Hydrothermal conversion of ZnO₂ to ZnO flowers: A mechanistic investigation and characterization

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In this article, we report a novel but simple method for the phase transformation of ZnO₂ to flower-like ZnO microstructures hydrothermally at 90 °C with and without the assistance of hexadecylamine as surfactant. The generation of zincate ion ZnO₂²⁻ as a growth unit from the reaction between ZnO₂ and peroxide ion O₂²⁻ *in situ* plays a key role in the phase transformation of ZnO₂ to ZnO. The morphology, structure, and composition of the products have been investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Powder X-ray diffraction (PXRD) and energy dispersive X-ray analysis (EDX). It has been demonstrated that the as-fabricated ZnO flowers are composed of self-assembled brooms and rods in the presence and absence of hexadecylamine respectively. On the basis of experimental results, a possible reaction mechanism and the growth processes involved in the formation of flower-like ZnO microstructures are discussed.

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1 Introduction

Synthesis of fine, structured semiconducting materials, particularly nano/micro structured metal oxides attracts a great deal of attention because of their extensive applications in catalysis, photonics and electronics [1–4]. Among the fine, structured semiconducting materials, ZnO is a wide direct band gap (3.37 eV) semiconductor material with a large exciton binding energy (60 meV). Besides, its nontoxicity, inexpensive and chemical stability has made ZnO a promising material in various fields including room-temperature ultraviolet laser [5], gas sensors [6], varistors [7], light-emitting diodes [8], solar cells [9], photo electronics [10], and so on. Over the past few years, much effort has been devoted to obtain nano/micro structured ZnO with controlled size and architecture because the optical, physicochemical and electric properties of ZnO are intimately dependent on its size and shape. Several strategies have been developed for the controlled synthesis of ZnO structures, such as direct thermal physical evaporation, catalysis assisted vapor-liquid-solid growth, and solution-based chemical routes [11–15]. In addition to the conventional solid-state process, several other synthetic routes such as spray-drying method, sol–gel process, thermal evaporation process, emulsion strategies, self-assembly techniques, precipitation, hydrolysis, pyrolysis, and hydrothermal methods [16–23] have also been successfully explored for the preparation of a variety of morphologic ZnO nanostructures. Upto now, various kinds of ZnO particles in different sizes and morphologies including nanowires, nanorods, nanotubes, nanoribbons, nanoneedles, nanocables, tetrapods, comb-like structures, tower-like structures [24–26], etc. have been reported. However, there have been a few reports on the synthesis of flower-like ZnO structures [27–31]. More recently, Mavundla et al. fabricated the solar cell devices from flower-shaped ZnO structures synthesized by microwave annealing of zinc nitrate and KOH at 180 °C [32]. Chen et al. reported a dye-sensitized solar cell based on a flowerlike ZnO nanorod array photo anode fabricated by low temperature hydrothermal method [33]. Wang et al. obtained ZnO nanoflowers via a simple low-temperature route in the absence of surfactants and showed that ZnO with different morphologies such as flowers and rods could be obtained via altering the concentration of NaOH

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[34]. Huang et al. synthesized ZnO crystals through a simple solution route at low temperature and ambient pressure [35]. Hong-Ju Zhai et al. synthesized spindle-like, pencil-like, branch rod-like and frizzy flower-like shaped ZnO in a mixed solvents of ethanol and water via hydrothermal method [36]. Qi Xiao synthesized ZnO microrods and flower-like 3D superstructures simply by tuning the volume ratio of Zn(OH)₄²⁻ precursor solution to the volume ratio of ethylene glycol to water via a template-free hydrothermal method [37].

Recently, Chin-Cheng Hsu and Wu reported the complete phase transformation of ZnO₂ to ZnO at 180 °C using the hydrothermal technique [38]. Cheng et al. converted ZnO₂ to ZnO hollow spheres through heat treatment at 180 °C in air [39]. However, the investigation of the reaction mechanism involved in the fabrication of ZnO by phase transformation of ZnO₂ at low-temperature remains a significant challenge to material scientists. In the present study, the flower-like ZnO structures were synthesized at 90 °C via hydrothermal method by the phase transformation of ZnO₂. In brief, ZnO₂ was prepared at room temperature in the presence and absence of hexadecylamine and these mixtures were used as precursors for the synthesis of ZnO flowers under hydrothermal treatment at different temperatures. The generation of soluble zincate ion ZnO₂²⁻ from the reaction between ZnO₂ and peroxide ion O₂²⁻ *in situ* as a growth unit plays a key role in the transformation of ZnO₂ to ZnO. Moreover, the growth process and the possible reaction mechanism involved in the formation of ZnO products are investigated.

