

## NANOSCALE MATERIAL SYSTEMS

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### Summary

Nanoscale materials have attracted significant attention in recent years. The focus has been on materials with morphological dimensions smaller than one tenth micrometer. A number of unique properties of materials emerge at this scale, such as size effect, Coulomb blockage, quantum tunneling, giant magneto-resistance effect, ballistic transportation, and so on. Based on these distinct properties, numerous effects have been made by material scientists and chemists to explore the future applications of nanomaterials in medicine, electronics, biomaterials, energy production and catalysis. In this chapter, our discussion is confined to four kinds of nanomaterials, namely oxides, semiconductors, noble metals, and fluorides.

## 1. Oxide and Complex Oxide Nanomaterials

### 1.1. Introduction

Oxides are the compounds with oxygen as one of the main chemical compositions. It is the largest existence in mass in the world, and closely related to our everyday life. Due to the existence of 22% of oxygen in air, there usually exist thin oxide shells at the surface of metal or other substrates.

Oxides can be divided into 2 groups from chemical point of view: **main group oxides and subgroup (transition metal) oxides**. The properties of main group oxides are relatively simple and less functional. One simple and obvious fact is: most main group oxides are colorless, usually shown as white powder. While oxides of subgroup

elements, which are exclusively metals (transition metals) they are often colorful (red, green, yellow, pink, etc.), and rich in functions, including superconducting, semiconducting, magnetic, fluorescent properties, etc. These properties are commonly related to their non-filled electronic configurations, or nonstoichiometric compositions, etc. Thus, they become the main reservoir for exploring novel oxide functional materials.

**Properties of oxides** include dielectric, magnetic, fluorescent, superconducting and semiconducting properties etc. These properties, however, are found usually closely related to the spin/transition of unpaired electrons, or nonstoichiometry of oxide materials, but less related to the size and dimensions, in spite of the fact that making them into nanoscale can often make them a bit more efficient, especially in surface-related properties, like sensor.

**Complex oxides:** When elements (both the main group and subgroup ones) are chemically bonded to oxygen atoms, they are usually considered cations. The cations are surrounded by oxygen atoms to form, in most cases, octahedra and tetrahedra, depending on the cationic diameters. The octahedra or tetrahedra link to form oxide solids by sharing vertices, edges, or occasionally faces. The octahedral or tetrahedral units can be homogeneous or heterogeneous. When multiple elements are incorporated into one solid with regular periods, the ternary (or more) compound is called complex oxides. The examples include transition metal complex oxides, silicate, etc.

**Dimension of oxides:** When the size of oxides goes down to less than 100nm in one dimension, their properties, including electric, optical, magnetic or catalytic properties, turns to be relative to the dimensional confinement, and the materials can thus be called oxide nanomaterials. Depending on the confined dimensions and the structural characteristics, the oxide nanomaterials can be zero-dimensional (0D, quantum dots), one-dimensional (1D, quantum wire), and two-dimensional (2D, quantum wells, sheet-like) oxides. Among them, 1D nanomaterials are considered bridges linking the macro- and meso- world and attracted most attention. Nanorods, nanobelts, nanoribbons, nanotubes, are counterparts of nanowires, often considered as quasi-one-dimensional nanostructures.

But the definition of nanomaterial is argued by some other material scientists that one material can be claimed nanomaterial only if their properties changed significantly depending on their size and dimension. But here we used the former traditional definition because materials show distinct size related properties in very different size range: some are larger than 200nm (e.g. Ag or Au), while some refuse to change their properties significantly even at less than 50nm (e.g. SiO<sub>2</sub>). Besides above classification, oxide nanomaterials are also defined according to their pore structures: zeolite (molecular sieves, microporous structures, usually pore size <2nm), mesoporous (pore size 2-50nm), macroporous (pore size >50nm) oxides. Hollow microsphere is another macroporous structure, but it is not included inside this classification due to lack of regulation on pore structures.

## 1.2. Synthetic Methods

Oxide nanomaterials are available from a series of synthetic ways. A general requirement for a successful preparative methodology is to be able to achieve nanoscale control in size and shape while maintaining a good overall crystallinity. During the 1990s, many methodologies have been developed to synthesize oxide nanostructures, such as CVD, Sol-gel, pyrolysis, reverse micelles method, etc. There are different ways to classify the above synthetic routes, but here we divided them into two major parts based on the growth force that were used during the preparation: template confined method and template-free methods.

