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Enhancement of optical bandgap and luminescent characteristics of one-dimensional ZnO nanoparticles

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One-dimensional ZnO nanoparticles were successfully synthesized from $Zn(CH_3COO)_2.2H_2O$ as well as CTAB-assisted NaOH and CTAB-assisted HMTA solutions. The entire calcined ZnO nanoparticles indexed with the hexagonal or wurtzite structure. Branch rod-like and columnar hexagonal-like ZnO structures were shaped when aqueous NaOH and HMTA solutions were used as the precipitating agent, respectively. In this study, the crystallite size decreased as the CTAB concentration was increased. By using an aqueous NaOH solution as the precipitating agent, the E_g value varied in a range of 3.222-3.235 eV. While the E_g value varied in a range of 3.206-3.216 eV when an aqueous HMTA solution was used. The emission peaks fitted with a Gaussian function at 390, 510, 620 and 730 nm and the defects in ZnO crystal were decreased by modifying the precursor solution with CTAB.

Key words: Nanostructured materials, Zinc oxide, Precipitation, Optical properties, X-ray diffraction.

Introduction

In the past few years, research and development effort in controlling the shape and size of ZnO particles have been extensively investigated due to their numerous applications. As we know, ZnO is a semiconducting compound that has been used increasingly in various fields due to its outstanding physical and chemical properties. ZnO is an n-type II-VI semiconductor with a wide band gap energy of 3.3 eV and large exciton binding energy of about 60 meV at room temperature which provides a great potential in applications such as gas sensors [1], surface acoustic devices [2], as a rubber additive [3] in solar cells [1] and as a photocatalyst with high chemical activity [4]. It is wellknown that the optical properties of ZnO depend closely on its structural properties such as crystallite size, orientation, aspect ratio and particle shape. Therefore, morphological control is a challenge to prepare different ZnO shapes with few agglomerations and a narrow size distribution. Recently, the utilization of a capping agent to control the morphology of ZnO is an interesting route for reducing the size and also providing monosized particles. To date, a number of capping agents have been investigated, for example, polyvinylpyrrolidone (PVP) [5], triethanolamine (TEA) [6], polyol [7] and cetyl trimethyl ammonium bromide (CTAB) [8]. Among them, much interest has been focused on the effect of CTAB because it is easily made into a clear solution. So, a number of researchers have paid attention on controlling the ZnO shape via a CTABmodified precursor solution. A variety of one-dimensional (1-D) ZnO structures such as rod-like, whisker-like, branch rod-like and sword-like shapes were prepared from different zinc salts and precipitating agents by a hydrothermal method at a high reaction temperature (>150 °C) [9-16]. Furthermore, many researchers also presented the influence of CTAB on the formation of ZnO by other techniques. Ishikawa et al. [17] showed that a rod shape was formed by a pulse laser ablation technique at low temperature (40, 60 and 80 °C) and a short reaction time (40 minutes) while Ni et al. [18] reported that a columnar structure was shaped by a microwave irradiation method. Noticeably, only a few studies displayed the role of CTAB in the size and shape control of ZnO particles by a precipitation method so far. For example, a spherical ZnO shape was formed from the reaction of CTAB-assisted ZnCl₂ and ammonia solution at room temperature with stirring for 96 h [19]. Meanwhile, a flake shape was formed if a CTABmodified NH₄OH solution was mixed with a ZnCl₂ solution and this mixed solution was agitated for 450 h [20]. Moreover, Chen et al. [8] reported that a flower-like structure was shaped when a mixture of ZnSO₄.7H₂O and NaOH solution was aged in the oven at 60 °C for 14 h.

In this study, we report the effect of CTAB on the formation of 1-D ZnO structures via a precipitation route from a Zn(CH₃COO)₂.2H₂O precursor solution when hexamethylene tetramine (HMTA) and NaOH solution were used as precipitating agent and the mixed solutions

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were stirred continuously at 70 °C for 3 h. The authors hope that the results obtained can complete the missing information on the preparation of ZnO nanoparticles by a precipitation method when CTAB was selected as the capping agent.

