Chapter 2

Basic Introductory Concepts

Current research has been focused on understanding and tuning the functional properties of metal oxide (MO) nanomaterials with finest physical and chemical (physico-chemical) properties that are suitable for specific applications. The control over the properties of MO nanomaterials is very essential as it determines the wide range applications of these materials. The optimization of physical and chemical properties of nanomaterials can be done by tuning its size, shape, phase composition, morphology and surface structure. The precise control over the above said factors helps to achieve high-throughput MO nanoparticles with desired property and application [61]. To have a good control over the properties of nanomaterials synthesized through bottom-up solution based methods, the process parameters like precursor, surfactant, mineralizer/chelating agent, solvent and its pH and crystallization temperature has to be optimized [62]. In the present chapter, different types of synthesis methods and the various process parameters which can be controlled to obtain desired structure, morphology and surface properties of MO nanomaterials have been
2.1 Synthesis Methods of Transition Metal Oxide Nanomaterials

Generally two techniques have been adopted for the synthesis of nanomaterials namely; top-down (physical methods) and bottom-up (chemical methods) techniques (Fig. 2.1). In top down technique, bulk materials are brought down to nanometer size by means of physical methods such as ball milling, lithography, laser ablation, inert gas condensation, electro spraying, and laser pyrolysis [63, 63–67]. However in bottom up approach the nanomaterials are obtained through coalescence of atoms or molecules from gas/liquid phase.

![Diagram of top-down and bottom-up approaches](image)

Figure 2.1: Schematic of top-down and bottom-up approaches, [adapted from [68]]

On comparing, the liquid phase synthesis methods is more convenient technique to fabricate nanomaterials with desired properties by controlling the nucleation rate through several process parameters which in turn determines its
structure, morphology, particle size, and surface defects [61, 69]. Thus the process parameters like precursor, surfactant, mineralizer/chelating agent, solvent and its pH and crystallization temperature has to be optimized during the synthesis of nanomaterials through bottom-up liquid phase synthesis methods. The major liquid phase synthesis methods like hydrothermal, microemulsion, sol-gel and chemical precipitation [62] are discussed under this section.

2.1.1 Hydrothermal method

Hydrothermal method is generally used to synthesize homogenous / composite nanostructures of high purity, good crystallinity, uniform size distribution, controlled morphology and microstructure. In this method, ceramic / non-ceramic oxide nanostructures are synthesized by taking a mixture of precursor solution (aqueous / non-aqueous) and mineralizer in an autoclave and then it is heated to a temperature above the boiling point of solvent under high pressure conditions. This high temperature and pressure hydrolyze water and dehydrate the metallic salts which results in the formation of metal oxides having low solubility in the solvent. The morphology and crystallinity of the as synthesized powders is determined by the hydrothermal temperature and pressure [70]. The increased solubility of the metal salt precursor can lead to the formation of crystalline materials at substantially reduced reaction temperatures without any post annealing treatments. The process is referred to as hydrothermal when water is used as the solvent and as solvothermal when solvent used is organic. Hydrothermal method facilitates the possibility to produce various metal (Pd, Pt, Ag, Au, Si, Ge, Cu, Co, Ni), alloy (Pt-Ni, Ni-Cu, Ag-Pd, Au-Pt), semiconductor (CdS, ZnS, HgS), composite (hydroxyapatite, CeO$_2$-ZrO$_2$, C-TiO$_2$)
and metal oxide (ZnO, CuO, NiO, TiO$_2$, CeO$_2$, ZrO$_2$, Al$_2$O$_3$, Co$_3$O$_4$), nanostructures with modified physico-chemical properties by controlling process parameters such as reaction temperature, pressure, process duration, solvent, pH, type of precursor and mineralizer, precursor concentration etc. Nanostructures fabricated through hydrothermal method are highly crystalline and homogeneous, and at a relatively low process temperature in liquid environments the process results in well dispersed nanoparticles with narrow size distribution. This technique leads to direct conversion of molecular precursors to crystalline metal oxide nanostructures with well-controlled dimensions and morphology. Besides, it is difficult to control the structure and composition of complex metal oxides.