*Template-Confining Methods:* Templates have been widely used to provide sterical confinements. These templates could be nanoscale channels within mesoporous materials or porous alumina and polycarbonate membranes, or even tubular materials like carbon nanotubes. The nanoscale channels can be filled using solution, sol-gel or electrochemistry with the action of capillary force or electronic field to generate nanoscale objects. The produced nanoparticles can then be released from the templates by selectively removing the host matrix. Many oxide nanomaterials have been fabricated using this templating process, including  $\text{TiO}_2$ ,  $\text{MnO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ . Furthermore, this templating methodology has been quite successful in term of controlling the material morphology into nanowires, even for preparing ordered nanowires or nanotube arrays. For instance, highly ordered  $\text{TiO}_2$  single crystalline nanowire arrays could be prepared within the pores of anodic aluminum oxide (AAO) template by a cathodically induced sol-gel method. Until now, as far as we know, oxides of vanadium, molybdenum, tungsten, antimony, ruthenium, iridium, and germanium have been successfully synthesized.

As a counterpart to the above template-assisted synthesis, microemulsions, reverse micelles as well as liquid crystal have also been applied to guide the growth of nanomaterials, and correspondingly they might be named as “soft-template” method. In typical soft template synthesis, surfactants were usually used. Surfactants are able to self assemble to form water in oil droplets and the reactants are confined inside the droplet. For most materials, the droplet size controls that of the produced nanomaterial. When the reactants are in their ionic form, amorphous nanoparticles are formed. Conversely with functionalized surfactants, nanoparticles characterized by a very high crystallinity are obtained. Under these conditions, both electrostatic interactions and steric confinements act to produce well-defined nanocrystals. Hopwood JD et al. used organized reaction microenvironments of BaNaAOT reverse micelles for barium sulfate nanoparticles and nanofilaments. Li M et al. described synthesis of ordered microarrays of nanocrystals of barium chromate, a complex oxide, in microemulsions of water and AOT. Guo L et al prepared  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$  nanorods by using the system of AOT–water–toluene. Micelles and microemulsions usually dominate at low surfactant concentration (e.g., 0.1 M) while lyotropic liquid crystalline phase can be obtained at high surfactant concentrations. Attard and co-workers demonstrated that normal hexagonal liquid crystalline phase could template bulk mesoporous  $\text{SiO}_2$  by hydrothermal synthesis. And  $\text{Cu}_2\text{O}$  nanowires have been electrodeposited from AOT reverse hexagonal crystalline liquid phases.

In the template-confined synthesis approaches mentioned above, it seems that, in case of hard-template synthesis the main driving force for the growth of nanoparticles can be attributed to the space-confined effect, however, as far as soft-template-assisted synthesis is concerned, especially microemulsion, reverse micelles, etc, there still lack of a general comprehension on the formation process, especially in case of nanowires.

**Template-free methods** Take advantage of intrinsic crystallographic anisotropy, oxide nanomaterials with controlled size and morphology can be obtained without any template. Hence the crystal structure of the oxides or the possible intermediates may be the underlying factors that will determine the formation of nanostructures with various shapes and dimensions. Crystal structures with a preferential axis may be preferable for the growth of oxide nanowires, for example, hexagonal ZnO, Mg(OH)<sub>2</sub>, lanthanide hydroxide nanowires have been successfully synthesized through a hydrothermal/solvothermal synthetic way. Also, the influence of ion concentrations cannot be neglected, which may have different influence on the growth rate of different crystal faces.

One of the general strategies for the oxide nanomaterials is co-precipitation or redox reactions in a solution. Several parameters like ion concentrations, reaction temperature and time are used to control the nanoparticle size, while surfactants, salts and pH are the major factors to control the particle shape. In this process, stabilizing agent such as a surfactant or polymer often acted as growth reduced agent for purpose crystal surface through the electrostatic interactions with the reactants. Two approaches have been developed: a) One of the reactants interacts with a stabilizing agent whereas the other evolves freely in the solution. The stabilizing agent molecules are present to control the growth of the nanocrystalline particles and to give the NCs solubility in polar or nonpolar solution after their synthesis owing to its hydrophilic nature. The adsorption of additives on certain crystal surfaces plays a crucial role in the shape-controlled growth for some materials. b) Functionalized surfactants (the counter ion of the surfactant is a reactive agent) are used.

