1. METAL OXIDE NANOMATERIALS

Introduction – Titanium oxide nanomaterials – Zinc oxide Nanomaterials – Tin oxide nanomaterials – Tungsten oxide nanomaterials – Tin oxide/Indium oxide nanomaterials – Formation mechanism of the metal oxide nanomaterials – Magnetic metal oxide nanomaterials – Nano phosphors.

Introduction

Metal oxide nanomaterials such as zinc oxide (ZnO), magnesium oxide (MgO), copper oxide (CuO), nickel oxide (NiO), iron oxide (Fe_2O_3), titanium oxide (TiO_2), tin oxide (SnO_2), lanthanum oxide (La_2O_3), cerium oxide (CeO_2), chromium oxide (Cr_2O_3),samarium oxide (Sm_2O_3), manganese oxide (Mn_3O_4), tungsten oxide (WO_3), cobalt oxide (Co_3O_4), zirconium oxide (ZrO_2), indium oxide (In_2O_3), etc. are of considerable importance in various practical applications. Nowadays, transition and rare-earth metal oxide nanoparticles has been the subject of much interest because of their optical, electrochemical and magnetic properties, which often different from bulk.

Among all the functional materials synthesized on the nanoscale, metal oxides are particularly attractive candidates, from a scientific as well as from a technological point of view. Metal oxides including the semiconductor, transition and rare earth metals are able to form a large diversity of oxide compounds, giving the inspiration for designing new materials. They can display a wide variety of complex structures and interesting electronic, magnetic and optical properties associated with the changes in the electronic structure and bonding, and in the presence of ordered defect complexes or extended defects.

The metal elements are able to form a large diversity of oxide compounds. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts. In the emerging field of nanotechnology, a goal is to make nanostructures or nanoarrays with special properties with respect to those of bulk or single particle species.

Metal oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites. They are attractive for a large variety of applications, including the fabrication of microelectronic circuits, coatings for the passivation of surfaces against corrosion, gas sensors, piezoelectric devices, energy storage (e.g. lithium batteries), fuel cells, solar cells, transistors, optoelectronic devices, catalysis, drug delivery and biomedicines.

There are two main classes of applications of metal oxide nanoparticles: high surface area materials and materials taking advantage of the size-dependence of the physical properties. Catalytic applications are an example, where both the high surface area and size-dependent properties play a role. The surface energy and energy of the surface sites are expected to depend on the particle size, and hence, the catalytic activity may be enhanced due to a change in the (surface) physical properties with size.

Metal oxide nanoparticles, with sizes less than 100 nm, have been developed as contrast agents for magnetic resonance imaging (MRI) as hyperthermia agents, and as carriers for targeted drug delivery to treat several types of cancer. *E.coli* is one of the most common human pathogens, and leads to many types of infection. This bacterium is responsible not only for local infections, such as wounds or postoperative infection, but also for prosthetic infection, such as through the use of catheters, endotracheal tubes, and other biomaterials. *E.coli* is also known to possess an increasing ability to resist antibiotics (such as penicillin, methicillin, tetracycline, erythromycin, and vancomycin). Thus, it is necessary to find an alternative treatment for *E.coli* infection that is directed to the site of infection, localized, and difficult for bacteria to formulate resistance. Along this line, some have hypothesized that reactive oxygen species (ROS) generated by metal oxide nanoparticles could kill bacteria without harming the non-bacterial cells.

In recent years, the photocatalytic decomposition of pollutants in water has received much attention. This process is of particular interest due to its ability to use solar energy. With industrial advancement, many organic pollutants are continuously emitted into the environment; hence, a lot of effort has been made to deal with the pollution caused. The challenge of photocatalytic degradation of organic pollutants would be to synthesize an efficient metal oxide photocatalyst.

Among the metal oxide nanomaterials, the effective versatile metal oxides such as titanium oxide (TiO_2), tin oxide (SnO_2) and zinc oxide (ZnO) nanomaterials have been attracted much attention in the scientific and technological point of view.

1.1 Titanium oxide nanomaterials

Titanium oxide, also known as titanium (IV) oxide ot titania is the naturally occurring oxide of titanium, chemical formula TiO_2. Titanium oxide (TiO_2) is a versatile functional metal oxide material. Titanium is the simplest of the transition metals having electronic structure $3d^2 4S^2$. It is present in the earth's crust and constitutes 0.6 % of it. It is mainly present as ilmenite ($FeTiO_3$) and the binary metal oxides. TiO_2 is the most important material amongst binary metal oxides which has three phases; rutile, anatase and brookite. These phases are characterized with high refractive index (anatase = 2.488, rutile = 2.609, brookite = 2.583), low absorption and low dispersion in visible and near-infrared spectral regions, high chemical and thermal stabilities. The crystal structure of titanium oxide is shown in Fig. 2.1. As compared to bulk material, nanostructured TiO_2 has improved properties and it is an important material in all disciplines of science including material engineering and biomaterials.