Du et al. [71] reported the synthesis of Pt nanoparticles with excellent electrocatalytic properties by a hydrothermal method using P123 as reducer and stabilizing agent. Following a hydrothermal method, Kometani et al [72] synthesized Ag nanoparticles from the aqueous solution of silver nitrate, polyvinyl pyrrolidone (stabilizer), and sodium citrate (reducing agent) and found that reaction temperature of 300 °C and pressure of 20-23 MPa are the optimum conditions to obtain fine and homogeneous Ag nanoparticles. Hydrothermal method brings the possibility of synthesizing bimetallic alloys by the simultaneous addition of two metallic precursor solutions. For instance, Carpenter et al [73] explained the solvothermal synthesis of Pt-Ni alloy from platinum and nickel acetylacetonates using N, Ndimethylformamide (DMF) as both solvent and reducing agent and established that this alloy is suitable as catalyst for oxygen reduction reaction in fuel cell cathodes with 15 times more activity than the normal Pt/carbon catalyst. Cao et al [74] reported the hydrothermal
synthesis of optically active CdS nanoparticles with controllable size, phase, and morphology obtained by varying the reaction time and surfactant concentration. Zhang et al [75] reported a hydrothermal strategy for the controlled synthesis of CeO$_2$-ZrO$_2$ nanocomposites of cauliflower like morphology by using urea as the mineralizer. Reports on synthesis of zirconia and nickel oxide nanoparticles by hydrothermal method shows that process parameters and reaction temperature inside the autoclave have significant effect on their structure and morphology [76]. Kolen'ko et al [76] showed that at low hydrothermal temperature, pressure, precursor concentration and processing time, amorphous zirconia is formed from zirconyl nitrate precursor due to low recrystallization speed. But on increasing the processing time, crystalline monoclinic zirconia is formed. However tetragonal zirconia is formed at higher hydrothermal temperature, pressure, precursor concentration and low processing time. Wang et al [77] demonstrated that various concentrations of ammonium fluoride (NH$_4$F) mineralizer is more effective in the formation of size controlled ZrO$_2$ nanorods than other ammonium halide (NH$_4$Cl, NH$_4$Br) mineralizers due to increased solubility of zirconium precursor in presence of fluoride ions. Chintaparty et al [78] found that nature of precursor can cause variation in nucleation rate and hence tunes the size and electrical properties of zirconia nanostructures. The same group [79] has studied that effect of calcination temperature on zirconium hydroxide obtained through hydrothermal method. It is found that at low crystallization temperature cubic phase is formed and at intermediated temperatures (600-800 °C) both cubic (67 %) and monoclinic (33 %) phase co-exist. However at high temperature (1100 °C) monoclinic phase zirconia is formed. This shows that zirconia phases are temperature dependent and hence
determines its dielectric constant. Reports show that the surface morphology, porosity and surface area of NiO nanoparticles greatly influence its specific capacitance. By varying surfactants, the porosity, morphology and average grain size of NiO nanoparticles can be tailored to get desired capacitance [80]. Reports shows that the theoretical specific capacitance of Ni(OH)$_2$ is higher than NiO. The specific capacitance of 3D flower like $\beta$-Ni(OH)$_2$ is higher because of its larger surface area and improved pore size which enhance the transmission rates of electrons and ions [81].