2 Experimental

Materials ZnO, glacial acetic acid (CH₃COOH), hexadecylamine (HDA), sodium hydroxide (NaOH), hydrogen peroxide (H₂O₂) were purchased from Merck Limited and used as received without further purification. Double distilled water was used throughout the experiments. The typical procedure we followed for the synthesis of flower-like ZnO structure is described as follows. 1.0 g of ZnO powder was added to a solution mixture of 0.1 g hexadecylamine dissolved in 2 ml glacial acetic acid and mixed homogeneously. Then, 25 ml of H₂O₂ (30%) was added into the above solution. After a few minutes, a clear, pale yellow solution was formed. To this solution, 10 ml of 5 M NaOH was introduced resulting in the formation of a pale yellow precipitate. The exothermic reaction occurs slowly during the reaction. And then, the reaction mixture was kept for 24 h at room temperature to ensure the completion of the reaction. Afterwards, the reaction mixture was transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 ml, then sealed and maintained at different temperatures ranging from 70–180 °C for 24 h in a preheated electric oven. For comparison, a similar experiment was carried out in the absence of hexadecylamine. After hydrothermal treatment, the autoclaves were naturally cooled to ambient temperature. The yellowish crystalline products were harvested by centrifugation, washed several times with distilled water and absolute alcohol to remove any possible residual impurities and finally dried at 60 °C in an oven for 2 h.

Characterization The phase purity and crystal structure of the obtained products were characterized by powder X-ray diffraction, which was recorded on a Philips X'pert PRO X-ray diffractometer with graphite monochromatized Cu K α radiation source ($\lambda = 1.541 \text{ \AA}$) operated at 40 kV and 30 mA. The morphologies of the products were examined by JEOL (JSM-6490LV) scanning electron microscope. The nano/microstructure of the products was observed by transmission electron microscopy equipped with an energy dispersive X-ray spectroscopy and selected area electron diffraction (SAED) which was performed on a Hitachi model H-600 instrument operating at 100 kV. The absorption spectrum was recorded using Shimadzu visible spectrometer (UV-3101) at room temperature. The room temperature photoluminescence (PL) study was carried out on a Perkin-Elmer LS-55 luminescence spectrometer using Xe lamp with an excitation wavelength of 325 nm at room temperature.

3 Results and Discussion

Powder X-ray diffractions The PXRD patterns of the products prepared at different temperatures are shown in figure 1. All the diffraction peaks of the PXRD pattern (figure 1a) of the product synthesized at room temperature can be perfectly indexed to a pure cubic phase of ZnO₂ with lattice constant $a = 4.8680 \text{ \AA}$ (Pa3, JCPDS 13–311). Figures 1b–d shows the powder X-ray diffraction patterns of the products synthesized under hydrothermal treatment in the temperature range of 70–90 °C for 24 h. From XRD results, it can be seen that the product

Fig. 1 PXRD patterns of the products prepared at (a) room temperature, (b) 70 °C/24 h, (c) 80 °C/24 h and (d) 90 °C/24 h.

obtained after hydrothermal treatment at 70 °C (figure 1a), exhibits the diffraction peaks at $2\theta = 34, 47.5, 56.7, 66.2, 67.9$ and 69.1 corresponding to (002), (102), (110), (200), (112), and (201) planes which had started to appear, significantly indicating the formation of ZnO. Therefore, at 70 °C the diffraction peaks could not be indexed to any known single compound indicating, that this may be identified as a mixture of the cubic phase of ZnO_2 and hexagonal phase of ZnO. On prolonging the reaction at 90 °C for 24 h (figure 1d), the existing peaks for the cubic phase of ZnO_2 were completely disappeared, which has been considered to be accountable for the complete transformation of ZnO_2 into ZnO. Figure 1d is the PXRD pattern of the ZnO phase which is indeed, well crystallized. All the peaks can be perfectly indexed to a wurtzite structure, and the measured lattice constants of c and a of this hexagonal phase are 5.21 and 3.25 Å (P63mc, JCPDS 36-1451) respectively.

