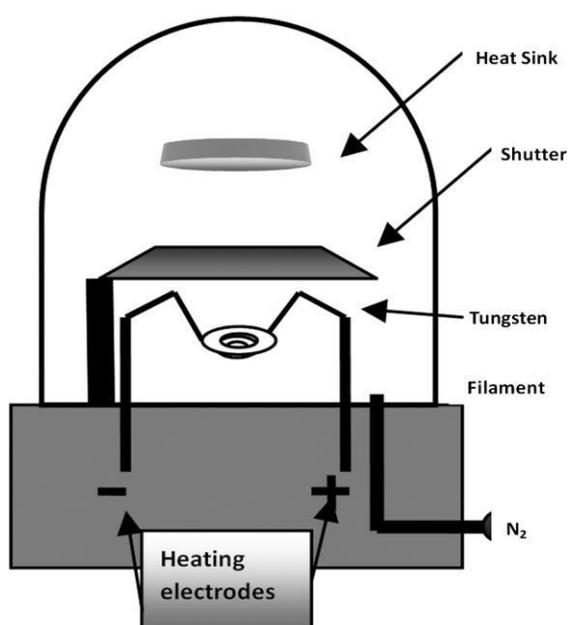


Figure 1.7 Schematic diagram of thermal evaporation process

The material to be deposited is loaded into a heated container called a crucible. The crucible is resistively heated by applying a large current. As the material in the crucible becomes hot it gives off a vapour in which atoms travel in straight lines until they strike a surface where they accumulate as a film. The substrates for collecting the desired nanostructures are usually placed down-stream following the carrier gas. The substrates can be silicon wafer, poly-crystalline alumina or single crystal alumina [60,61].

During the experiments, the system is first pumped down to around 10^{-2} Torr. Then, the furnace is turned on to heat the tube to the reaction temperature at a specific heating rate. An inert carrying gas, such as argon or nitrogen is then introduced into the system at a constant flow rate to bring the pressure in the tube back to 200-500 Torr (different pressures are required by different source materials and final deposited nanostructures). The reaction temperature and pressure are held for a certain period of time to vapourize the source material and achieve a reasonable amount of deposition. Source materials can be vapourized at the high temperature and low pressure condition. The vapour is then carried by the inert carrying gas down to the lower temperature region, where the vapour gradually becomes supersaturated. Once it reaches the substrate, nucleation and growth of nanostructures will occur. The growth is terminated when the furnace is turned off. The system is then cooled down to room temperature with flowing inert gas [61].

The thermal evaporation process is basically a physical vapour deposition process and has been successfully used for synthesizing a variety of oxide and non-oxide nanobelts and nanowires. Moreover, this system can also be used for chemical vapour deposition (CVD) by simply applying reaction gases instead of the carrier gas and placing substrates in the middle of the tube. For example, multi-wall and single-wall carbon nanotubes have been successfully fabricated in this system using hydrogen and methane/acetylene as reactants. Metal catalysts, such as gold, tin, copper, etc. have also been used to achieve size control and alignment. All though thermal evaporation is one of the simplest and most popular synthesis methods, thermal evaporated films have a very poor ability to cover the complex pattern which yields a discontinued film on the vertical wall patterns. Besides this, it is also difficult to produce well-controlled alloys by evaporation [60].

1.5.1.6 Sputtering Deposition

Sputtering is the primary alternative to the thermal evaporation for metal film deposition in thin film fabrication technique. This technique has better step coverage than thermal evaporation and is much better at producing layers of compound materials and alloys. In sputtering process, the high energy ions in plasma of an inert gas strike a target containing the material to be deposited. Because of the momentum exchange between the ions and the atoms in the target, material is ejected from the target. The amount of material ejected from each ion collision is dependent on the target material, yielding a highly material with specific deposition rate. In the case of deposition of elemental metals, simple dc sputtering is usually favoured. During the deposition of insulating materials RF plasma must be used. By the addition of reactive gasses e.g. oxygen in the plasma during the sputtering process, a thin film with atoms incorporated from the reactive gas can be achieved. Figure 1.8 represents the schematic diagram of sputtering deposition technique [60].

