

Semiconductor Oxide Nanoparticles

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ABSTRACT

The nanoparticle hybrid systems are improved semiconductors. They are compared with their isolated counterparts. We report the preparation of MO₂ (M = Ti, Ce, and Sn) and their synthesis. We report the controlled-size semiconductor oxide nanoparticles based on the impregnation and decomposition of transition-metal 2-ethylhexanoate-based precursors in mesoporous hosts. The pore size of the host material plays significant role to control the size of the material synthesized within it. The mass gain after each cycle in the synthesis process determined the control of nanoparticle growth via a layer-by-layer assembly. X-ray diffraction, transmission electron microscopy, and Raman spectroscopy techniques were used to characterize SnO₂, TiO₂ and CeO₂ nanocrystals. Raman spectroscopy measured nanocrystal size as characterization tool.

Keywords: semiconductor, oxides, nanoparticles, size control

1 INTRODUCTION

Nanotechnology defines as the creation of functional materials, devices and systems through control of matter at the range of 1-100 nm scale. The term 'nanosemiconductor' covers metal oxide and hybrid materials in one dimension (quantum dots and thin films etc.), two dimension (nanofibers, nanowires, nanotubes, etc.), and three dimension (nanoparticles/nanopowders, nanocapsules, fullerenes, dendrimers, molecular electronics, nanostructured materials, nanoporous materials etc.). Due to their small grain size, these materials exhibit unique mechanical, chemical, physical, thermal, electrical, optical, magnetic, biological and also specific high surface area properties, which cannot be found in their bulk counterpart turn define them as nanostructures, nanoelectronics, nanophotonics, nanobiomaterials, nanobioactivators, nanobiolables, etc. Metallic nanoparticles (Ag, Au, Ge, Mo, Si, Pt, Pd, and Ru etc.), semiconductor metal oxide (Al₂O₃, CeO₂, CdO, CoO, Co₃O₄, CuO, Cu₂O, FeO, Fe₂O₃, Fe₃O₄, Ga₂O₃, Hf₂O₃, In₂O₃, Ln₂O₃, MgO, MoO₃, MnO₂, Mn₂O₃, Mn₃O₄, Nb₂O₅, NiO, PbO₂, Pr₂O₃, Sb₂O₃, SiO₂, SnO₂, V₂O₅, WO₃, TiO₂, ZnO, ZrO₂, Ln₂O₃, LnVO₄, NaYF₄, NaYF₄:Ln, NaLnF₄, NaLnF₄:Ln, LnPO₄, LnPO₄:La-Lu, semiconductor quantum dots (AgS, AlN, CdS, CdSe, CdTe, CuS, GaN, GaP, PbS, PbTe, ZnS, ZnSe, ZnTe etc caught

attention in electrodes, catalysis, solar energy conversion, field emission, photonic devices, drug delivery, biosensors(DNA, optical, chemical, gas and immunosensors. Semiconductor crystals exhibit a broad spectrum of strong size dependent properties for particle sizes below the Bohr radius of their bulk exciton. The size dependence of the nanocrystal electronic energy level has attracted special interest. It allows one to tailor the materials optical and electronic properties by controlling particle size, and many potential new applications such as nanocrystal bio-tags, quantum dot lasers, polymer-based nanocrystal solar cells, and single electron transistors.

How semiconductor works?

Quantum confinement of classical particle in a box explains this problem. The effective mass of m^* confined in a crystal with a one dimension barrier at a distance of L , the movement of the particle can be described with the Schrödinger equation:

$$\frac{\partial^2 \Psi(x)}{\partial x^2} = -\frac{2m^* E}{(\hbar/2\pi)^2} \Psi(x) \dots\dots\dots(\text{Eq.1})$$

where $\Psi(x)$ is the wave function and E is the energy of the particle. This equation can be solved by using the boundary conditions that $\Psi(x) = 0$ at $x = 0$ and $x = L$:

$$\text{for } E_n = \frac{\hbar^2 k_n^2}{2m^*} = \frac{n^2 \hbar^2 \pi^2}{2m^* L^2} \quad n = 1, 2, 3, \dots\dots\dots(\text{Eq.2})$$