Nanostructured titanium oxide (TiO_2) particles have been intensively studied because of their outstanding chemical and physical properties, which are of interest for such applications as gas sensors, catalysts, photocatalysts, pigments, optics, photovoltaic cells, and precursor materials for mesoporous materials. It is important in earth sciences, plays a role in the biocompatibility of bone implants, is being discussed as a gate insulator for the new generation of MOSFETs and as a spacer material in magnetic spin-valve systems, and finds applications in nanostructured form in Li-based batteries and electrochromic devices. Depending on the application, the titania components must fulfill a wide variety of requirements in terms of particle size, size distribution, morphology, crystallinity and phase. For many applications particle size might be considered the most important parameter because it has a tremendous effect on the mechanical, electronic, magnetic, and optical properties. Ultra-small TiO_2 particles with diameters between 1 and 10 nm have been reported to fall into the transition state of molecular and bulk material properties exhibiting quantization effects and unusual luminescence properties. Size quantization effects for anatase have been reported for particles as large as 22 nm.

In the synthesis of titania, nonhydrolytic sol-gel processes usually apply the reaction of titanium chloride with a variety of different oxygen donor molecules. The formation of the Ti-O-Ti bridges results from the condensation between Ti-Cl and Ti-OR. The alkoxide functions can be provided by titanium alkoxides or can be formed in situ by reaction of the titanium chloride with alcohols or ethers. However, the oxide formation requires temperatures of 80 °C, 150°C or even 300 °C.

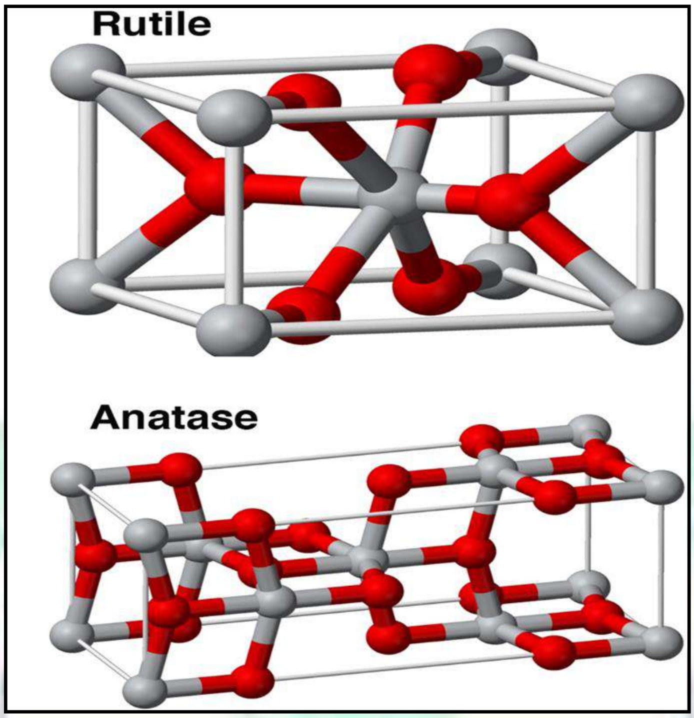

Fig. 2.1 Crystal structure of TiO_2

Titanium dioxide (TiO_2) is one of the most studied materials in the field of antibacterial applications due to its unique abilities such as photocatalytic bacterial-disrupting, nontoxicity, and self-cleaning properties. A better understanding and improvement of catalytic reactions is one main driving force for surface investigations of TiO_2.The photocatalytic disinfection performance of TiO_2 can be explained by the following mechanism. First, the photo-excited TiO_2 nanoparticles produce electron-hole pairs when exposed to UV light. Then, photo-generated holes and electrons in the TiO_2 surfaces can react with adsorbed substances and consequently generate reactive oxygen radicals. Finally, these oxygen species attack and disrupt the bacterial cell wall, resulting in cell death. Though several TiO_2 nanocomposites with antimicrobial capabilities have been reported, there are still barriers in their antibacterial application under dark conditions. In the TiO_2 nanocomposites, biocidal efficiencies depend on their light absorbance under UV and visible light. Therefore, most TiO_2 compounds exhibit no antimicrobial performances in the dark condition. For this reason, some approaches with metal-doped TiO_2, i.e., silver, palladium, and copper coated titania compounds, have been reported to provide efficient antibacterial activities without light irradiation. However, a significant disadvantage of these metal-doped composites is that the released metal ions from the TiO_2 surfaces may be an origin of an undesired environmental problem. Therefore, it is desirable to develop eco-friendly TiO_2 nanocomposites with enhanced antibacterial properties with and without the light irradiation.

1.2 Zinc oxide nanomaterials

Zinc oxide (ZnO) is a versatile functional material. It is the most important nanomaterials, due to its superior and diverse properties. Compared to other II-VI compound semiconductors, ZnO has a wide band-gap of 3.37eV, and a rather large exciton binding energy, which makes the exciton state stable even at room temperature. ZnO nanomaterials have received considerable attention due to their distinguished performance in electronics, optics, and photonics. It has unique optical and acoustic properties, as well as electronic properties of II-VI semiconductor with large exciton binding energy (60 meV). ZnO has achieved applications in photo catalysts, solar cells, chemical sensors, piezoelectric transducers, transparent electroluminescent devices and ultraviolet laser diodes. ZnO is also used as a sensing material for various gases with satisfactory environmental stability. Further, it demonstrates improved performance as a promising material for dye-sensitized solar cells. It can be made a highly transparent and conductive material, or a piezoelectric component.