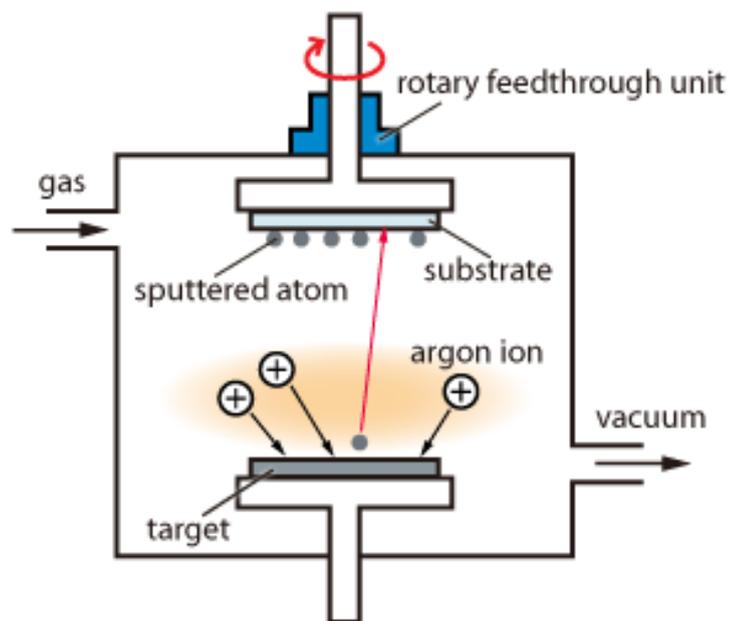


Figure 1.8 Schematic diagram of sputtering deposition

Before starting the sputtering process, the parts in the vacuum chamber for coating are first heated. They are then ion etched by bombardment with argon ions. This renders the metal surface pure and clean, free from any atomic contamination - an essential condition for coating adhesion. Then, a high negative voltage is applied to the sputtering sources which contain the coating material. The resulting electrical gas discharge leads to the formation of positive argon ions that are accelerated in the direction of the coating material which is atomised by the bombardment. The evaporated particles of atomised coating material are deposited on the substrate. The result is the deposition on the substrates of a thin compact coating with the desired thickness and structure. High step coverage, medium pressure process and synthesis of different alloys and compound materials are the advantages of the sputtering method [1,60,61].

1.5.2 Bottom-Up Approach

In general, bottom-up is widely used and less energy intensive. Bottom-up approach is nothing new in materials synthesis. Typical materials are building up atom by atom on a large scale with control of size and shape of the materials. This approach is just opposite of top-down approach. The materials are synthesised, taken care of it from atomic levels. So the nanomaterials are formed from the bottom levels atom by atom, molecule by molecule or cluster by cluster. In organic chemistry or polymer science, we know polymers are synthesised by connecting individual monomers together. In crystal growth, growth species such as atoms, ions and molecules, after impinging onto the growth surface, assemble into crystal structure one after another. It plays an important role on fabrication and processing of nanostructure and nanomaterials. Bottom-up approach also promises a better chance to obtain nanostructures with less defects, more homogeneous chemical composition

and better short and long range ordering. This is because the bottom-up approach is driven mainly by the reduction of Gibbs free energy, so that nanostructures and nanomaterials such produced are in a state closer to a thermodynamic equilibrium state [1,64,65].

Both approaches play very important role in modern industry and most likely in nanotechnology as well. There are advantages and disadvantages in both approaches. The biggest problem with top-down approach is the imperfection of surface structure and significant crystallographic damage to the processed patterns. These imperfections lead to extra challenges in the device design and fabrication. But this approach leads to the bulk production of nanomaterials. Attrition or Milling is a typical top-down method in making NPs where as the colloidal dispersion is a good example of bottom-up approach in the synthesis of NPs [2].

Bottom-up approach allowed the advantages of individual building blocks into integrated materials at the atomic/molecular level. The use of this protocol is expected to result in the discovery of new multifunctional materials allowing for wide range of applications. Several methods have been developed to synthesis of NPs in bottom-up approach. The method used to synthesis can be categories into liquid phase synthesis or vapour phase synthesis. The most common method is liquid phase synthesis. There are various methods belong to liquid phase synthesis like sol-gel method, hydrothermal, simple reaction methods (aqueous solution) and polyol method etc. But in vapour phase synthesis, the chemical vapour deposition is the most common method.