where k_n is the allowed wave factors and $k_n = n\pi / L$. When this simplified solution is extended to a semiconductor nanocrystal with a size close to the Bohr radius a_B , the resulting expression for the energy shift from the ground state of the corresponding bulk materials is:

$$\Delta E_n = n^2 \hbar^2 \pi^2 / 2m^* a^2 \quad (\text{Eq.3})$$

where a is the size of the nanocrystal, m^* is the reduced effective exciton mass which is defined by $1/m^* = 1/m_e^* + 1/m_h^*$. m_e^* and m_h^* are the effective mass of electron and hole of the material, respectively. The Bohr radius of a semiconductor can be obtained from the dielectric constant ϵ and the reduced exciton mass m^* : $a_B = \epsilon \hbar^2 / m^* e^2$. Thus, the band gap of the material can be engineered to a desired level by changing the size of the nanocrystals: $E_{g, \text{nanocrystal}} = E_{g, \text{bulk}} + \Delta E = E_{g, \text{bulk}} + \hbar^2 \pi^2 / 2m^* a^2$ (Eq.4) The band gap energy increases with a decrease in the size of the nanocrystals. Since the optical transition is directly related to the band gap, it is possible to tune the absorption and photoluminescence wavelength of the nanocrystals just by manipulating their size. Semiconductor metal oxide nanocrystals show distinct properties shown in Figure 1.

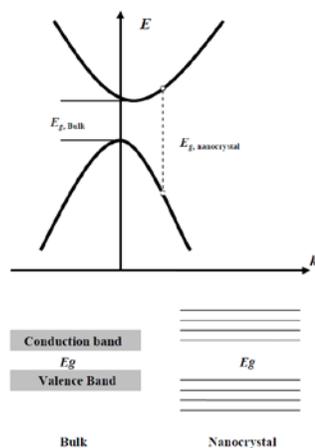


Figure 1. Illustration of a semiconductor band structure showing shift of energy band gap.

2. NANOCRYSTAL SYNTHESIS

Preparation methods are incorporation and thermal decomposition of metal carbonyl clusters and alkoxides, ion-exchange, metallo-organic decomposition (*MOD*), and sol-gel processes. Layered solids, zeolites and, recently, carbon nanotubes are the most popular porous hosts. *MOD* method can be successfully used for producing inorganic powders and thin films as technique does not require either vacuum processing or gel preparation. The metallo-organic precursor is treated under the appropriated conditions (temperature, atmosphere, time) to yield the desired final oxide. The advantages of this process include simplicity, easy composition control, and lower temperatures of synthesis, shorter times, better compositional uniformity and high specific surface areas. *MOD* methodology is appropriate for preparing materials in confined environments because it is a wet based-method and the liquid precursor can be efficiently inserted into the porous host. This methodology is suitable for adjusting what is called the impregnation-decomposition cycle (*IDC*) in order to get good control of crystallite size as a function of the number of *IDC*. The *IDC* method has been shown to be a versatile bottom-up nanofabrication technique. In Figure 2 we show a scheme on how this technique is used for preparing nanocrystals inside a porous host.

2.1. METALLO-ORGANIC-DECOMPOSITION TECHNIQUE

The integrated chemical systems (nanocrystals anchored on porous hosts) that we are going to discuss in the next sections have two different hosts. We now shall briefly describe the main properties of these hosts.

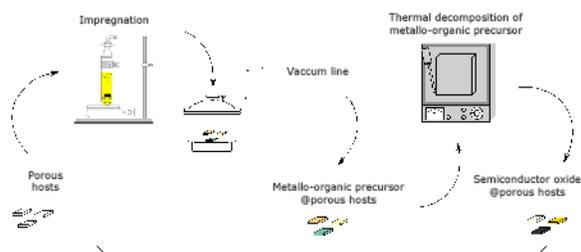


Figure 2. Scheme showing the steps used for preparing the nanocrystals inside the porous hosts using the metallo-organic decomposition method (*MOD*). Each cycle is called “one impregnation-decomposition cycle – *IDC*”.