Assisted with surfactant molecules, there are also other strategies for the synthesis of oxide nanomaterials. Two more detailed examples may illustrate this:

### **1D Rolling Process**

Rolling process is the basic concept of which is that layer (natural or artificial) structures may roll from the edges under elevated temperature and pressure and the as-obtained tubular structures may serve as the original driving force for the growth of 1D nanostructures. This inspiration may originate from the synthesis of inorganic nanotubes such as Carbon nanotubes. A rational assumption is now that the graphite sheets can be rolled up into tubes, other inorganic layered structure materials might also do this. It is reasonable since the layers are held together mainly by weak van der Waals' forces. Several layer structures of binary or ternary oxides have been investigated by Li et al., such as Na<sub>x</sub>H<sub>2-x</sub>Ti<sub>3</sub>O<sub>7</sub>, MoO<sub>3</sub>, MnO<sub>2</sub>, K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>, etc, and artificial lamellar structures of VO<sub>x</sub>-surfactan and WO<sub>3-x</sub> have also been employed to prepare nanotubes or nanowires structures.

### **Liquid–Solid–Solution (LSS) Process**

LSS process based on phase transfer and separation synthetic strategy was developed to prepare monodispersed oxide nanocrystals by Li's group. In this approach, a water–ethanol mixed solution is adopted as the main continuous solution phase. Since water is an ideal solvent for most inorganic species, and ethanol is a good solvent for most of the surfactants including fatty acids, most soluble inorganic salts can be adopted as the starting materials and long alkyl chain surfactants such as octadecylamine or oleic acid can be used as protecting reagents for the nanocrystals. Along with the reactions and the ion exchange process of sodium linoleate and the metal ions across the different phases, linoleic acid can be released during the reactions, and the in-situ generated nanocrystals will be covered with the long alkyl chains and thus have hydrophobic surfaces, which is incompatible with the hydrophilic surrounding of the aqueous solution. Since they are covered with long alkyl chains, these nanocrystals usually have hydrophobic surface properties, and can be redispersed into nonpolar solvents such as cyclohexane and chloroform. By carefully designing the chemical reactions that occur at the interfaces of different phases or at the water/oil interfaces, a huge group of monodisperse nanocrystals with sizes in the range of 2–50 nm, which have quite different crystal structures, compositions and properties have been obtained, including oxides ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CuO}$ ,  $\text{Fe}_3\text{O}_4$ , etc.) and complex oxide ( $\text{CoFe}_2\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{CaCO}_3$ ,  $\text{LaVO}_4$  etc.)

### **Vapor–Liquid–Solid (VLS) Process**

Besides the solution-based template-free approach, CVD and PVD have been adjusted to prepare oxides of nanowires, and most of them follow a VLS growth mechanism. Based on the phase diagram, one can choose appropriate catalysts for the growth of target products. In the oxides-related growth process, metal powders or the corresponding oxides have been used as the starting materials, and the oxygen are usually provided through wet carrying gas.  $\text{MgO}$ ,  $\text{ZnO}$  and  $\text{SiO}_2$ , etc, have been prepared through the VLS mechanism. By properly patterning the catalysts, arrays of  $\text{ZnO}$  nanorods have also been prepared. Since the catalyst droplet alloy directs the nanowires' growth and defines the diameter of crystalline nanowires, the nanowires obtained from the VLS process typically terminates at one end in a solid catalyst nanoparticle with diameter comparable to that of the connected nanowires.

As an analogy to VLS growth, Liu et al. have developed a SLS (solid-liquid-solid) growth mechanism to prepare  $\text{SiO}_x$  nanowires, in which Si are not from the vapor or liquid phase of Si sources but from the Si substrate. Meanwhile, Yu et al. have also reported the synthesis of  $\text{GeO}_2$  and  $\text{Ga}_2\text{O}_3$  following VS growth mechanism. As another enrichment to VLS, Wang et al. have found that, in the growth of  $\text{SiO}_2$  nanowires by employing Ga as the catalysts, an alloy droplet of Ga-Si may simultaneously serve as catalysts for hundreds of  $\text{SiO}_2$  nanowires and the diameter of the obtained nanowires is much smaller than that of the catalysts, which is apparently far different from VLS growth mechanism. In the synthesis of semiconducting oxides nanobelts simple evaporation method has also been applied. Since it involves no catalysts or templates, it seems that it is totally based on the anisotropic crystallization nature of corresponding samples under overcooling temperature, and meanwhile, high purity can be expected.