1.6 Liquid Phase Synthesis Methods

1.6.1 Sol-Gel Process

The terms sol-gel processing involves the transition from a sol (very finely divided solid particles dispersed in a liquid which will not settle out) to a gel (a dispersion of a liquid throughout a solid matrix). It is a long established process with the key controlling processing steps being sol formation and gelling, drying, curing and sintering. Starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds such as metal alkoxides. Typically, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension. This suspension can be further processed to make materials in different forms from thin films and aerogels to nanocomposites and NPs. The reactions involved in the sol-gel method based on the hydrolysis and condensation of metal alkoxides can be described as follows:



Where R is the alkyl group and M is the metal ion. The advantages of the process are perceived to be (i) low processing temperatures (ii) high homogeneity and purity of products and (iii) versatility with respect to the materials that can be formed. In particular, sol-gel process offers unique opportunities to generate gels of organic-inorganic materials [64]. The majority of sol-gel focus has been on producing glass ceramic powders, coatings and thin films. The increasing interest for these methods is that particles of high purity, controlled particle size and new composition may be produced. Particles of interest range from alumina, zirconia, titania and silica to titanates, phosphors, pigments and encapsulated pigments, optical materials, ferroelectrics and catalyst supports [2,65,66].

The new generation of sol-gel produced hybrid materials was initiated by the preparation of non-crystalline organic–inorganic materials. The physical and mechanical properties of these materials can be tailored by manipulating the ratio of inorganic–organic components. Resultant „super-repellent“ surfaces are based on a physical structure rather than chemical character [65]. Another new group is biological composite, an organic dye could be entrapped in a porous silica cage led to the greater aspiration of incorporating biologically active materials in inorganic matrices to control reactions arising from the transport of materials in or out of the matrix [66]. In the formation of sols, it is desirable to achieve a homogeneous colloid matrix. Material properties (including particle size) may be controlled by pre-reacting the slower reactive components or chelating the faster components to achieve homogeneity. Mechanical treatments and the use of ultrasound to generate a more homogeneous distribution of the nucleation sites for NPs have been used. The drying stage is perhaps the most critical in influencing the properties of the final product (especially in catalyst supports, films and coatings). The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.