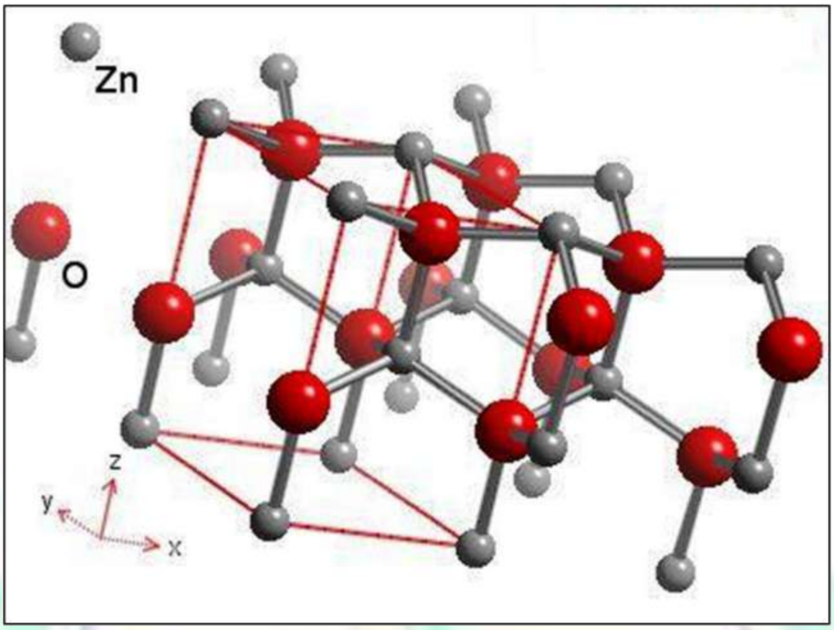

Fig. 2.2 Crystal structure of ZnO

Zinc Oxide crystallizes in three forms, such as hexagonal wurtzite, cubic Zinc blende, and the rarely observed cubic rock salt. The wurtzite structure with the lattice constant a = 3.25 Å and c = 5.2 Å is most stable at ambient conditions, and thus most commonly used (shown in Fig. 2.2). There are two ZnO molecules in a unit cell, and the atomic positions are Zn at [000] and [1/3, 2/3, 1/2], and O at [0 0 u] and [1/2, 2/3, u+1/2], where u=0.346; each atom is surrounded by a tetrahedron of four atoms of the opposite atoms. The structure can be conveniently, though rather artificially, considered as composed of ZnO_4 or tetrahedral OZn_4. The structure of ZnO consists of alternating planes composed of O^{2-} and Zn^{2+} ions, which are tetrahedrally coordinated and stacked along the z-axis on an alternate basis.

The initial interest in these materials started with studies of the lattice parameter by M.L. Fuller in 1929 and C.W.Bunn's study in 1935, but there was difficulty in producing high quality crystalline material. During the last decade, the ZnO related research has increased rapidly. The number of articles published on ZnO has increased every year; it has become the second most popular semiconductor material after Silicon. On one hand, its popularity is mainly due to the improvements in the growth of high quality, single crystalline ZnO, in both epitaxial layers and in bulk form. On the other hand, especially since the emergence of the nanotechnology, novel electrical, mechanical, chemical and optical properties have been introduced, with the reduction in size, which is largely believed to be the result of surface and quantum confinement effect. Size and shape controllable semiconductor nanostructures were achieved, based on the understanding of the nucleation and growth process of ZnO nanocrystals. Many researchers have focused their studies to enhance the useful features of ZnO nanostructure and their morphology, especially with their particle size. Therefore, studies with respect to the synthesis and properties of ZnO nanostructures have been devoted to meet the demands of their potential application, based on the morphology of the materials. So far, synthetic strategies, including physical process-related methods, such as thermal decomposition, sputtering and pulse laser ablation , hydrolysis, electrochemical deposition, arc plasma, chemical vapor deposition and various chemical routes, such as hydrothermal, solvothermal, sol-gel, precipitation processes etc., have been employed to manufacture ZnO nanostructures.

One dimensional ZnO nanostructures such as nanotubes, nanowires, nanorods, nanobelts, tetrapods and nanoribbons stimulate considerable interests for scientific research due to their importance in fundamental physics studies and their potential applications in nano-electronics, nano-mechanics, and flat panel displays. Particularly, the optoelectronic device application of 1D ZnO nanostructure becomes one of the major focuses in recent nanoscience researches. During the last decade, ZnO epilayer and various ZnO nanostructures have been grown by various techniques. A major advantage for ZnO nanostructures, e.g. nanorods and nanotubes, is that they can be easily grown on various substrates and non-lattice materials including flexible polymers. In addition, ZnO nanostructures can be advantageous with a low density of defects. The growth of defect-free structures is more likely for nanostructures in comparison with epilayers, since the strain in the nanostructures can be efficiently relieved by elastic relaxation at the free lateral surfaces rather than by plastic relaxation.

