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Induced synthesis ZnO nanoparticles using novel amphiphilic Zinc precursor complex with mono-octadecyl cis-butene dicarboxylate

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Zinc oxide (ZnO) nanoparticles were synthesized using novel amphiphilic zinc complexes with mono-octadecyl cis-butene dicarboxylate (MAO) as precursors, for which can form nanosized micelle-like aggregates by special self-assembly. The amphiphilic zinc complex was fabricated with MAO which was achieved by the modification of maleic anhydride with long chain 1-octadecanol. The synthesized ZnO samples were further studied by Fourier transform infrared spectroscopy (FT-IR), Diffuse reflectance ultraviolet–visible spectra (DRUVS), X-ray diffraction (XRD), Scanning electronic microscopy (SEM) and Transmission electron microscopiy (TEM). Results show that the nanosized ZnO semiconductor material exhibits the hexagonal (wurtzite) crystal structure and presents regular and well dispersion nanoparticles with average particle size in the range of 40-70 nm. Besides, the corresponding photoluminescence (PL) demonstrates a strong and dominant peak at 395 nm with a suppressed and broad green emission at 545 nm, suggests that the ZnO nanostructures have good optical properties with very few structural defects.

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1. Introduction

In recent years, nanoscale inorganic semiconductor materials have attracted much more interest in various fields of chemistry due to their desirable properties and various applications in science and technology [1, 2]. On the other hand, recent studies suggested that, in addition to size and dimension, the shape of nanostructured materials also has a great influence on their properties [3-5]. As a result, much effort has been made in designing rational methods for synthesizing nanoscale inorganic semiconductor materials with different shapes [6-9]. Zinc oxide (ZnO), an inexpensive, nontoxic, n-type II-VI semiconductor with a direct wide band gap (3.37 eV at room-temperature) and large exciton binding energy (60 meV) which can ensure an efficient exciton emission at room temperature [10], is one of the most promising materials for numerous applications such as optoelectronic devices and gas sensors owing to their high surface-to-volume ratio [11-15]. Up to now, various morphological of one-dimensional (1D) ZnO nanostructures (e.g. nanowires, nanotubes, nanobelts, nanorings, nanorods and star-shaped nanostructures) have been fabricated and investigated [16-21] by a variety of techniques, such as sol–gel method [22], electrochemical [23], spray pyrolysis [24], thermal decomposition [25], wet chemical synthesis, combustion method [26-28], etc. However, its nanoscale crystals tend to aggregate or to undergo Ostwald ripening [29] because of their high surface energy, which can allow to readily alter the structural characteristics of the solid powders [30, 31]. Moreover, it is well known that intrinsic defects such as the oxygen vacancies (VO) are formed in ZnO crystal due to the difficulty of its growth. Therefore, in order to stabilize NCs, limit the agglomeration of particles effectively and control the morphology and microstructures of nanoscale ZnO, shape-controlled synthesis of ZnO with various morphologies is of potentially significant importance [32-36]. The deep understanding of the nucleation and growth processes enables us to control the shape and size of ZnO [37-39], and extensive research has paid more attention on the design and assembly of precursors with special organic ligands during these years. Here, we choose amphiphilic molecules as the precursors to prepare nanoscale ZnO semiconductor materials because the amphiphilic molecules could form nanosized micelle-like aggregates with various morphologies in aqueous medium by special self-assembling. In principle, the micellization can be viewed as a process that drives the packing of all junction points into a high density array, and influences the shape, structure, epitaxy and property of the precursors [40, 41].

In this paper, using maleic anhydride as starting material, 1-octadecanol was grafted in order to achieve a new type of amphiphilic mono-octadecyl cis-butene dicarboxylate (MAO), with carboxylic acids as the hydrophilic segments and organic long-chain as the lipophilic segments. Then the corresponding amphiphilic zinc complexes with MAO ligands were synthesized. By selecting the amphiphilic zinc complexes as the precursors, we obtained nanoscale ZnO semiconductor materials. We expect that the special amphiphilc molecular ligands of the zinc complexes can control the morphology and microstructures of ZnO materials. The microstructure and photoluminescence of the nanosized ZnO semiconductor materials was discussed in detail.