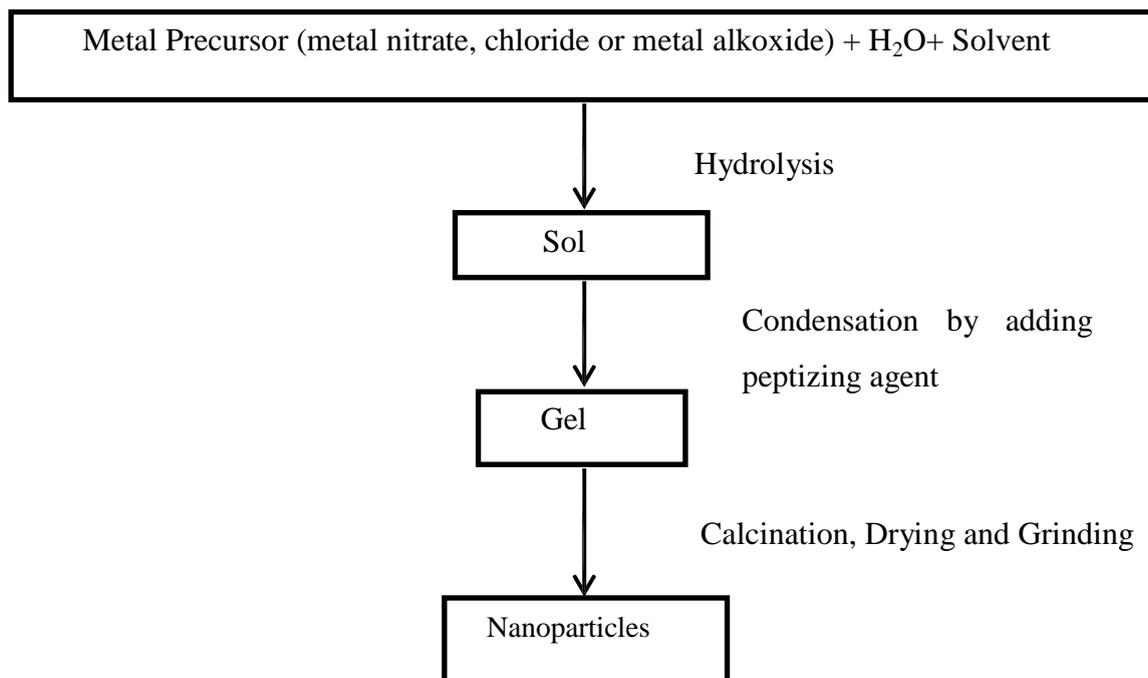


Figure 1.9 Flow chart of a typical sol-gel process

Advantages of the sol-gel process are that it is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth metals can be introduced in the sol and end up uniformly dispersed in the final product. The main advantage is one can get uniform NPs by any bottom up approach [65,66].

1.6.2 Solvothermal/Hydrothermal Process

Solvothermal synthesis is a process that utilizes single or heterogeneous phase reactions in a particular solvent media at elevated temperature ($T > 25\text{ }^{\circ}\text{C}$) and pressure ($> 100\text{ kPa}$) to crystallize anhydrous inorganic materials directly from solution. From the solvothermal synthesis, variety of nanomaterials can be prepared such as metals, semiconductors, ceramics and polymers. The process involves the use of a solvent under moderate to high pressure (typically between 1 atm and 10,000 atm) and temperature (typically between $100\text{ }^{\circ}\text{C}$ and $1000\text{ }^{\circ}\text{C}$) that facilitates the interaction of precursors during synthesis. If water is used as the solvent, the method is called

“hydrothermal synthesis”. The synthesis under hydrothermal conditions is usually performed below the supercritical temperature of water (374 °C). Figure 1.10 represents the schematic diagram of solvothermal process set-up. The process can be used to prepare different geometries including thin films, bulk powders, single crystals and NCs. In addition, the morphology (sphere (3D), rod (2D), or wire (1D)) of the crystals formed is controlled by manipulating the solvent supersaturation, chemical of interest concentration and kinetic control. The method can be used to prepare thermodynamically stable and metastable states including novel materials that cannot be easily formed from other synthetic routes [67-71].

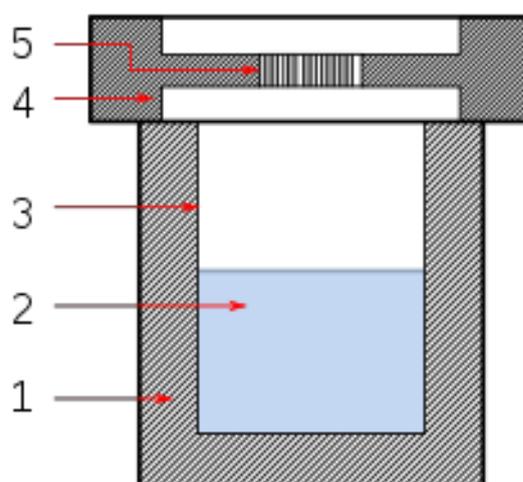


Figure 1.10 Schematic diagram of solvothermal synthesis set up: (1) stainless steel autoclave, (2) precursor solution, (3) Teflon liner, (4) stainless steel lid and (5) spring

Solvothermal reactions using non-aqueous solvents have also been considered to be useful for various materials and chemical processing. Often non-aqueous solvent may contain impurity water and/or by product water during the processing. Similarly, hydrothermal reactions may include non-aqueous components during their processing. Therefore, hydrothermal and solvothermal are overlapping in many cases. Moreover, hydrothermal/solvothermal reactions can contain almost all species of liquids, gases

and solids. Therefore, they are having the following features: Wide variety of liquid media [67], additional gases and solids [68], wide variety of temperature and pressure [69], static and dynamic [70], flowing and circulating systems [71]. Figure 1.11 illustrates the flow chart of a typical sol-gel process.

1.6.2.1 Advantages

(1) The most materials can be made soluble in a proper solvent by heating and pressurizing the system close to its critical point. (2) Significant improvement in the chemical activity of the reactant and in producing materials that cannot be obtained from other chemical route. (3) Products of intermediate state, metastable state and specific phase may be easily produced novel products of metastable state and other specific condensed state. (4) Easy and precise controlled reaction.