2.2. TEMPLATE-ASSISTED SYNTHESIS METHODS

Synthetic methods for nanomaterials by template methods are widely used which confine the growth of materials within a template (such as pores), followed by removal of the template, provide a flexible synthetic route for a variety of nanostructured materials. Both hard-templates (e.g. porous materials, mesoporous silica, track-etched polycarbonate film and carbon nanotubes) and soft-templates such as polymer, self-assembly of surfactant molecules and solvents could be used. Now biomolecules such as DNA, tripeptide glutathione (GSH) and lysozyme as template can be used for the synthesis of nanoparticles. Figure 3 illustrates how nanotubes or nanowires can be formed using porous materials template. Firstly, the substrates are loaded into these nano-channels by various methods such as vapor phase sputtering, liquid phase injection, solution-phase deposition or electrochemical deposition. Nucleation, growth and crystallization are confined in these nanometer sized channels. Selective removal of the porous template results in the formation of nanorods, nanowires or nanotubes. The most commonly used porous materials are porous polymer and alumina films. One typical example is the use of porous anodic alumina (PAA) templates to prepare ZnO nanowires and nanotubes. The zinc-based sol particles were loaded into the PAA nano-channel due to the electrostatic attraction. The ZnO nanowires and nanotubes can be fabricated when the sol particles sintered inside the channels. Outstanding examples of arrays that has been generated by this route are those of oxides nanotubes like TiO₂, In₂O₃, Ga₂O₃, BaTiO₃, PbTiO₃, In₂O₃ and Fe₂O₃, as well as nanorods of MnO₂, WO₃, Co₃O₄, V₂O₅, and ZnO. Other widely applicable route to inorganic nanotubes and nanorods is to use CNTs as templates. CNTs have been coated with a thin film of secondary materials that builds up the tube wall of the desire inorganic nanotube followed by removal of the carbon nanotube. Most oxide nanotubes and nanorods, such as V₂O₅, Al₂O₃, WO₃, MoO₂, Sb₂O₃ and MoO₃, ZrO₂, RuO₂,

SiO₂, and TiO₂ have been prepared using CNTs as templates. Self-assembly of surfactant molecules is another important class of templates. Surfactant molecules can be classified into cationic, anionic, non-ionic and zwitterionic according to their polar head groups. When the concentration of surfactant molecules is below its critical micelle concentration (CMC), the surfactant molecules will only lie up at the liquid-vapor interface or dissolve into the liquid. However, once the concentration is over CMC, these surfactant molecules can self-assemble into spherical micelle, cylindrical micelle or lamellar structure depending on the concentration and types of surfactant molecules. Figure 3 depicts the structure of these micelles. These self-assembled structures can be used as templates for the growth of nanomaterials as shown in Figure 4. Reactants can load into or grow outside the cylindrical template. Subsequently removal of surfactant molecules gives nanorods, nanowires or nanotubes. The uses of surfactant as a template for nanomaterials synthesis have been widely explored. Existing 1D nanomaterials such as nanowires and nanotubes can also be used as a template for the synthesis of other 1D nanomaterials. The substrates can coat onto the nanowire or nanotubes for growth. Removal of the template results in the formation of nanotubes. The substrates can also react with the nanowires so that growth of the new materials is directed by the existing nanowires. For example, single-walled carbon nanotubes (SWNTs) were used as a template for the synthesis of one-dimensional SiC, BN nanostructures, ZnO nanorods, CoFe₂O₄ nanowires, β -zeolite nanowires.

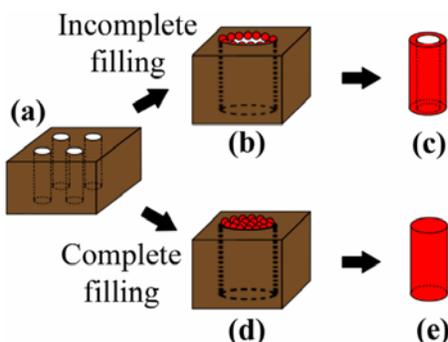


Figure 3. Schematic diagram showing the formation of 1D nanomaterials using porous materials as templates. (a) Porous materials such as porous anodic alumina with nanometer scale channels. (b) Incomplete filling of the substrates in the channel. (c) Formation of nanotube due to incomplete filling. (d) Complete filling of the substrates in the channel. (e) Formation of nanorod or nanowire due to complete filling.