In addition, one of the significant differences between ZnO nanostructures and an epilayers is the larger surface area of the former. This large surface area can be an advantage for some applications, for example sensor devices. However, it can also be a problem in other applications, for example, optoelectronic devices such as light emitting diodes and solar cell devices, since the surface recombination rate may become dominating, resulting in a short carrier life time. So far, the knowledge about surface recombination or other surface effects in ZnO nanostructures is still limited, which is necessary and urgent to be investigated. In the case of ZnO epitaxial layer, on one hand, it is well known that an important issue for designing ZnO-based optoelectronic devices is the realization of bad gap engineering so that people can create barrier layers and quantum well in the heterojunction devices. In addition, heterostructures and quantum wells have also been realized, proving the feasibility of ZnO based optoelectronic devices. Among these ternary compounds, ZnMgO alloy has attracted more attention and apparently becomes the focus in recent years due to the similarity in ionic radii between Zn^{2+} (0.74Å) and Mg^{2+} (0.71Å) which allows for the substitution of magnesium within the wurtzite ZnO lattice. The fundamental band gap energy of ZnMgO is mainly depended on the alloy composition, which has been realized the modulation from 3.37 to 4.0 eV. However, due to the different lattice symmetries of ZnO (wurtzite) and MgO (rocksalt), the growth process and mechanism of ZnMgO is complicated. On the other hand, usually, the ZnMgO are grown at relative higher temperature in order to achieve epitaxial layers with good crystal quality. In another way, a post-deposition annealing process is carried out on as-grown ZnMgO epitaxial layer to improve its crystalline perfection and increase conductivity. It is obvious that ZnMgO/ZnO heterostructure is a very good candidate to get the diffusion information due to its simple structure. However, so far, the investigation of Mg diffusion in the ZnMgO/ZnO heterostructure is still limited. Therefore, the corresponding systemic investigation is necessary and significant for not only fabrication but practical application.

1.3 Tin oxide nanomaterials

Tin oxide (SnO_2) crystallizes with the tetragonal rutile structure (cassiterite in its mineral form) with the (110) surface being the most stable one, wherein the tin atoms are 6 coordinate and the oxygen atoms are three coordinate, as shown in Fig. 2.3. Being an important n-type semiconductor with a wide band gap (E_g = 3.6 eV at 300 K), rutile cassiterite (SnO_2) possesses excellent chemical stability, and many unique optical and electronic properties: high optical transparency in the visible range, remarkable receptivity variations in a gaseous environment, etc. These properties make it a suitable candidate for the applications of catalysis, sensing, transistor devices, electrodes of lithium-ion batteries, and optoelectronic devices. It is well-known that the physical and chemical features of SnO_2 are intimately associated with the particle size, geometric shape and exposed crystallographic facets. The properties of SnO_2 nanostructures can be enhanced in several ways like impurity doping, coating with surfactants and annealing.

Doping of transition metal ions in SnO_2 systems is of great interest due to their ability in tuning the electrical, optical and microstructure properties, which find their applications in sensors, photocatalytic and other optoelectronic devices. Tin oxide nanoparticles have been successfully doped with transition metal ions such as Fe, Co, Mn and Cu and rare earth ions Tb^{3+}, Eu^{3+} and Ce^{3+}. The results of the above have shown that the dopants, Co, Fe and Cu, can lead to an increase in the surface area of SnO_2, by reducing the grain size and crystallinity. Thus the final properties of impurity doped SnO_2 nanoparticles are related to both the composition and processing method. A number of methods such as co- precipitation, sol–gel, hydrothermal, chemical vapour deposition, VLS method, laser ablation, and thermal redox process have been developed for the preparation of SnO_2 nanoparticles.

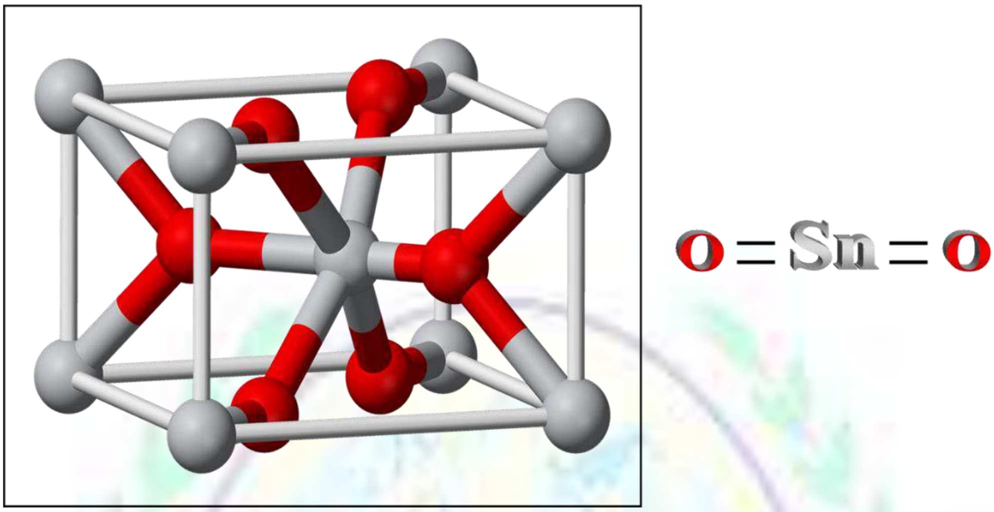

Fig. 2.3 Crystal structure of Tin oxide

The solution-based hydrothermal process is a facile method to synthesize SnO_2 with various morphologies. Chiu and Yeh et al have reported that the hydrothermal synthesis of SnO_2 nanoparticles with the size of 3 nm in the presence of iso-propanol and Cheng et al have synthesized a slim nanorod like morphology with a diameter of ~3.4 nm and a length of ~7 nm under similar conditions. Firooz et al have also fabricated nanostructured SnO_2 with prism-like, nanoflower-like, cubic-like or nanosheet-like morphology by using a surfactant-assisted hydrothermal method. The pH value, temperature and additions of a co-solvent, the surfactant, are the main factors to manipulate the morphology of SnO_2 in hydrothermal synthesis. But how to tune these factors reasonably to fabricate SnO_2 with the desired structures is still a challenge.