### 2.1.2 Microemulsion method

Microemulsion method enables the fabrication of homogenous and monodispersed nanostructures of metal, metal oxide, core shell, and composite by regulating the structural characteristics through variation of several process parameters. This technique depends on the thermodynamically stable system formed from the combination of polar phase (water), non-polar phase (oil), and a surfactant. The surfactant forms an interfacial layer which separates the polar and non-polar phase in a microemulsion formed by a mixture of oil-in-water or water-in-oil which results in the formation of micelles. The micelles consisting of nanosized water droplets surrounded by hydrophilic head of surfactant with its hydrophobic tail pointing outwards act as nanoreactors during nanoparticle synthesis. In the confined region, the nanoreactors regulate the nucleation and particle growth with unique structure and excellent properties. Generally for the synthesis of nanostructures, one microemulsion method and two microemulsion methods are adopted. In one microemulsion method, a triggering agent initiates the nucleation of single microemulsion. Besides, the nucleation
can also be initiated by adding another reactant to the emulsion containing the first precursor. The trigger/reactant diffuse through the interfacial layer and initiate the chemical reaction between the precursor and trigger/reactant inside the reactor to produce desired nanoparticles. However in two microemulsion method, the two microemulsions carrying the reactants separately are mixed together in specific ratio. The collision between two micelles of sufficient energy results in the mixing of the two micellar components and once the critical number of molecules is reached inside the micelle nucleation is initiated resulting in the formation of nanoparticles [82]. Through microemulsion method, it is possible to obtain diverse range of nanoparticles with precise control over the morphology and particle size by varying the nature and amount of surfactant. But this technique requires a high concentration of surfactant for the formation of microemulsion and consequently the presence of residual surfactants in the system adversely affects the particle properties. Moreover stability of microemulsion is influenced by parameters such as high temperature and pH and these conditions result in uncontrolled grain growth and particle morphology.

Reports show that physiochemical properties of nanostructures can be tailored through specific control over process parameters like concentration of precursor, surfactant, mineralizer, nature of micelle formation and calcination temperature. Extensive work has been reported on the synthesis of metal (Cu, Pt, Pd, Au), metal sulphide (CdS, CuS, Cu$_2$S, PbS), metal salts (sulphate, carbonate, halide), composite (Au-Ag, Pd-Pt, CuO-ZrO$_2$, CdS-ZnS, CdSe-ZnS, CdSe-ZnSe, CdS-CdSe, CdS-Ag$_2$S) and metal oxide (NiO, SiO$_2$, TiO$_2$, ZrO$_2$, Fe$_2$O$_3$) nanostructures through microemulsion method. The surfactant regulates the nucleation rate during the synthesis of various types of nanostructures.
Besides, the structure and morphology can be tuned by varying the reaction temperature [88], water to surfactant molar ratio (R_w) [89–91], pH [92], type of surfactant [93], nature of mineralizer/reducing agent [91], and calcination temperature [94].

### 2.1.3 Sol-gel method

Sol-gel method, a solution based synthesis technique, is most suitable for the preparation of homogenous inorganic and ceramic metal oxide nanomaterials with high purity and well controlled properties [95]. In this technique, a sol is formed from precursor solution through hydrolysis and partial condensation of monomeric units which on further polycondensation forms a 3D network structure (gel). The so-formed gel is then subjected to syneresis/aging which is followed by drying to form xerogel/aerogel. Generally in the synthesis of metal oxide nanoparticles, a sol is formed from the aqueous solution of inorganic salt/alkoxide precursors. In the case of alkoxide precursor, the alkoxy group is replaced with hydroxyl group which on condensation form oxygen bond between metallic ions (M-O-M, metaloxane bonds) to produce a sol. As the reaction proceeds, polymerization of the sol happens through mutual aggregation and it forms a cross-linked 3D network structure in solution called gel. The gel is then allowed for aging, where the condensation process continues in the gel network to form a solid mass which is followed by shrinkage of the gel matrix and the progressive expulsion of solvent. Now the gel, which is devoid of solvent and other volatile liquids, is dried at different conditions to generate various morphologies such as xerogels or aerogels. Finally dehydration of the gel to remove surface hydroxyl groups is carried out by calcina-
tion at higher temperatures and the final crystalline material is obtained. For preparing dense ceramics and glasses this step is followed by densification at temperatures higher than 800 °C [96]. To synthesize the metal oxides from its salt, a chelating agent (for instance citric acid) is used for the hydrolysis of metal ions in aqueous solution. The hydrolysis takes place through the coordination of water molecules with the metal via electrons in their bonding orbitals. The charge on the metallic ion, pH and nature of the solvent (aqueous / non-aqueous) determines the rate of hydrolysis. In the case of less reactive metallic ions in aqueous solution the hydrolysis rate can be controlled through pH. The metal oxides can be obtained directly by heat treatment of metallic salt solution which result either in precipitation of the original metal salt, or amorphous oxides / hydroxides. This approach results in larger crystals and this can be avoided by using chelating agents to form stable aqueous metal complexes [97]. The hydrolysis and condensation of metal ions is controlled by organic additives / chelating agents like glucose, fructose and citric acid [98, 99].