Experimental

Materials

All chemical agents employed in these experiments were analytical grade and they were used without further purification. The chemical agents were composed of zinc acetate dihydrate (Zn(CH₃COO)₂.2H₂O, Fluka), hexamethylene tetramine (HMTA, C₆H₁₂N₄, Fluka), cetyl trimethyl ammonium bromide (CTAB, C₁₉H₄₂BrN, Fluka) and sodium hydroxide (NaOH, Carlo Erba).

Synthesis of branch rod-like ZnO particles

0.16 mol NaOH was dissolved in 100 ml of distilled water and each of the solutions was stirred at room temperature for 10 minutes until a clear solution was obtained. Then, 0.01 and 0.02 mol CTAB was added separately into the previous NaOH solutions and they were stirred continuously for 1 h. Finally, 0.02 mol Zn(CH₃COO)₂.2H₂O that was dissolved in 100 ml of distilled water was added dropwise into the CTAB-assisted NaOH solutions. White precipitates were formed and they were still stirred at a constant temperature of 70 °C for 3 h. After the precipitates were cooled to room temperature, they were filtered, rinsed with distilled water several times and ethanol, then collected and calcined at 600 °C in air for 1 h.

Synthesis of columnar hexagonal-like ZnO particles

0.16 mol HMTA was dissolved in 100 ml of distilled water and each of the solutions was stirred at room temperature for 10 minutes until clear solutions were obtained. The other processes were followed as in preparing branch rod-like ZnO particles.

Characterization

The structural and phase formation were identified by an X-ray diffractometer (XRD, X'Pert MPD, PHILIPS). The morphological study was evaluated by a scanning electron microscope (SEM, JSM-5800LV, JEOL). The molecular structure was characterized by IR spectroscopy (Spectrum BX, Perkin Elmer). The optical absorbance was determined by a UV-vis spectrophotometer (UV-vis 2450, Shimadzu) and room temperature photoluminescence (PL) spectra were measured by a luminescence spectrometer (LS/55, PerkinElmer).

Results and Discussion

Structural study

The phase identification of all samples was, first of all, studied in order to examine the purity of the calcined samples. Fig. 1 showed that the XRD patterns of all the



Fig. 1. XRD patterns of calcined ZnO particles prepared from CTAB-modified base solutions (a) NaOH solution with 0 (A), 0.01 (B) and 0.02 (C) mol CTAB as well as (b) HMTA solution with 0 (D), 0.01 (E) and 0.02 (F) mol CTAB.

samples indexed only as the diffraction pattern of the hexagonal or wurtzite structure without any diffraction peaks of a secondary phase neither $Zn(OH)_2$ nor CH_3COONa in accordance with the JCPDS database 36-1451. Applying to the Debye-Scherrer formula [21], the average crystallite size was calculated and the results are presented in Table 1.

It is noteworthy that the type of precipitating agent and concentration of capping agent (CTAB) are the crucial parameters in this system. It is evident that the crystallite size decreased gradually as a function of the CTAB concentration. In the crystallization process, it could be considered that CTAB played an important role in diminishing the crystallite size by two different ways. Firstly, CTAB is a cationic surfactant and it can ionize completely in water. CTA⁺ could then adsorb on the surface of ZnO nuclei, giving rise to a reduction of the surface energy [22]. As a matter of fact, the surface energy of a material relates closely to the grain boundary energy. Usually, the grain boundary energy is assumed to be about 1/3of the surface energy of a material. From this point of view, it could be concluded that the grain boundary energy decreases if the surface energy decreases, resulting in a reduction of the driving force for particle growth [23]. Secondly, The CTA⁺ ions could interact with a unit growth $[Zn(OH)_4]^{2-}$ after the zinc precursor solution was introduced

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obtained						-
Table 1.	Information	of the	synthetic	conditions	and ZnO	particles

precipitating agent	CTAB concentration (mol)	Crystallite size (nm)	Particle size (diameter) (nm)	Particle shape
HMTA	0 0.01 0.02	49.48 47.17 45.41	501 473 436	Columnar hexagonal
NaOH	0 0.01 0.02	46.81 42.85 41.26	274 202 148	Branch rod

into the CTAB-assisted NaOH and CTAB-assisted HMTA solutions due to the electrostatic interaction and then the strong interaction between positively charged CTA⁺ and negatively charged plane of the ZnO nuclei brought about either the inhibition of ZnO dissolution (that could promote the crystalline growth) or inhibition of the adsorption of dissolved Zn species on the ZnO particle. So, the growth process was suppressed and a smaller crystallite size is formed as a higher CTAB concentration was used [17]. The reduction of crystallite size does not only depend upon CTAB concentration, but also the type of precipitating agent used. It is evident that a smaller crystallite size was obtained when an aqueous NaOH solution was used as the precipitating agent. This result can be explained by a strong reaction of Zn²⁺ and OH⁻ ions as well as more ZnO nuclei could nucleate due to a different mechanism as described in [24, 25], so a smaller crystallite size was formed.