1.4 Tungsten oxide nanomaterials

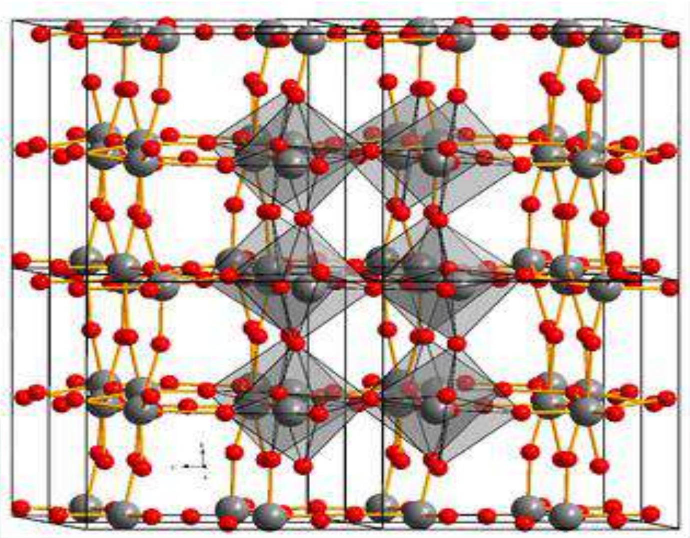

Fig. 2.4 Crystal structure of WO_3

Tungsten (VI) oxide, also known as tungsten trioxide or tungstic anhydride, WO_3 is a chemical compound containing oxygen and the transition metal tungsten. The crystal structure of tungsten trioxide is temperature dependent as shown in Fig. 2.4. It is tetragonal at temperatures above 740°C, orthorhombic from 330 to 740°C, monoclinic from 17 to 330°C, and triclinic from -50 to 17°C. The most common structure of WO_3 is monoclinic with space group $P2_1/n$. Tungsten oxide (WO_3) is an n-type semiconductor with a reported band gap of about 2.6–2.8 eV. The intrinsic conductivity arises from its non-stoichiometric composition giving rise to a donor level formed by oxygen vacancy defect in the lattice. Such electronic properties make the tungsten oxides suitable for various applications such as electrochromic, photochromic, photocatalyst, and gas sensor. The WO_3 nanoparticles or nanocrystallites have been synthesized by various techniques such as spray pyrolysis, thermal decomposition, and wet chemical processes such as sol–gel, colloidal process, and ion-exchange method.

1.5 Tin oxide/Indium oxide nanomaterials

Tin oxide/ Indium oxide (SnO_2/ In_2O_3) nanocomposites are of great interest due to their ability in tuning the electrical, optical and microstructure properties, which find their applications in sensors, photocatalytic and other optoelectronic devices. The results of the above have shown that the metal composites, can lead to an increase in the surface area of SnO_2, by reducing the grain size and crystallinity. A number of methods such as co-precipitation, sol–gel, hydrothermal, chemical vapour deposition, laser ablation, and thermal redox process have been developed for the preparation of SnO_2/In_2O_3 nanocomposites. The pH value, temperature and additions of a co-solvent, the surfactant, are the main factors to manipulate the morphology of SnO_2/In_2O_3 in hydrothermal synthesis. But how to tune these factors reasonably to fabricate SnO_2/In_2O_3 with the desired structures is still a challenge. The strong size-dependence observed for the electrical conductance in the context of gas-sensing devices has been recently reviewed for the SnO_2/In_2O_3 nanocomposites.

1.6 Formation mechanism of the metal oxide nanomaterials

Obviously, the solution phase synthesis has become a promising approach to prepare metal oxide nanomaterials, in particular for crystal sizes of less than 50 nm. The size and shape of the colloidal nanocrystals can be controlled by varying the surfactant such as cationic, anionic and nonionic. The surfactants play multiple roles in nanocrystal synthesis: (1) they can affect the rate of nucleation and growth and consequently control the nanocrystals size; (2) they can stabilize the nanocrystals and prevent inter-particle agglomeration by increasing the steric barrier; (3) they can improve the nanocrystal solubility in conventional solvents. The following characteristics of the surface modification of nanoparticles are:

- To promote the stability of the particles in liquid media
- To alter hydrophylicity of particle surface to hydrophobicity
- To couple biomaterials for biological purpose (recognition, delivery, manipulation)
- To produce building blocks for assembly (devices)

- To obtain functional nanoparticles (core-shell structure)