The method offers many advantageous during the synthesis of nanoparticles such as homogeneity of the product up to atomic scale, control over composition and structure, high purity, and it can be scaled up for large scale production [100]. Moreover the choice of several synthesis parameters such as precursor, catalyst, calcination temperature, pH value, additive to precursor molar ratio etc. permits the synthesis of semiconductor nanoparticles (CdS, CdSe, ZnB₂) [101], magnetic alloy nanoparticles (Fe-Co, Fe-Ni, Co-Ni) [102, 103], composite nanoparticles (PbTiO₃) [104], and metal oxide nanoparticles (ZnO, NiO, SiO₂, ZrO₂, TiO₂, SnO₂, Ta₂O₅). The type of precursor, hydrolysis catalysts, organic additives and molar ratio of precursors [99, 105]
and calcination temperature [106, 107] used in a sol-gel method has a significant effect on the morphology, crystalline size and phase stability of ZrO$_2$ and NiO nanoparticles. For instance, use of chloride precursor promotes the stability of monoclinic phase with formation of bigger sized ZrO$_2$ nanoparticles [108]. However, in case of nitrate salts, nitrate ions prevent the nucleation and growth of monoclinic domains and reduce the tetragonal to monoclinic phase transformation rate [109].

### 2.1.4 Chemical precipitation method

Chemical precipitation method is a simple and cost effective method commonly employed for the synthesis of micro and nanostructured materials of metals, semiconductors, metal oxides and composites with specific chemical composition. Generally in precipitation method, the products of precipitation are sparingly soluble metal ions formed under supersaturated conditions and through suitable chemical reaction nucleation can be initiated which results in the formation of large number of particles. The metal hydroxides so formed will have low solubility in aqueous / non-aqueous solvent. Since the nanoparticles are in metastable state, its size and morphology depends on Oswald ripening and coarsening of the particles [100]. The structure and morphology of the nanostructures can be tuned by using surfactant. The surfactant stabilizes the metal ions against agglomeration and directs the growth of nanoparticles along preferred crystallographic directions [110]. The hydroxides obtained can be separated from the solution by centrifugation / filtration. The unwanted by-products from the reaction are washed away during this process. Depending on the complexity of the final product, precipitation reaction can be either
direct precipitation or co-precipitation. In direct precipitation the product contains one or two elements and the reaction is straightforward (e.g., metal and metal oxides) precipitating a single species. However, in co-precipitation the products are complex (e.g., ternary or quaternary oxides) due to simultaneous precipitation of multiple species [100].

Reports show that the structure and physiochemical properties of nanostructures [61, 111–118] can be tailored to suit specific applications by controlling the process parameters such as precursor, solvent, mineralizer, concentration of precursor / mineralizer [26, 111], pH [119], surfactant and calcination temperature [120]. The surfactants act as structure directing agents through its stabilizing action and thereby control the phase, crystalline size and structure of ZrO$_2$ and NiO nanoparticles [52, 54, 110, 121]. Besides, higher precursor concentration can promote the formation of crystalline molecules with a larger particle size [119, 122]. Reports show that low temperature calcination of hydrous amorphous zirconia stabilizes the tetragonal and monoclinic phase zirconia nanoparticles [123], whereas raising the calcination temperature enhances particle size [122, 124, 125] and thereby stability of monoclinic phase [119].