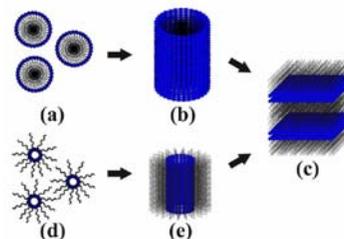


Figure 4. Schematic diagram showing the structures of self-assembled surfactant molecules. Arrows stand for the change of structure as the concentration of surfactant molecules increases. (a) Structure of spherical micelle; (b) Structure of cylindrical micelle; (c) Lamellar structure; (d) Structure of spherical reverse micelle; (e) Structure of cylindrical reverse micelle.

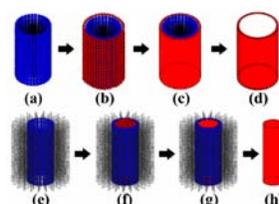


Figure 5. Schematic diagram showing the formation of nanorods, nanowires and nanotubes by cylindrical template. (a) Cylindrical micelle formed by self-assembly of surfactant molecules. (b) Substrate molecules attach onto the outer wall of the cylindrical micelle. (c) Sintering of the substrate molecules form a wall outside the cylindrical template. (d) Selective removal of the surfactant molecules gives the desired nanotubes. (e) Cylindrical reverse micelle formed by self-assembly of surfactant molecules. (f) Substrate molecules load into the cylindrical reverse micelle. (g) Nucleation, growth and crystallization occurs inside the cylindrical template. (h) Selective removal of the surfactant molecules gives the desired nanorods or nanowires.

X-ray diffraction (XRD) is a noncontact and nondestructive technique which can be used to determine the crystalline phases present in materials, the structural properties of these phases, the thickness of thin films, and atomic arrangements of amorphous materials. The geometry of diffraction in a single grain is described through the reciprocal lattice. If the crystal lattices are defined by three vectors \mathbf{a} , \mathbf{b} , and \mathbf{c} , there are three reciprocal lattice vectors defined as:

$$\mathbf{a}^* = 2\pi \mathbf{b} \times \mathbf{c} / \mathbf{a} \cdot \mathbf{b} \times \mathbf{c} \quad (\text{Eq.12})$$

as cyclic permutations thereof for \mathbf{b}^* and \mathbf{c}^* . These vectors define the reciprocal lattice, with the significance that any three integers (hkl) define a family of lattice planes with spacing $d = 2\pi / |h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*|$, so that the diffraction vector $\mathbf{K} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ satisfies $|\mathbf{K}| = 2\pi / d = 4\pi \sin\theta / \lambda$ (most chemists and some physicists define $|\mathbf{K}| = 1 / d = 2\sin\theta / \lambda$). The intensity of the diffracted beam is governed by the unit cell structure factor, defined as:

$$F_{hkl} = \sum_j e^{i\mathbf{K}\cdot\mathbf{R}_j} f_j e^{-2W} \quad (2)$$

where \mathbf{R}_j is the position of the j^{th} atom in the unit cell, the summation taken over all atoms in the unit cell, and f_j is the atomic scattering factor, tabulated in, e.g. the International Tables for Crystallography, and is equal to the number of atomic electrons at $2\theta = 0$, decreasing as a smooth function of $\sin \theta/\lambda$.

3 STRUCTURE OF NANOCRYTALS

TEM is the most useful method to provide direct observation of pore structures and parameters. Details of 50nm can be resolved by scanning SEM.

Raman spectroscopy analyzes metal oxide infrared bands at around 500-300 cm^{-1} due to O-M stretching. The energy range for infrared spectra measurements is 400-4000 cm^{-1} and the resolution 4 cm^{-1} .