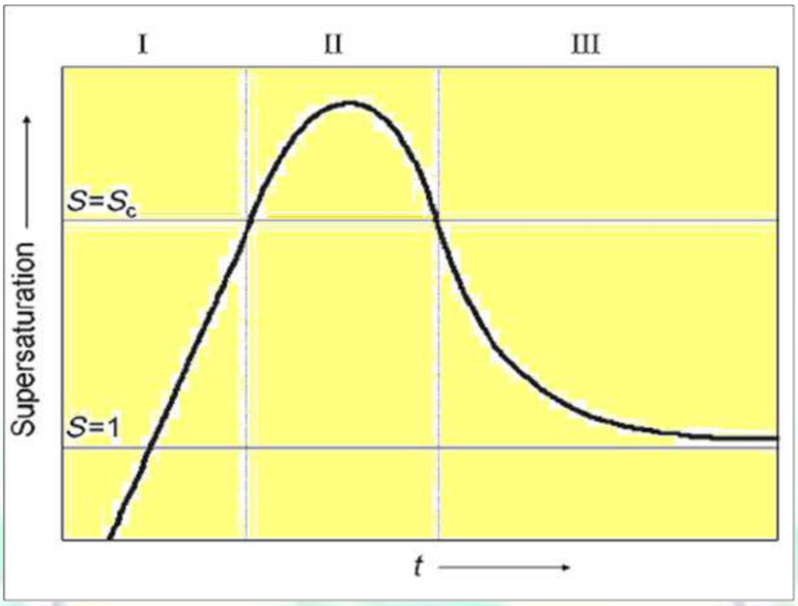

Fig. 2.5 LaMer Plot: change of degree of supersaturation as a function time

The formation of colloidal nanocrystals is simply considered to occur in two key steps: (1) nucleation and (2) growth. Theoretically, there is an extremely high energy barrier for spontaneous homogeneous nucleation. Nucleation does not initiate until the nucleation threshold is reached. The LaMer plot (Fig.2.5) reveals how the energy barrier works to induce a "burst of nucleation" In stage I, some nuclei may form under supersaturated conditions of active atomic or molecular species (monomer) (S=1). But these nuclei are thermodynamically unstable and are readily re-dissolved. In stage II, a burst nucleation is initiated by abruptly increasing the concentration of the monomer over the threshold (S=Sc). This may be achieved by swiftly injecting the precursor into the solvent at a relatively high temperature, such as in the hot injection method. When the monomer concentration is depleted owing to the nucleation process, the system moves into the growth stage (nucleation rate = 0, stage III)

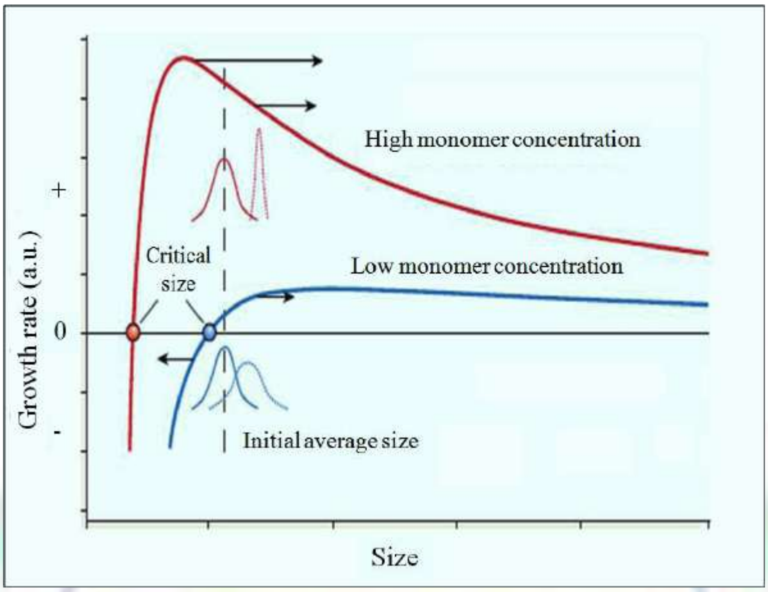

Fig. 2.6 The growth rate as a function of nanocrystal radius

The growth process of nanoparticles can be either” diffusion-controlled” or”kinetically controlled” and it is highly dependent on the concentration of the monomer present. At high monomer concentrations, the critical radius (or size), which is the minimum radius of a nucleus that can grow spontaneously in the supersaturated solution, is small (Fig. 2.6) so that all the particles grow. According to the”growth by diffusion” model, the growth rate of a particle is inversely proportional to its radius which results in the”focusing” effect in the particles size distribution and results in a nearly monodisperse product. In contrast, large critical radius exists at low monomer concentrations. Based on the “kinetic model (precipitation and dissolution)”, small particles tend to shrink while big particles grow. This is called Ostwald ripening (Fig. 2.7) which leads to a”defocusing” effect in size distribution.