Scanning Electron Microscopy and Transmission Electron Microscopy In order to understand the formation mechanism of the ZnO products, temperature-dependent experiments were carried out and the morphology of the products were studied by SEM. Figure 2a–e shows SEM images of the resulting products synthesized hydrothermally with the assistance of HDA at different temperatures. Figure 2a shows the SEM image of the sample obtained at 70 °C which is a mixture of ZnO_2/ZnO and does not indicate any regular, well-defined shaped structure. At this temperature the conversion of ZnO_2 to ZnO is very minute. When the experiment was performed at 80 °C, it was found that the nest-like morphology of the product was constituted by rods and on close examination, the morphology revealed the existence of a small number of irregular shaped ZnO_2 particles (figure 2b). When the temperature was increased to 90 °C, the flower-like morphology made of ribbons was obtained (figure 2c). On further increasing the reaction temperature to 180 °C, it was found that the product exhibits the large-scale micro-meter sized ZnO flowers shown in figure 2d. It can be observed that the majority of ZnO particles were uniformly distributed in the form of flowers with a higher aspect ratio. Figure 2e represents the SEM image of the product obtained at 180 °C for 48 h. It was found that the flower-like assemblies were disassembled to individual brooms possibly due to the stress-strain existing in the center. It implies that each individual flower is composed of well-aligned bundles of brooms which are radially oriented to the center. Figure 2f is the TEM image of selected individual ZnO brooms. The ZnO broom nanorods resemble a sword. The selected area electron diffraction (SAED) pattern taken from the same broom as shown in the figure 2g clearly demonstrates that the broom can be indexed as a single-crystalline hexagonal wurtzite ZnO.

Figure 3a–c shows the SEM images of the resulting products synthesized hydrothermally in the absence of HDA at 180 °C for 24 h. The products also exhibit flower-like morphologies composed of a large number of self-assembled hexagonal nanorods homocentrically. On ultrasonication for 10 min, the flower-like morphology was destroyed and the self-assembled hexagonal nanorods were disassembled to discrete nanorods. Figure 3d shows the TEM image of selected individual ZnO nanorods. It indicates that a ZnO nanorod is of hexagonal shape with a smooth surface.

Energy-dispersive X-ray Spectroscopy The chemical purity of ZnO as well as its stoichiometry was investigated by EDX analysis. Figure 3e presents the EDX spectrum of the ZnO flowers. The EDX spectrum clearly

Fig. 2 SEM images of the products prepared using hexadecylamine at (a) 70 °C, (b) 80 °C, (c) 90 °C, (d) 180 °C (24 h from a–d), (e) 180 °C for 48 h, (f) TEM image and (g) SAED pattern of single ZnO broom.

indicates that the flowers are composed of only Zn, and O, without any trace of impurity. The copper signal in the spectrum arises from the copper grid of TEM. The elemental analysis reveals that the atomic ratio of Zn:O is 65.3:34.7, indicating the presence of oxygen deficiency, which might have been caused during the rapid formation of ZnO flowers under hydrothermal process. The crystal defects (oxygen vacancy) in ZnO flowers are potentially good for making new chemical sensors and solar cells.

Fig. 3 SEM images of the products prepared in the absence of hexadecylamine at 180 °C for 24 h: (a, b) the low-magnification, (c) the high-magnification, (d) TEM image of single ZnO hexagonal rod and (e) EDX spectrum of ZnO.

Reaction and growth mechanisms The basic reactions occur at room temperature and the hydrothermal process can be described as follows:

At room temperature:

Fig. 4 Schematic representation of the formation mechanism of microstructured ZnO flowers.