Fig. 2 shows the IR spectra of calcined ZnO powders prepared from CTAB-modified precursor solutions. Four major absorption peaks were clearly observed in each spectrum. The broad absorption peak located at 3298-3657 cm⁻¹ corresponds to the O-H mode. The absorption peak at 2270-2382 cm⁻¹ is due to the CO₂ molecule in air. The absorption peak located at 1560-1693 cm⁻¹ corresponds to the symmetric C = O stretching mode and the absorption peak located at 460-530 cm⁻¹ is the stretching mode of ZnO [26]. Noticeably, the absorption peaks around 2924 and 2854 cm⁻¹ because of the stretching modes of methylene



Fig. 2. IR spectra of representative ZnO particles where (a) presence of 0.02 mol CTAB in NaOH solution and (b) presence of 0.02 mol CTAB in HMTA solution.

groups in the long chains of CTAB were not present in the IR spectra. This indicates that CTAB was completely removed from the calcined samples [27].

The particle shape of ZnO precipitated from different precipitating agents was clearly distinct. A columnar hexagonal-like shape was formed when using an aqueous HMTA solution whereas a branch rod-like shape was formed when an aqueous NaOH solution was employed. The dependence of the shape on the precipitating agent can be explained by different paths of the mechanism. Providing NaOH solution as the precipitating agent, Zn(OH)₂ precipitates can dissolve under the strong alkaline conditions and then the growth unit $[Zn(OH)_4]^{2-}$ with different growth rate of planes was found to be $v_{(0001)} > v_{(\overline{1}01\overline{1})} > v_{(\overline{1}010)} >$ $v_{(\bar{1}011)} > v_{(000\bar{1})}$ were formed in the solution. Finally, the ZnO was precipitated if the ZnO nuclei in the solution reached supersaturation. In this study, we propose that the formation of a branch rod-like shape was similar to the flower-like formation as reported in [22]. By contrast, if the zinc precursor solution was introduced into an aqueous HMTA solution, the particles were shaped differently compared to the NaOH solution. Initially, ZnO nuclei were formed following the mechanism presented in [25]. In this case, the growth rate along the (0001) plane of ZnO nuclei is very much slower than that of the branch rod-like formation. Furthermore, the six side facets of the $(10\overline{1}0)$ family could promote their growth [28], resulting in the formation of columnar hexagonal-like structure as shown in Fig. 3.

Optical study

The optical properties strongly depended upon the particle size and crystallite size of ZnO and the UV absorption of ZnO related to the electronic transition from filled valence states to empty conduction states. The direct optical bandgap of calcined ZnO particles could be evaluated through the well-known relationship as follows [29]:

$$\alpha E = D(E - E_g)^{1/2} \tag{1}$$

where E is the photon energy, α is the absorption coefficient and D is a constant. In this evaluation, the photon energy was calculated by the relationship:

$$E = \frac{1240}{\lambda} \tag{2}$$

where λ is the measured wavelength in nanometers. For the final term, the absorption coefficient could be estimated from:

$$\alpha = A/d \tag{3}$$

where A is the measured absorbance and d' is the thickness of cell.

Fig. 4 showed the extrapolation of the straight line down to $\alpha E = 0$ (where $E = E_g$) for all samples. By using the NaOH solution as the precipitating agent, E_g values of about 3.227, 3.229 and 3.235 eV were obtained as the CTAB concentration was increased from 0 to 0.01 and



Fig. 3. A SEM images of calcined ZnO particles prepared from CTAB-modified base solutions (a) NaOH solution with 0 (A), 0.01 (B) and 0.02 (C) mol CTAB as well as (b) HMTA solution with 0 (D), 0.01 (E) and 0.02 (F) mol CTAB.