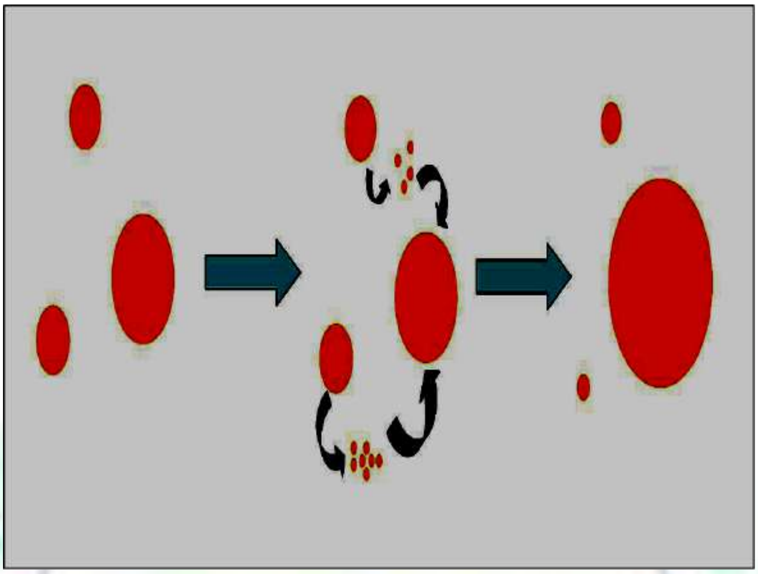

Fig. 2.7 Schematic diagram of Ostwald ripening process

The geometric shape of colloidal nanocrystals is determined by three critical factors: (1) the crystalline phase of the seed at nucleation stage; (2) the surface energy effect and (3) the control of the growth regime at the growth stage. The nucleation seed can have a variety of potential crystallographic phases from the isotropic structure of a cubic to an anisotropic structure of orthorhombic or hexagonal but the stable phase is highly dependent on its environment, such as temperature and the choice of surfactant. After the determination of a preferred crystalline phase, the subsequent growth process governs the final geometry of nanocrystals. The growth rate in different directions is strongly dependent on the surface energy of the crystallographic faces of the nucleation seed. The growth rate is exponentially proportional to the surface energy. Generally, facets with higher surface energy grow much faster than others. The surface energy of the crystal facet can be tailored by the type and the amount of adsorbed capping molecules present. In addition, the shape of nanocrystals is also determined by the delicate balance between the kinetic and the thermodynamic growth regimes. Anisotropic growth of nanocrystals normally occurs under kinetic growth regimes while isotropic growth of nanocrystals is preferred under thermodynamic growth regimes. The control of the growth regime between kinetic and thermodynamic growth can be achieved by varying the reaction parameters such as the monomer concentration and the temperature.

1.7 Magnetic metal oxide nanomaterials

Magnetic metal oxide nanomaterials such as NiO, CuO, Co_3O_4, Cr_2O_3, Mn_3O_4 etc. in particular, have been developed and optimized for fundamental scientific interest but they have also found many biomedical applications ranging from contrast agents in magnetic resonance imaging to bio-sensing applications. The large surface area to volume ratio results in a substantial proportion of atoms having different magnetic coupling with neighboring atoms leading to differing magnetic properties. Bulk gold and platinum are non magnetic but at the nano size they act as magnetic particles. Au nanoparticles become ferromagnetic when they are capped with the appropriate molecules such as thiol. Giant magneto-resistance(GMR) is a phenomenon observed in nanoscale multilayer consisting of strong ferromagnet (Fe, Co, Ni)and a weaker magnetic or non magnetic buffer(Cr, Cu).It is usually employed in data storage and sensing.

The magnetic metal oxide nanomaterials have been extensively studied and used in high-density magnetic recording devices, instrumentation and computer data storage, spin valves, ferro-fluid technology, magneto-caloric refrigeration, magnetic resonance imaging and in memory devices.

The classification of bulk materials with respect to magnetic properties is usually based on their magnetic susceptibility (χ), defined as the ratio between the induced magnetization (M) and the applied magnetic field (H). In diamagnetic materials, magnetic dipoles are oriented antiparallel to H resulting in small negative susceptibility (-10^{-6} to -10^{-3}) and the magnetization is not retained when the external field is removed. Paramagnetic materials possess permanent magnetic dipoles that align parallel to H and the susceptibility is positive and temperature dependent according to Curie law (at high temperatures).

For ferro, ferri and antiferromagnetic materials collective magnetism is crucial due to the fact that permanent magnetic dipoles show exchange interactions. This leads to a definition of a critical temperature (Curie temperature for ferromagnetic materials and Néel temperature for antiferromagnets) below which a spontaneous magnetization is exhibited.

The susceptibilities of these materials depend on their atomic structures, temperature, and the external field H. In bulk materials and large magnetic particles there is a multi-domain structure, where regions of uniform magnetization are separated by domain walls. If the particle size is decreased, there is a critical volume below which it costs more energy to create a domain wall than to support the external magneto-static energy (applied field) of the single-domain state. Below this critical size, typically in the order of tens of nanometers, materials that exhibit collective magnetism become a single magnetic domain. This is observed for magnetic nanoparticles, and in particular for iron oxide systems developed for bio-medical applications. For spherical magnetite particle the critical diameter has been determined to be ca 120 nm. A single-domain particle is uniformly magnetized with all the spins aligned in the same direction. The magnetization can be reversed by spin rotation since there are no domain walls to move. This is the reason for the very high coercivity observed in small nanoparticles.

Magnetic single-domain nanoparticles possess another important property, the anisotropy energy, which refers to the preference of the magnetization to lie along particular directions (with respect to the crystallographic directions) within the nanoparticles. These directions minimize the magnetic energy and are called anisotropy directions or easy axes.

For superparamagnetic nanoparticles, the magnetization evolution with the external magnetic field is proportional to the Langevin function that takes into account the Boltzmann distribution of the energy level corresponding to the possible orientations of the particle magnetization moment. This function is commonly used to fit experimental magnetization curves of nanoparticles and to determine the size of the crystals and its specific magnetization.

The characteristic features of superparamagnetic nanoparticles are their response to a magnetic field, where there are no coercivity field, no remanent magnetization and very high field saturation of the magnetization.