### 2.2 Fabrication of thin films through solution based techniques

Generally thin solid films refer to a layer of material of thickness ranging from few nanometers to several micrometers deposited on a substrate. There are two categories of thin solid films: passive and active films. Passive thin films
serve as protective/aesthetic/decorative coatings applied on a structure to protect it against adverse environments and mechanical forces from corrosion and surface damage. However active thin solid films respond to specific triggering effects like heat, light, and contact with gases and biological analytes and generate a response for energy conversion, sensing and mechanical actuation. Hence suitable combination of active and passive thin films results in thin film device such as thin film solar cells, transistors, thermoelectric devices, sensors and actuators. Deposition of high-$k$ and p-type thin film metal oxides can be achieved by physical and chemical evaporation-based techniques like sputtering and chemical vapor deposition, as well as by solution-based wet chemistry methods. Out of these techniques, physical and chemical vapor deposition routes are well analyzed and would produce uniform and intact films. But controlling the correct stoichiometry in these techniques is quiet challenging and ultra-high vacuum working environment is required. However solution processed mechanical techniques like spin, spray and dip coating are of low cost and at the same time provide better control over the stoichiometry of the metal oxide thin film. To achieve a thin film with desired composition through solution based techniques, the feedstock for film fabrication should be prepared using effective solvent and surfactants/bindners to control solubility of precursor, surface tension and viscosity.

### 2.2.1 Spin-coating technique

Spin coating is a non-vacuum based mechanical technique employed for thin film deposition on a rotating substrate. Using this fast and simple method, homogeneous films can be deposited on flat substrates. First the precursor re-
quired for desired film fabrication is dissolved in a suitable solvent. Then the homogenous precursor solution taken in a syringe or pipette is dispensed onto the center of a substrate kept on the spin coater. The spin coater is allowed to rotate at a controlled speed to ensure a slow outflow of the solution to cover the entire substrate surface thus leaving a thin deposition of the precursor solution on the substrate. The film thickness and its uniformity are determined by the ramping rate and final speed of the spin coater. After deposition, the film is dried and annealed at desired temperature to evaporate the organic solvent residues. This process has to be repeated to obtain thin films of desired thickness. In this technique, the film thickness depends on: feedstock solution viscosity, concentration, density and its evaporation rate; nature of substrate (hydrophobic/hydrophilic) determines the coverage of the dispensed feedstock solution during spinning; and surfactant which facilitate the complete coverage of dispensed feedstock solution. Besides, during deposition as the substrate starts to spin the dispensed feedstock solution flows radially due to the action of centrifugal force and the extra feedstock solution spun off the substrate. Hence by increasing the spin speed, the centrifugal force increases which results in very thinner fluid film. The environmental humidity and temperature determines the evaporation rate of the film. If the solvent dries very fast before the dispensed solution covers the entire substrate or if the viscosity change significantly as the feedstock solution spreads over the substrate the as-deposited film will not be uniform. This can be avoided through relatively slow drying rate of the dispensed solution which facilitates the fluid to cover the substrate with constant viscosity.