4 HYBRID NANOSEMICONDUCTORS

$\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0.04\text{--}0.1$) with a stable chemical composition provide a highly dense CdTe and $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ceramics with distinct characteristics shown in Figure 7.

5 EMERGING NANOELECTRONICS

Silicon nanotechnology is replaced with hybrid nanocomposites. CMOS and MOSFET technology based on Si-SiO₂ interfacen will be replaced by single electron MOS memory(SEMM) to provide quantized threshold voltage with terabyte area on chip. Other development is in single wall CNT graphite technology as transistors rectifiers. Nanowires, quantum dots are new faces. Graphene combines most exciting features from carbon-nanotube, single-electron and molecular electronics as alternatives to the silicon-based technology. Semiconductor laser technology is wider hope in improved plasmon, optical, photon technology.

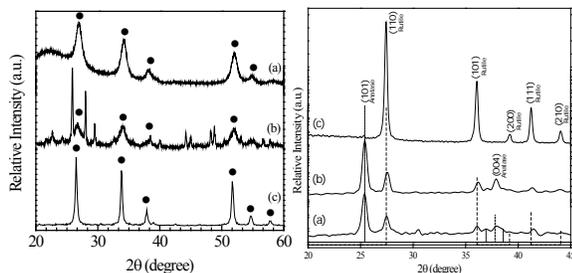


Figure 6. (left) X-ray powder diffraction measurements of SnO₂ nanoparticles. (a) SnO₂@PVG, (b) SnO₂@ α -NbPO₅ obtained with 10 IDC and (c) free SnO₂. The solid circles identify the peaks from the rutile SnO₂ phase taken from a crystallographic database. (Right) Powder XRD patterns of the decomposition product of free Ti(OnPr)₂(hex)₂ at (a) 500 °C; (b) 600 °C; (c) 700 °C. Dotted and dashed lines stand for TiO₂^A [58a] and TiO₂^R [58b], respectively [1].

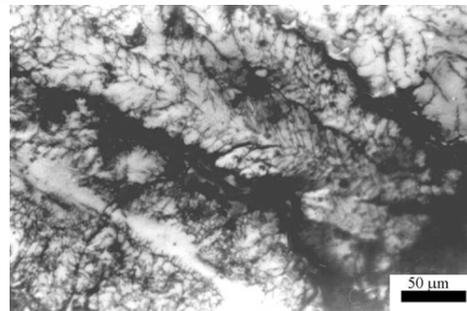
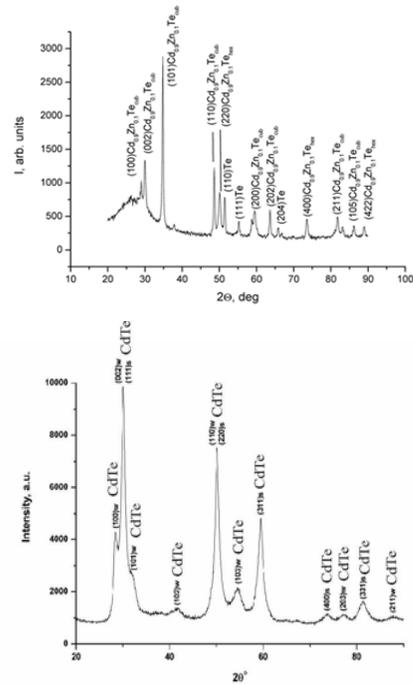


Figure 7. (top row) XRD is shown for Cd_{0.9}Zn_{0.1}Te ceramics produced at T = 20°C, p = 400 MPa on top; CdTe ceramics produced at T = 200°C, p = 650 MPa. In middle; and (bottom row) CdTe ceramics produced at T = 20°C, p = 650 MPa, time under pressure t = 10 min[3].

6 CONCLUSION

Metallic organic decomposition technique is advancing in synthesis of nanosemiconductors. A technique is reported for CdTe and Cd_{1-x}Zn_xTe ($x = 0.04\text{--}0.1$) nanopowders consisting of 8-10-nm particles for hard ceramic materials. 1D nanomaterials such as nanowires, nanotubes, nanomicelles are excitements.

7 REFERENCES

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