### 1.3. Applications of Oxide Nanomaterials

Oxides are the most commonly seen minerals in the earth and have now been widely used in various areas, from ceramics, catalysis, sensor, to electronics, optics, and magnetic fields. With reduced size and dimensionalities, more new and exciting physical and chemical contains were discovered.

**Catalysis applications** Transition metal oxide is an important catalyst support in many catalytic reactions and less costly as a substitute for the precious transitional noble catalyst. Nanophase transition metal oxides, with small particle size, high surface area, and perhaps more importantly, more densely populated surface coordination unsaturated sites, could potentially provide significantly improved catalytic performance over traditional granular catalysts. The catalytic activity of these nanocatalysts was highly influence by their size, crystal structure, even different crystal surface distribution. For example,  $V_2O_5$  supported on  $TiO_2$  (anatase) shows superior activity over the  $V_2O_5/TiO_2$  (rutile) in the partial oxidation of *o*-xylene. The catalytic activity of microcrystalline MgO is higher than high surface area nanocrystalline MgO because of the former exposing the most active (100) face surface.  $CeO_2$  nanorods predominantly exposing (001) and (110) planes show higher catalytic activity for CO oxidation than  $CeO_2$  nanoparticles. Unusually high index (112) crystal planes of  $Co_3O_4$  NCs are more reactive than the basic (001) and (011) planes for methane combustion by studying of  $Co_3O_4$  with a different shape. Together with novel approaches to nanomaterials synthesis, the understanding of the relationship between oxide nanoparticle structure properties and catalytic performance would lead the design and development of new catalysts.

**Gas Sensor** Semiconductor gas sensors have been developed based on kinds of n-type metal oxides such as  $SnO_2$ ,  $In_2O_3$ ,  $WO_3$ ,  $ZnO$  and  $Fe_2O_3$ . In particular,  $SnO_2$  has been widely used. Oxide grain size and grain boundaries could influence their sensor performance. Meanwhile, area surface is also a key factor. The grains located deep inside may remain intact or inaccessible for the gas under certain conditions, leading to reduced gas response. As an improvement from traditional thick-film sensor, Li's group has demonstrated a high sensitivity and 'quick-recovery' property of macroporous  $WO_3$  and  $SnO_2$  hollow microspheres when using as gas sensors. In addition to the nanoparticles and bulk sensor materials, one-dimensional nanostructure materials have been investigated to produce new semiconductor gas sensors. It has been reported that the nanobelts of semiconducting oxides are very promising for sensors due to the fact that the surface-to-volume ratio is very high, the oxide is single crystalline and the size is likely to produce a complete depletion of carriers inside the belt.

**Fluorescence** The luminescence of inorganic oxides can be traced to two mechanisms: luminescence of localized centers and luminescence of semiconductors. The first case is represented by transitions between energy levels of single ions (e.g., f-f transitions of  $Eu^{3+}$  in  $Y_2O_3:Eu^{3+}$ ) or complex ions (e.g., the charge-transfer transition on  $[WO_4]^{2-}$  in  $CaWO_4$ ). Luminescence of semiconductors normally occurs, after band-to-band excitation, between impurity states within the band gap (e.g., donor-acceptor pair luminescence in ZnS). The first luminescent devices contained only a single phosphor material. The emitted light was normally not white, but colored. For instance,

blue-emitting  $\text{CaWO}_4$ , which is a highly efficient phosphor, was used in X-ray-intensifying screens in first fluorescent lamps by Edison. Nowadays, luminescent materials are applied for a wide variety of applications, including displays such as television tubes, computer monitor tubes, and displays in electron microscopes. There are also many lighting applications, such as fluorescent lamps. For all these purposes, tens of thousands of phosphors have been synthesized and characterized. However, factors such as efficiency, emission color, and decay time, quenching effects, stability, reproducibility and cost prices have to be considered. There are new technologies aiming at flat displays: plasma display panels (PDPs), field-emission displays (FEDs) and new techniques such as LEDs. Commercially available white LEDs are comprised at present of highly stable garnet phosphors,  $(\text{Y, Gd})_3(\text{Al, Ga})_5\text{O}_{12}:\text{Ce}^{3+}$ , as sole wavelength converters. Synthesis and assembly technique of monodispersed nanocrystals endow the luminescence oxides new applications. For instance, colloidal luminescent  $\text{Ln}^{3+}$  doped  $\text{LaVO}_4$  nanocrystals (NCs) could be made into a transparent luminescent thin film by a simple coating method, or even be made into a film just tens of nano- meters thick by the self-assembly of NCs into a monolayer, which is important for the miniature size and flexibility of the device, and shows some potential in applications such as antiforgery technology. It was also reported that the above luminescent  $\text{Ln}^{3+}$  doped  $\text{LaVO}_4$  film could greatly improve the cell performance when applied in dye-sensitized solar cells by absorbing UV light and down-converting it to visible light.