2. Experimental

Synthesis of mono-octadecyl cis-butene dicarboxylate (MAO) by the modification of maleic anhydride:

The synthesis of amphiphilic mono-octadecyl *cis*-butene dicarboxylate (MAO) was adopted as the similar procedure in ref. [42]. Maleic anhydride (0.98 g/10 mmol) was mixed with equimolar amount of long chain 1-eicosanol (2.98 g) in a flask. Then the solid mixtures were placed in an oil bath at the temperature 110 – 115 °C and react for 16h. Finally the samples were recrystallized with n-hexane three times to afford the white powder amphiphilc MAO (Fig. 1 (A)). Anal. Calcd. for $C_{22}H_{40}O_4$ (mono-octadecyl cis-butene dicarboxylate (MAO), mp: 66 °C): C, 71.70; H, 10.94; Found: C, 671.47; H, 10.63.

Synthesis of nanosized ZnO by amphiphilic zinc complex with MAO:

The synthesis of nanosized ZnO by amphiphilc zinc complex with MAO was described in the following way. The corresponding amphiphilc zinc complex ($Zn(MAO)_2$) with this ligand (MAO) was prepared by homogeneous precipitation. Excess MAO (2.1 mmol) over $Zn(CH_3COO)_2{\cdot}2H_2O$ was dissolved into ethanol solution and its pH value was adjusted to be about 7.0 with ammonia solution. Then the alcohol solution of $Zn(CH_3COO)_2{\cdot}2H_2O$ (1 mmol) was added very slowly to the above solutions and mixed homogenously. After that, the above mixed solution were heated under 60 °C, whose pH value became alkalescent by dipping 1 mol % ammonia solution. After that, the temperature was increased to 100 °C to evaporate the excess solvent until the solution becomes viscous, dried and the amphiphilic zinc complex precursors were achieved finally (Fig. 1 (B)). At last, the samples were heat-treated at 700 °C for about 3 hours, respectively, in order to remove the organic component from the zinc complex systems and form the material. The typical scheme of the synthesis can be shown as below:

$$1.00\ Zn(CH_3COO)_2\cdot 2H_2O + 2.10\ MAO + NH_3\cdot H_2O$$
$$\rightarrow [Zn(MAO)_2]\ \text{complex} + x'\ NH_3\cdot H_2O$$
$$\rightarrow ZnO + CO_2\uparrow + H_2O\uparrow + NH_3\uparrow$$

Physical measurements of ZnO

Elemental analyses (C, H, N) of MAO were carried out by the Elementar Cario EL elemental analyzer. Infrared spectroscopy of MAO with KBr pellets was performed on a Nicolet Nexus 912 AO446 model spectrophotometer in the 4000 ~ 400 cm^{-1}. The nanometer particles were synthesized by means of X-ray powder diffraction (XRD, 40 kV and 20 mA, Cu K*a*, Philps PW1710, reflections peaks for 100, 002, 101, 102, 110, 103, 200, 112 and 201 directions were used in our measurements). The morphology, microstructure were characterized by scanning electronic microscope (SEM, Philps XL-30), transmission electron microscopic (TEM, H-800). Excitation and mission spectra for solid powders of this phosphor were determined with Perkin-Elmer LS-55 model fluorophotometer (excitation wavelength 400 nm, scan rate 1000 nm/s, excitation slit width = 5 nm, emission slit width = 5 nm).

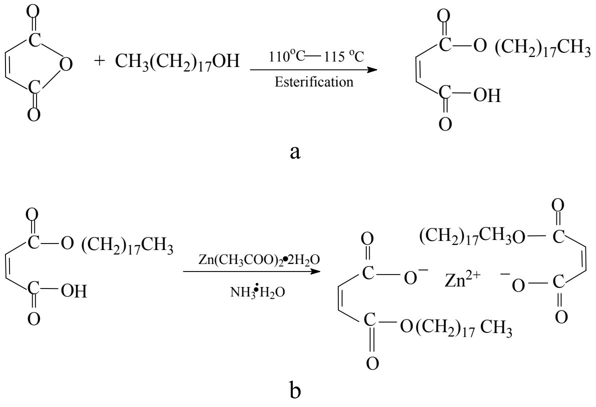


Fig. 1. Scheme of the synthesis of mono-octadecyl cis-butene dicarboxylate (MAO) by the modification of maleic anhydride (A) and zinc complexes with long chain mono-octadecyl cis-butene dicarboxylate (MAO) (B).