When the crystallite sizes are reduced to a few nanometers then single domain particles are more stable which could lead to superparamagnetism and weak ferromagnetism. Another interesting aspect of small-sized magnetic particles is the observation of field reversal due to quantum tunneling. CuO nanoparticles are of special interest because of their efficiency as nano fluids in heat-transfer applications. The magnetic, structural and transport properties of the different manganese oxides (MnO_2, Mn_2O_3, and Mn_3O_4) are of considerable interest. These oxides have been used as electrochromic materials and have a wide range of applications in catalysis and battery technologies. Size and shape controlled synthesis of CuO nanoparticles has received considerable attention because the physical and chemical properties of nanostructure materials are strongly related not only to their sizes but also to their shapes. In the past decades, different methods have been proposed to synthesize CuO nanoparticles with different sizes and shapes, such as thermal oxidation, electro-deposition, hydrothermal treatment, high-temperature combustion, gas-phase oxidation and quick-precipitation. Nickel oxide (NiO) has been of interest due to its interesting magnetic properties. It is known that bulk crystals of NiO possess a rhombohedral structure and exhibit antiferromagnetic behavior below 523 K (T_N) and is paramagnetic above that temperature. Cobalt oxide (Co_3O_4) is another transition metal oxide of importance because of its application as gas sensors, catalysts, magnetic materials, electrochromic devices and high-temperature solar selective absorbers. Cobalt oxide has been proposed as alternative anode materials due to their Li-storage capacities. However, the cycling performances and rate performance of the bulk cobalt oxides are very poor due to the huge volume change during the charge-discharge processes and low conductivity. Cobalt oxides with nanostructures have high specific surface and short lithium diffusion distance, which is beneficial for the specific capacity and rate performance. On the other hand, the nanostructures of cobalt oxides can sustain more volume change during the electrochemical cycling process. In the past decades, cobalt oxides of different nanostructures including nano-tubes, nano-wires, nano-belts, nano-needles and films have been prepared. These efforts have resulted in better electrochemical performances of cobalt oxides. The dependence of the properties (like band gap) on the size of particles has led to many interesting applications in optical devices of these nanomaterials.

1.8 Nanophosphors

Lanthanide-based phosphors have applications in multi-component phosphor lighting applications. Current lanthanide-based inorganic phosphors such as Y_2O_3**:** Eu typically absorbs 254 nm radiations effectively. For this reason, the lanthanide-based inorganic phosphors are useful in mercury discharge applications, such as fluorescent lighting. The use of lanthanide in photophysics for optical refrigeration is yet another demonstration of the richness of effects that can be observed with the large number of different energy levels inherent to the 4f electrons of lanthanide ions. It may very well be stated that fundamental studies on the photonics of materials containing one, two or more different types of interacting lanthanide ions will lead to the observation of new effects. High thermal stability and high melting point of rare earth phosphates, especially lanthanum phosphate was known for a long time. The phosphor paint for lamp coating using Lanthanide phosphate as a green-emitting component is more homogeneous than that made of CMAT ($Ce:Mg:Al_{11}O_{19}:Tb$). Hence color uniformity between two ends of tubular fluorescent lamps such as T_5, T_8 and cold cathode fluorescent lamps is better than that using CMAT green phosphor. The particle size of a phosphor affects the amount of phosphor particles needed to produce an optimal coating for a particular application. In addition to its high quantum efficiency and stability at high temperature, the advantage of LAP over $MgAl_{11}O_{19}$: Ce, Tb (abbreviated as MACT) is that specific gravity of LAP (5.07 gcm^{-3})

which matches well with Y_2O_3: Eu phosphor (5.20 gcm^{-3}) as compared with MACT whose specific gravity is 4.2 gcm^{-3}. Recent studies proved that they can act as excellent hosts for rare earth ions, which in turn generated great interest for this material in the field of optics and photoluminescence. Each type of host for lanthanide ions has its strengths and weaknesses for the construction of luminescent materials. Organic ligands generally induce efficient non-radiative deactivation of lanthanide ions, in particular for highly excited states. It offers tunability their physicochemical and biological behaviour through molecular chemistry. Inorganic hosts give rise to richer lanthanide photophysics through reduced non-radiative deactivation channels, but are not as easily processed as organic materials and are often bio-incompatible. And also the photostability of lanthanide complexes is expected to be superior to that of organic fluorophores, since the excitation energy only remains on the organic ligand a very short time before it is transferred to the lanthanide ion which usually does not undergo any photochemical transformations. When making use of the lanthanide luminescence for the detection of biological molecules, the luminescent material needs to be compatible with the biological and aqueous environments and the individual light emitters should be small enough not to interfere with any of the biochemical processes in the sample under study. Lanthanum phosphate ($LaPO_4$) is mainly used as a green emitting phosphor for fluorescent lamp due to its high quantum efficiency, high intensity, thermal stability at high temperature and sharp emission around 543 nm. It may very well be stated that fundamental studies on the photonics of materials containing one, two or more different types of interacting lanthanide ions will lead to the observation of new effects. The catalytic activity of rare earth phosphates also received wide attention. Rare earth complexes have already been under investigation for stereo selective catalysis. In recent years, the synthesis and characterization of the supported materials such as Sm, Pr, Ce, Tb, Eu, Er and Gd doped $LaPO_4$ nanophosphors have been investigated.

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The luminescence of trivalent lanthanide ions has found applications in lighting, lasers, optical telecommunications, medical diagnostics and various other fields. The practical application of lanthanide luminescence requires incorporation of lanthanide ions in the matrix of $LaPO_4$. The luminescent powders called phosphors can be used to convert the UV radiation, generated by the mercury or xenon plasma inside fluorescent lighting, to deliver a homogeneous and stable light output even after prolonged exposure to this highly energetic radiation. Similarly, phosphors for cathodoluminescence, found in the cathode ray tubes, need to resist the continuous electron bombardment. Conventional televisions and computer screens use the lanthanide doped phosphors to convert the cathode rays into visible information. Currently, the most important commercialized use of luminescent lanthanide complexes is in medical diagnostics and clinical tests. The most common type of lanthanide based luminescence material find application in the field of detection of biological molecules.

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