**Lithium-ion batteries** Rechargeable solid-state batteries have long been considered an attractive power source for a wide variety of applications, and in particular, lithium-ion batteries are emerging as the technology of choice for portable electronics. Up to now, most positive electrodes of Lithium-ion battery are made of complex oxides like  $\text{LiCoO}_2$ . Other candidates, like  $\text{LiMn}_2\text{O}_4$  is also investigated. One of the main challenges in the design of these batteries is to ensure that the electrodes maintain their integrity over many discharge-recharge cycles. Improvements in the performance of lithium-ion batteries were brought by the use of transition-metal oxide nanoparticles to enhance surface electrochemical reactivity. P. Poizot reported that electrodes made of nanoparticles of transition-metal oxides ( $\text{MO}$ , where M is Co, Ni, Cu or Fe) demonstrate electrochemical capacities of  $700\text{mAhg}^{-1}$ , with 100% capacity retention for up to 100 cycles and high recharging rates. The mechanism of Li reactivity differs from the classical Li insertion/deinsertion or Li-alloying processes, and involves the formation and decomposition of  $\text{Li}_2\text{O}$ , accompanying the reduction and oxidation of metal nanoparticles (in the range  $1\pm 5$  nanometers) respectively. Furthermore, by combining the oxide nanoparticles and carbon materials, for example, embedding  $\text{SnO}_2$  nanoparticles in a carbonaceous shell, which ensures that formed  $\text{Li}_2\text{O}$  and Sn contact well without other separation, and internal  $\text{Li}_2\text{O}/\text{Sn}$  products are electronically contacted directly with the carbonaceous shell during cycling, unusually high reversible capacity was achieved.

**Opto-electronic conversion ( $\text{TiO}_2$  for solar cells)** Dye-sensitized solar cells (DSSC) first reported by Grätzel and O'Regan in 1991 are an innovative, low-cost alternative to silicon-based solar cells. A typical DSSC comprises a **mesoporous nanocrystalline  $\text{TiO}_2$  film** sensitized by dye molecules and a liquid electrolyte containing an iodide/triiodide redox couple. The nanocrystalline  $\text{TiO}_2$  electrode provides a high

specific surface area for the adsorption of a large number of dye sensitizers. Alternative wide band gap oxides such as ZnO and Nb<sub>2</sub>O<sub>5</sub> have also given promising results. It has been reported that the use of a network structure of TiO<sub>2</sub> nanorods instead of TiO<sub>2</sub> nanoparticles results in significant improvements, achieving rapid electron transfer and high efficiency. Or enhance the penetration of the quasi-solid electrolyte because of the macroporous structure of the electrospun web. A photoanode for DSSC made from ZnO nanowires was also reported by Yang P. Coating TiO<sub>2</sub> nanoparticles with a different metal oxide has received much attention because the conversion efficiency of the cell is improved by employing a TiO<sub>2</sub> electrode consisting of a core-shell structure. When metal oxides such as ZnO, SrO, Nb<sub>2</sub>O<sub>3</sub>, and SrTiO<sub>3</sub> were used as the coating layer for TiO<sub>2</sub>, the short circuit current or the open circuit voltage of the solar cell increased, and the overall energy conversion efficiency improved.

#### 1.4. Conclusion

Oxides and complex oxides are the largest existence in the world, which are generally stable and multi-functional. Making those compounds into nanosized solids have made their intrinsic properties, including semiconducting, fluorescence, and magnetic properties more suitable for practical applications, and also significantly improved their performances in the surface-related applications, including catalysis and sensor.

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