During hydrothermal process:

From reactions 1–3 at room temperature, it is understood that sodium hydroxide reacts with hydrogen peroxide present in excess, producing peroxide (O_2^{2-}) ions. The peroxide ions in turn react with Zn^{2+} ions and lead to the formation of ZnO_2 precipitate which was confirmed by X-ray diffraction studies. During the hydrothermal process, formation of the growth unit in solution is the main factor for the transformation of ZnO_2 to ZnO. Previously, the existence of soluble zincate ZnO_2^{2-} ion has been reported [40–42]. Therefore, in our case, one can assume that the soluble zincate ion ZnO_2^{2-} is the growth unit which could be formed *in situ* owing to the reaction between ZnO_2 and O_2^{2-} as observed in reaction 4. During the hydrothermal process, the formation of ZnO crystal is proportional to the concentration of the growth unit ZnO_2^{2-} in solution according to reaction 5. At the beginning of the reaction, the quantity of ZnO_2 is larger compared to O_2^{2-} . So the nucleation rate of ZnO crystallite depends on the concentration of the soluble zincate ion ZnO_2^{2-} . This process is continued for as long as the complete quantity of ZnO_2 is converted to ZnO through the formation of soluble ZnO_2^{2-} ions (reactions 4 and 5).

The proposed growth mechanism of the flower-like ZnO microstructures is shown in the schematic diagram (figure 4). In the primary growth stage of ZnO during the hydrothermal process at 70 °C, a small amount of ZnO_2 precipitate can partly transform into ZnO nuclei via the formation of ZnO_2^{2-} ion. The generated ZnO particles serve as the seeds or nucleation centers. Aggregation of these particles leads to the formation of rods on the surface of the ZnO_2 particles. On increasing the temperature to 90 °C, the ZnO_2 precipitate could be completely transformed into ZnO as the final product and the crystal shape could be well developed into a flower-like morphology. On ultrasonication for 10 min or when the reaction time is increased to 48 h at 180 °C, the flower-like morphology was destroyed to individual brooms. The resulting brooms were made of radially aligned sword-like nanorods in the presence of hexadecylamine. The hexadecylamine molecules interact with zincate $[\text{ZnO}_2]^{2-}$ ion to form a complexing agent, this complexing agent adsorbs on the surface of ZnO nuclei, which leads to the formation of active sites. So that the secondary growth process occurs by the aggregation of ZnO particles at energetically favorable active sites on the surfaces of the rods, resulting in the formation of ZnO brooms. The ZnO broom-like structures undergo self-assembled and finally leads to the formation of well defined flower-like ZnO structures. From the crystallography, the structure of ZnO can be described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the *c*-axis. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (000 $\bar{1}$)-O polar surfaces. Under hydrothermal conditions the HDA molecules act as a ‘shape inducing reagent’ and may preferentially adsorb on the side walls of the ZnO which inhibit the radial growth of the nanorods relative to the longitudinal growth and promote the growth along the (0001) direction greatly and result in the formation of sword-like nanorods.

Fig. 5 Room-temperature (a) UV-Vis absorption and (b) PL spectrum of the obtained flower-like ZnO microstructures.

Optical properties The room temperature UV–Vis absorption spectrum of the ZnO flowers is shown in figure 5a. The spectrum shows an absorption peak located at 370 nm with a blue shift in comparison with that of bulk ZnO (400 nm), this shift may be ascribed to the size effect of the synthesized flower-like ZnO microstructures [43]. The room-temperature PL spectrum of the ZnO is shown in figure 5b. The following emission bands have been observed: The UV emission band at 399 nm in ZnO structure is also called near band edge (NBE) emission and is due to recombination of free-excitons via a process of exciton-exciton collisions. The violet band at 423 nm is believed to be due to radiative defects related to the interface traps existing at the grain boundaries and emitted from the radiative transition between this level and the valence band. While the blue band emission at 460 nm perhaps originated from the recombination of oxygen vacancies with oxygen interstitials or other defects [36]. The blue-green band emission at 485 nm corresponds to a single occupied oxygen vacancy in ZnO and also results from the recombination of photo-generated hole with single ionized charged state of this defect. The weak green emission band at 527 nm implies that there are few surface defects in the product [44–46].

4 Conclusions

In summary, we have successfully synthesized flower-like ZnO microstructures by complete phase transformation of ZnO₂ at 90 °C under hydrothermal process, with and without the assistance of hexadecylamine. The generation of zincate ion ZnO₂²⁻ *in situ* as a growth unit plays a key role in the phase transformation of ZnO₂ to ZnO. The flower-like ZnO microstructures made of self assembled individual brooms and hexagonal rods were obtained in the presence and absence of hexadecylamine respectively.

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