Spin coating is an efficient method for the fabrication of ultrathin ZrO$_2$ thin
film with controllable morphology and thickness. Chang et al reported that the porosity/smoothness and thickness of zirconia thin film can be controlled by changing the concentration of precursor solutions [126]. ZrO$_2$ thin films with high thermal stability and improved electrical properties can be fabricated through sol-gel based spin deposition technique. You et al [127] demonstrated that amorphous ZrO$_2$ thin films fabricated by sol-gel method were thermally stable up to annealing temperatures of 900 °C. Chu et al [128] demonstrated the integration of MIM capacitor device with high-$k$ ZrO$_2$ thin film of thickness 9.5 nm on a flexible polyimide substrate via spin coating method. Besides, the as-deposited ZrO$_2$ film subjected to oxygen plasma treatment and subsequent annealing exhibited low leakage current and maximum capacitance density (13.3 fF/µm$^2$). Further heterogeneous layer NiO$_x$/Al$_2$O$_3$ deposited on p$^+$-Si substrate through sol-gel technique possessed good electrical response to serve as TFT with low operating voltage of 3.5V and hole mobility of $\sim$ 25 cm$^2$V$^{-1}$s$^{-1}$ [40].

### 2.2.2 Dip-coating technique

Dip coating technique is based on the deposition of a liquid film on a substrate through precise and controlled withdrawal of the substrate from a solution using dip coater. The stages involved during dip coating process are: immersion, dwelling, withdrawal, drying and curing (optional). During thin film deposition first the substrate is fully/partially immersed into a solution at controlled speed under controlled temperature and atmospheric conditions. For short period of time, the substrate will remain in the solution and then it will be withdrawn from the solution at a constant speed and then dried and annealed to remove the organic residues. The film thickness depends on: initial fictionaliza-
tion of the initial substrate surface; immersion time; withdrawal speed; viscosity; number of cycles dipped; solution composition, its concentration, temperature, number of solutions in each dipping sequence and environment humidity.

This method of film fabrication is quite simple, inexpensive and suitable for fabrication of heterogeneous thin film with complex structures. The multilayered film ZnO/ZrO$_2$/ITO/glass fabricated through dip coating technique is found to be transparent with 60-85 % transparency in the visible region and exhibited field-effect transistor characteristics [129]. ZnO/ZrO$_2$ multilayer deposited on SiO/Si wafer too showed good transistor characteristics attributed to reduction in leakage current by high-$k$ ZrO$_2$ layer. The electrical response of thin film transistor with improved field effect mobility, low threshold voltage and high on/off current ratio is possible by introducing hybrid film PMMA-ZrO$_2$ between ZnO layer and SiO/Si wafer [130].

### 2.2.3 Spray technique

Solution based spray coating technique is quite suited for high-speed automated large scale production of thin and thick films. In general there are three main processing steps during film fabrication which includes: atomization; aerosol transport of the droplet; and then droplet evaporation and drying on the substrate. The atomization step generates droplets of feedstock spray solvent and the carrier gas transfer the atomized drop of feedstock to the substrate. The size of the droplet is determined by the atomizer and carrier gas pressure. If the carrier gas pressure is too low then the droplets fall down instead of reaching the substrate. As the droplet reach the substrate, the substrate has to be maintained at optimum temperature (depends on the boiling point of the sol-
vent). This is necessary for the droplet to evaporate at optimum period and then gets dried. Besides the optimization of x-y movement of spray head, distance between spray head and the substrate, and spray time would results in uniform spreading of the droplet over the substrate. Reports reveal that the dielectric properties of high-\textit{k} zirconia films obtained by spray technique depend on precursor concentration, substrate temperature and annealing temperature [131, 132]. Zirconia films deposited on silicon substrate exhibited dielectric constant varying from 10.9 to 17.5 and are capable of withstanding high electric fields up to 3 MV/cm, without undergoing destructive dielectric breakdown. Further, the spray parameters like substrate temperature, spray time and post annealing determines the structure of the zirconia film and hence its dielectric breakdown strength. It is possible to fabricate uniform thick layer of highly transparent p-type NiO film by spray pyrolysis. Further the NiO films are adherent with the substrate and are of uniform surface with resistivity as low as 5 $\Omega$cm. They exhibited almost 90\% transmission in the visible spectrum for 2 $\mu$m thick films. The conductivity of the films is reasonably stable and can serve as less expensive p-type transparent electrode for solar cells and displays.