3. Results and discussion

From the data of FTIR spectra, it can be seen that, the peak at 1783 cm^{-1} of cis-butene dicarboxyl (maleic anhydride, MA) presents the stretching vibration of C=O and the band at 3130 cm^{-1} corresponds to stretching vibration of C-H which belong to the backbone of maleic anhydride. While the IR spectra of MAO appears the vibration peaks of methyl group ($-CH_3$) at 2848 cm^{-1}, and shows that the $\nu_{(C\text{-}H)}$ of the long carbon chains changes to 2918 cm^{-1}, which proves that the long chain alcohols was successfully grafted to maleic anhydride. Additionally, the peak at 1726 cm^{-1} substantiates that the absorption of C=O was affected by the long chain groups. From the date of FTIR spectra recorded of ZnO derived from amphiphilc zinc complexes with MAO, we can see two bands located respectively at 443 cm^{-1}, 665 cm^{-1}, both of which are between 400 and 800 cm^{-1} (a very broad and strong band) and corresponded to the framework vibrations of pure zinc oxide. Compared with the date of FTIR spectra of ZnO in reference [43], it was found there is no apparent distinction between them, which confirms that the synthesized product is only ZnO. Therefore, we suppose that the organic component is decomposed completely.

Fig. 2 shows the diffuse reflectance ultraviolet–visible spectra (DRUVS) of ZnO synthesized by amphiphilic zinc complexes with MAO in the regime from 200 to 950 nm, respectively. It can be seen that the sample presents an absorption edge in the wavelength range ($250 < \lambda < 400$ nm). A prominent absorption band was observed near 250 nm, which shows that the absorption edge of ZnO powders is probably due to $O^{-2} \rightarrow Zn^{2+}$ charge transfer transitions from valence band to conduction band.

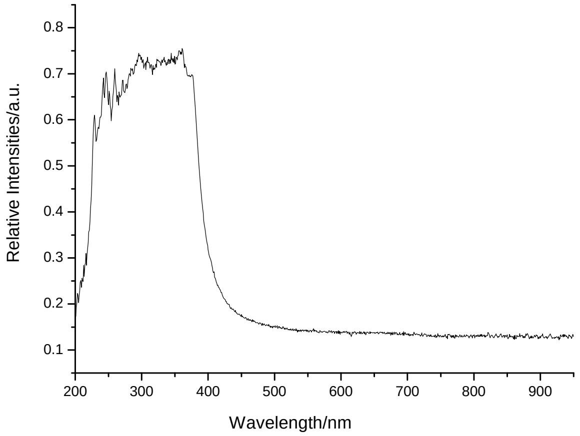


Fig. 2. DRUVS of ZnO derived from the zinc complex with MAO precursor.

The powder XRD patterns for synthesized nanosized ZnO is shown in Fig. 3 (the representative indices peaks have been indicated). All of the diffraction peaks in the obtained spectrum are well matched with that of ZnO (JCPDS Card No. 36–1451) and in agreement with the data obtained from the experimental results reported in Ref. [44], which confirms that the synthesized ZnO powder is single crystalline and possesses a wurtzite hexagonal structure. From the estimated data, the nanometer ZnO materials obtained from zinc complex precursors was a pure phase, and has a size distribution in the range of 40 – 70 nm.

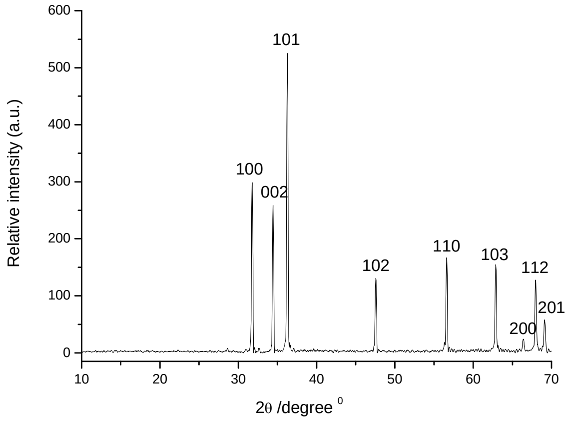
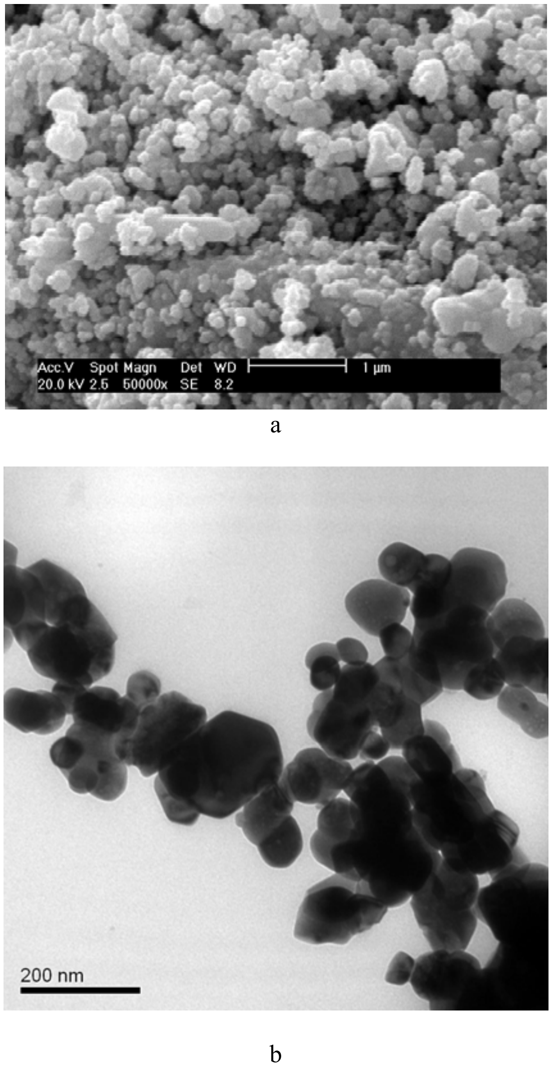