0.02 mole, respectively. Similarly, the E_g values increased from 3.206 to 3.210 and 3.216 eV when HMTA was used as the precipitating agent in the presence of CTAB with an amount of 0, 0.01 and 0.02 mole, respectively. It is clearly seen that the E_g value increased as a function of the CTAB concentration or crystallite size. This was explained by the modification of the band structure, i.e; narrowing of the valence and conduction bands [30]. Regarding the E_g values of ZnO particles precipitated from different bases, the E_g values obtained of the ZnO particles prepared from the NaOH solution were larger than that of the E_g values of the ZnO particles prepared from the HMTA solution. This is because a smaller crystallite size of the ZnO particles was obtained when using the NaOH solution as the precipitating agent in the precipitation process.

Considering the effect of the particle shape on the E_g value, it could be observed that the E_g value of branch rod-like particles with a larger crystallite size (46.81 nm) is wider than that of the E_g value of the columnar hexagonal-like shape particles with a crystallite size of 45.41 nm.



Fig. 4. Evolution of the $(\alpha h\nu)^2$ vs. hu curves of calcined ZnO particles prepared from CTAB-modified base solutions (a) NaOH solution with 0 (A), 0.01 (B) and 0.02 (C) mol CTAB as well as (b) HMTA solution with 0 (D), 0.01 (E) and 0.02 (F) mol CTAB.

In summary the particle shape affected directly the E_g value and thus the branch rod-like structure provided a larger E_g value compared to the columnar hexagonal-like structure.

Fig. 5 illustrates the room temperature PL spectra recorded from the branch rod-like ZnO (Fig. 5(a)) and columnar hexagonal-like ZnO (Fig. 5(c)). From Fig. 5, two strong luminescence bands which displayed a UV band and a visible broad band can be observed at about 390 nm and 640 nm, respectively. The emission spectrum of a representative sample was fitted with a Gaussian function and the result showed an emission peak at about 390 nm in the UV region. This peak is attributed to the direct recombination of excitons through an exciton-exciton collision process or exciton annihilation which is a characteristic near the band gap of ZnO. The broad band in the visible region showed three peaks centered at about 510, 620 and 730 nm. Herein, it could be said that the emission peaks centered at 390, 510 and 620 nm are basic PL emissions [31, 32] and the peak centered at about 730 nm is an overtone emission at about 390 nm [33]. An explanation of the emission in the visible region is still an important issue. Nevertheless, it is as yet not understood clearly. Many reports [34-37] considered that oxygen vacancies could be responsible for the visible emission. In this study, the peak at about 510 nm (green emission) is associated with an optical transition in a singly ionized oxygen vacancy and the emission peak located at about 620 nm (yellow emission) is attributed to a single negatively charged interstitial oxygen ion [38]. It is noteworthy that the room temperature PL intensity of ZnO particles prepared from



Fig. 5. (a) Room temperature PL spectra of calcined ZnO particles prepared from NaOH solution with 0 (A), 0.01 (B) and 0.02 (C) mol CTAB, (b) PL emission of sample C fitting with Gaussian function, (c) Room temperature PL spectra of calcined ZnO particles prepared from HMTA solution with 0 (D), 0.01 (E) and 0.02 (F) mol CTAB and (d) PL emission of sample F fitting with Gaussian function.

the CTAB-modified zinc precursor solution is lower than that of the PL intensity of ZnO particles prepared from the solution without any addition of CTAB, indicating that CTAB could help in reducing the defects in ZnO crystals.

Conclusions

Branch rod-like and columnar hexagonal-like ZnO particles were successfully fabricated by a precipitation method at low temperature. The type of precipitating agent strongly influenced the particle shape and crystallite size. A smaller crystallite size and branch rod-like shape were obtained when an aqueous NaOH solution was used whereas a columnar hexagonal-like shape with a larger crystallite size was obtained when using an aqueous HMTA solution as the precipitating agent. The shape and size of ZnO particles directly affected the Eg value obtained. A wider Eg value was obtained from the smaller crystallite size and branch rod-like shape. The room temperature PL emission showed four major peaks centered at about 390, 510, 620 and 730 nm when fitted with a Gaussian function. The PL intensity in the visible region decreased as a function of the CTAB concentration, indicating that the defects in the ZnO structure were decreased as CTAB was introduced into the precursor solution.

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