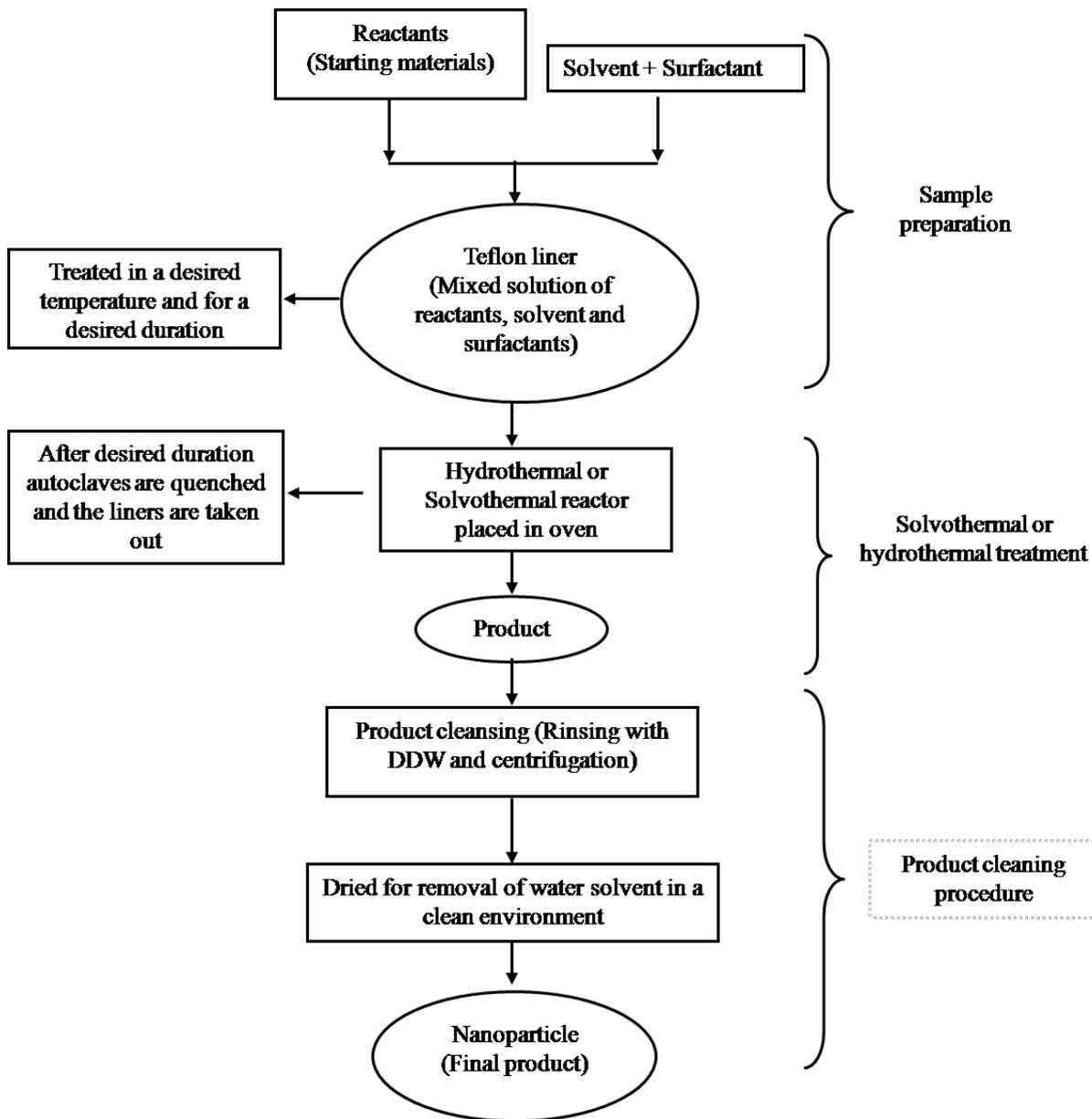


Figure 1.11 Flow chart of the hydrothermal and solvothermal method

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