Fig. 3. XRD of ZnO derived from the zinc complex with MAO precursor.

Morphology and particle size distribution of nanometer ZnO samples derived from the zinc complex with MAO precursors were investigated by scanning electron microscopy (SEM) (as show in Fig. 4a. It can be observed clearly that the products mainly consist of smaller granules in the SEM granules, most of which are uniform. We can also predict approximately that the material particle size is smaller than 100 nm, which are in agreement with the data from the XRD estimation. Further structural characterization was carried out by the transmission electron microscopy (TEM) (as shown in Fig. 4b). The TEM images of ZnO nanoparticles demonstrate fairly uniform size distributions and shows that the particles have a size distribution in the range of 40-80 nm, which is in agreement with SEM and the XRD value. Furthermore, a wurtzite hexagonal structure is evident from this image.



a

b

Fig. 4. SEM (A) and TEM (B) for ZnO derived from the zinc complex with MAO precursor.

In our work, we used the amphiphilic zinc complexes as precursor molecules to prepare ZnO nanoparticles, for which have the both hydrophilic and lipophilic groups. We selected maleic anhydride as starting material and grafted with long chain 1-octadecanol to achieve amphiphilic ligand (MAO) with carboxylic acids as the hydrophilic segments and organic long-chain as the lipophilic segments. Then the corresponding amphiphilic zinc precursor molecules were fabricated by complexing MAO with zinc ion. After calcinating precursor molecules at 700 °C, ZnO nanoparticles have been synthesized. We supposed that in the wet chemical process, amphiphilc molecule has special self-assembling: the hydrophobic segments of the complex form the core of the micelle while the hydrophilic segments form the corona or outer shell. The hydrophobic micelle core can serve as a microenvironment for the growth of the zinc complex, while the corona shell serves as a stabilizing layer between the hydrophobic core and the external medium. We further hypothesized that the same organization would occur if a particle were a junction point of many hydrophobic and hydrophilic arms. The incompatible flexible arms can undergo spatial separation by wrapping around the metallic core. The resulting multi-arm hybrid amphiphile would be driven to aggregate in order to minimize the entropically unfavorable contacts with water molecules [45-48]. Moreover, in high-temperature process, the organic groups of the zinc complex may also serve as a dispersing medium to form nanosized material, which can also limit the agglomeration of particles. This is quite different from other methods which require employing some organic polymers to serve as dispersing mediums [49]. Therefore, using the amphiphilc zinc complexes ($Zn(MAO)_2$) as precursors, we have successfully controlled the morphology and particle size of the ZnO nanoparticles after calcinating at 700 °C, by providing a better condition for growth of the grains, for it has both hydrophilic and lipophilic groups. This preparation technology used amphiphilc molecules as a control to synthesize solid-state nanometer material, which can be expected to be a candidate technology to obtain other nanoparticles by different amphiphilic precursors.

