Hydrothermal Assisted Synthesis of Hierarchical Nanostructured Metal Oxide Thin Film

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Introduction

Hydrothermal synthesis has been the most popular one, gathering interest from scientists and technology, particularly in the last fifteen years. Hydrothermal technology not only helps in synthesis of mono dispersed but also highly homogeneous nanoparticles. The term hydrothermal is purely geological and it was first used by the British geologist, Sir Roderick Murchison to describe the action of water at elevated temperature and pressure [1]. Hydrothermal processing can be defined as many heterogeneous reactions in the presence of aqueous solvent or mineralizes and re-crystallize material that are relatively insoluble conditions is usually performed below supercritical temperature of water (374°C) [2]. The hydrothermal methods can be used to prepare nearly any structure including thin film, single crystal, nanocrystals, and bulk powder. In addition morphology sphere (3D), nanosheets (2D) and wire, rods (1D) of the crystal is controlled by manipulating the solvent [3-5], chemical of concentration and kinetics control. The technique can be used to synthesize thermodynamically stable and metastable states including novel materials that cannot be easily formed by other synthetic route. The hydrothermal synthesis is carried out in autoclaves which is sealed steel cylinder that can withstand at high temperature and pressure for a long time [6-8]. In hydrothermal synthesis materials takes for a longer reaction time. The autoclave must be high temperature and pressure so the use most successful 316 series stainless steel, iron, nickel, cobalt based super alloy is used. To avoid corrosion of autoclave materials is coated with non-reactive Teflon materials.

Experimental setup for hydrothermal synthesis

The hydrothermal reactions are carried out at elevated pressure so specialized equipment is essential. Under such condition it is easy to work with sealable vessels. The vessel is referred as autoclaves or hydrothermal bomb that withstands in harsh chemical conditions. Due to the high pressure, such devices are usually manufactured from metal alloys. Stainless steel bombs are most common, but other materials like tantalum, hastelloy or titanium are employed as well for more corrosive liquids. The autoclaves had an inner wall coated with Teflon cylinder that is chemically inert. Hydrothermal system is shown in Figure 1. The autoclave was filled 80% to its total volume and sealed. The autoclave was heated, resulting in increase in the autogeneous pressure of solvent.

External pressure adjustment is not possible for we used system. The critical point for water lies at 374°C and 218 atm. Water is become supercritical above this temperature and pressure. Supercritical fluids show characteristics of both a liquid phase and a gas phase. There is very less surface tension at the interfaces of solids and supercritical fluids, so supercritical fluids exhibit high viscosities and easily dissolve chemical compounds that would be exhibit very low solubility's under ambient conditions. A hydrothermal process is simple take advantage of the increased solubility and reactivity of reactants at elevated temperatures and pressures without bringing the solvent to its critical point.

Factors affecting hydrothermal technique

Hydrothermal growth of different nanostructures depends on many factors such as deposition temperature, nature and concentration of precursors, addition of surfactants, solution pH value, crystal properties of the materials and nature of the substrate.

Solution pH value

The surface charge density of metal oxide will change the interfacial energy and affect the size and distribution of the nanostructures. When solution pH changed results in adsorption of protons or hydroxyl groups will change the surface charge density. So change in solution pH result in different charge densities and electrostatic forces which affect the aggregation and ripening of the nanostructures.

Concentrations of the reactants

The growth rate and quality of the thin film deposition was greatly influences by the nature and concentration of the reacting species. The growth kinetics also depends on the nature of reactants. The concentrations of the reactants have impact on the morphology of final product of nanostructures.

Addition of surfactants

When the precursors are mixed with organic surfactants, then formation of monomers takes place. As the monomers achieve the critical concentration (nucleation threshold), aggregation occurs to form nuclei. After formation of nuclei, the monomers concentration deceases below the critical concentration, and then the monomers can only add to existing nuclei for continuous growth of thin film.

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Nature of the substrate

In addition dimensional control of hydrothermally grown oxide nanostructures attract a lot of attention. It has been proposed that the control of the interfacial tension will affect the thermodynamics and kinetics of the nucleation and growth. The substrate nature affects the nucleation central and control the crystal growth in desired direction to the substrate to form a desired morphology for example control of nanorods perpendicular to substrate surface or parallel to the substrate surface.

Deposition temperature

To study the influence of synthesis temperature on the phase and morphology of metal oxides was prepared at different temperature while keeping other parameter constant. There is a possibility to developed well crystalline phase and decrease in the unit-cell volume. As deposition temperature increases the dissociation of complex increases. The kinetic energy of molecules also increases leading to greater interaction between ions which results into precipitation and give grained structure of thin films.

Deposition time

When the film growth was performed for different hours, noticeable difference in morphology or crystallite density was observed. This reveals that the majority of nucleation, growth of nanoparticles and large crystallites occurs within the few hours. The morphology can be tuned in desired shape e.g. nanorods with either pointed tips or flat tops can be produced by varying the deposition time.

In some cases, it is better to use the experiential rule which agrees with the fact that solubility becomes high in solvents with higher dielectric constant and types of chemical bond which are closer to solute substance. Deviation from this group has a place in the case where specific interaction between solid substance and the solvent occurs. The synthesis and recrystallization of a compound and growth of single crystals on seed are all carried out using different solvents on the basis of physico-chemical considerations. The following conditions are used in selecting the most suitable mineralizers:

1. The formation of readily-soluble mobile complexes in the solution.
2. A fairly sharp change in the solubility of the compounds with changing temperature or pressure.
3. A specific quantitative value of the absolute solubility of the compound being crystallized.
4. A specific redox potential of the medium ensuring the existence of ions of the required valence.
5. Analogy of the dissolution of the test compounds.

Conclusions

Hydrothermal synthesis method is a promising approach for the fabrication of low dimensional hierarchical structured metal oxide thin films. The hydrothermal route is facile, has control over the size, requires low reaction temperatures, and is economic for large scale production of materials with large surface areas and unique morphology.

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