Fig. 5 (A) shows the excitation spectra of the luminescence (λ_{em} = 400 nm) for the as-derived ZnO nanoparticles. Two excitation peaks were observed at 246, 355 nm, respectively, and other peaks were not apparently. The photoluminescence (PL) emission (excited at 246 nm) of the ZnO samples is shown in Fig. 5 (B). ZnO exhibited a wide band gap at room temperature with a large exciton binding energy, which is suitable for effective UV emission. As a result, an intense, sharp and dominated peak at 395 nm in the UV region corresponding to the near-band-edge emission (free exciton) is observed [50, 51]. In addition to the UV emission, a suppressed and weak band deep-level emission (DLE) extending from 500 nm to 600 nm and a very weak blue emission band of wavelength centered at ~ 465 nm have also been observed in this sample. The DLE can be de-convoluted into two main bands, one green band with peak maximum ~545 nm and orange band with peak maximum ~ 613 nm, is contributed to recombination at surface states (low-dimensional structures with reduced volume to surface ratio) [52, 53] and deep level defects, probably ionized charge states of oxygen vacancies [54-58]. The observation of blue band emission (centered at ~ 465 nm) of ZnO has been also reported using cathodoluminescence [59]. However, up to now, the mechanism of this emission is still a matter of debate. Generally, high crystalline quality ZnO shows a dominated UV emission with a suppressed and week green emission [60]. Bagnall et al. reported that the crystal quality of the deposited ZnO is important factor for the high UV emission and hence betterment in the crystal quality (less structural defects and impurities such as oxygen vacancies and zinc interstitials) may enhance the intensity of UV emission [60]. In our case, the near band edge emission is dominated over the deep level emission, which indicates that the grown nanostructures are good in crystal quality and exhibiting a good optical property.

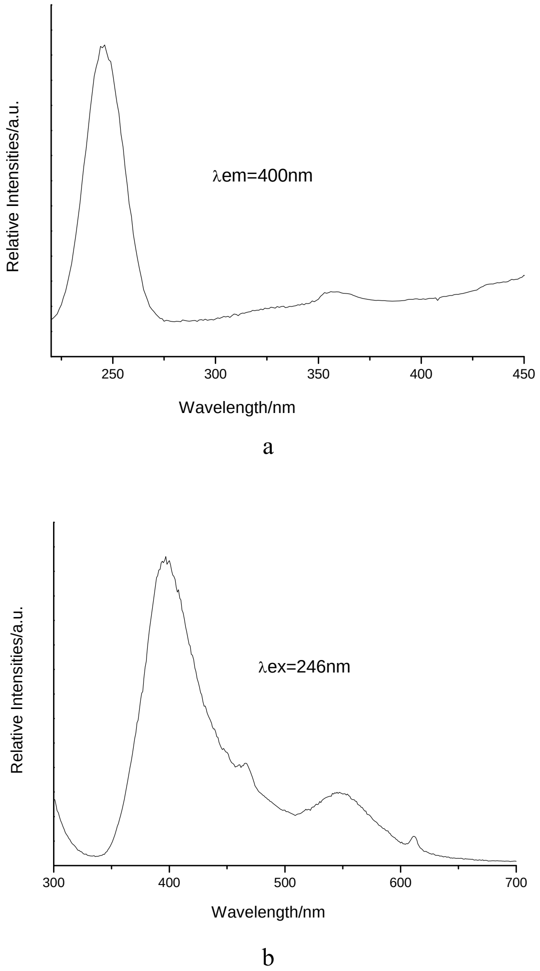


Fig. 5. Excitation spectra (A) and emission spectra (B) of ZnO derived from the zinc complex with MAO precursor.

4. Conclusions

In summary, the new synthesis method reported in this work yields the nanometer-scale ZnO semiconductor materials by using amphiphilc zinc complexes ($Zn(MAO)_2$) as precursors. After calcinating the precursors at 700 ℃, the morphology and particle size of the synthesized ZnO nanoparticles can be controlled because both the hydrophilic and lipophilic segments of amphiphilic zinc complexes can form nanosized micelle-like aggregates with various morphologies in aqueous medium by special self-assembling. The particles of this nanometer material exhibit uniform and well dispersed, hexagonal (wurtzite) crystal structure with the size in the range of 40–70 nm according to the results of SEM, TEM and XRD, which indicates that the amphiphilic zinc complexes have an influence on the shape of the ZnO after calcinations. Besides, the photoluminescence spectrum of the ZnO samples, containing four main bands, a sharp strong UV emission around ~395 nm, a weak broad green band with peak maximum ~545 nm, a very weak orange band with peak maximum ~615 nm and a very weak blue emission band of wavelength centered at ~ 465 nm, indicates that the synthesized products are single crystalline ZnO exhibiting good optical property. A candidate technology for the synthesis of nanometer materials is shown.

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