Surfactant-Free Fabrication of ZnO Spheres and Pseudospherical Structures

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ZnO spheres and pseudospherical structures have been synthesized by a surfactant-free wet chemical method. The products were formed by a dissolution/reprecipitation mechanism. Room temperature ferromagnetism has been observed in the products, which could be affected not only by annealing but also by ultrasonic treatment. Photoluminescence measurement reveals that the ferromagnetism may relate to the defects that cause the 469 nm emission, and the products mainly show blue emission in the visible band after annealing. The low-cost and high-yield synthesis method makes the products promising materials for optoelectro and spintronic devices.

Introduction

As an important inorganic functional oxide, ZnO has stimulated much interest for its wide application in electronics, optoelectronics, photocatalysis, sensors, etc.1-4 The theoretical prediction and experimental observations of room temperature (RT) ferromagnetism in ZnO-based diluted magnetic semiconductors (DMS) have added a new dimension to the application of this material.5,6 Recent research showed that pure ZnO could also show RT ferromagnetism,7,8 indicating that they are candidate materials for spintronic devices. Diverse methods have been employed to prepare ZnO nano- or microstructures, but large-scale use will depend on the development of simple, low-cost approaches.1 In this sense, solution-based methods under one-pot conditions may be the most effective and realistic way to prepare ZnO materials with controlled morphology. The “bottom-up” assembly paradigm in nanotechnology requires materials with lower crystal symmetries to serve as symmetric building blocks. Spherical structures are still the most favorable architecture because of their highest symmetry.9,10 However, due to its noncentrosymmetric structure, hexagonal wurtzite ZnO prefers to grow along the c-axis ([0001] direction) in solution media, resulting in the commonly observed one-dimensional (1D) ZnO nanostructures such as nanorods and nanowires.11,12 However, by using surfactants as crystal growth modifiers, ZnO spheres can be obtained. For example, by using PEG (polyethylene glycol) in a solution phase process, particle-assembled ZnO spheres have been obtained,13 and by adding PVP (poly(vinylpyrrolidone)) in a solvothermal reaction, ZnO/PVP nanocomposite spheres with two hemispheres have been obtained, in which the PVP phase can be moved by heating.9 On the other hand, by using templates, ZnO hollow spheres can be fabricated in solution.14,15 Although the formation of these symmetric structures is induced by templates or polymeric additives, a question arises as to whether or not the ZnO materials with an anisotropic crystals system can be directly prepared into isotropic structures by wet chemical synthesis. In this study, we report a simple way to fabricate ZnO spheres and pseudospherical structures by chemical bath deposition (CBD) without any additives. The method is environmentally benign, low-cost, and high-yield. RT ferromagnetism has been observed in the products, which makes them promising candidates for spintronic devices.

Experimental Section

Preparation. In a typical synthesis, Zn(NO3)2·6H2O and hexamethylenetetramine (HMT) with equal molar ratio were dissolved into 40 mL of ethanol to form a 0.1 M solution. The solution was pretreated in an ultrasonic water bath for 15 min, then transferred into a 50 mL flask, sealed, and placed into a water tank left at 70 °C for 20 h. The products were collected by centrifugation, then thoroughly washed with distilled water and ethanol, and finally dried at 70 °C in air. For further investigation, some of the as-prepared samples were immersed in ethanol and treated in the ultrasonic water bath for 2 h, and some were annealed at 400 °C in air for 2 h.

Characterization. All the samples were characterized using X-ray diffraction (XRD) (Philips X’Pert-MRD, Cu Kα, λ = 1.5406 Å), scanning electron microscopy (SEM) (Quanta 200FEG), transmission electron microscopy (TEM) (Tecnai F30) and high resolution TEM (HRTEM) (Hitachi H-9000NAR). Magnetic properties were measured using an alternative gradient magnetometer (Micromag TM2900). Photoluminescence (PL) studies were carried out at RT using a Hitachi F-4500 spectrofluorometer (Xe lamp, λex = 325 nm).

Results and Discussion

Structure and Morphology. Figure 1 shows the XRD patterns of the as-prepared and post-treated products. All the reflection peaks can be indexed into hexagonal ZnO (JCPDS 36-1451), and no impurity phase has been found. Size and morphology information of the as-prepared products are depicted in Figure 2. As shown in Figure 2a, the ZnO products consist of relatively uniform spherical structures in which the dominant products are monodisperse ZnO spheres, as shown in Figure 2b. Fewer twinning spheres with an interface are included, as shown in Figure 2c. The diameters of the spheres, including that in the twinning spheres, are about 700–800 nm. Multi-spherical structures, although very rare, could be also found in the products. As shown in Figure 2, panels d–j, these structures comprise more than three quasi-spheres, where each quasi-
sphere still has a diameter of 700–800 nm. Similar twinning spheres can be seen in ref 9, where the ZnO/PVP nanocomposite spheres comprise two mesocrystalline hemispheres. However, the multispherical structures have not been reported before. Some of the structures still show clear interfaces, as shown in Figure 2, panels d and f, whereas in others the interfaces are not clear (Figure 2, panels e and i) or entirely disappear (Figure 2j). Figure 3 shows the TEM images of the products. The spheres do not contain interior structures as indicated by Figure 3a, and they have some features of mesocrystals, as shown in Figure 3b. The spheres are assembled by rather small crystallites, but the crystallites are not obvious, and the spheres are not apparently porous as those in refs 9 and 13. HRTEM image in Figure 3c further demonstrate these features. The crystallites are highly crystalline with a lattice spacing of 0.26 nm, corresponding to an interlayer spacing of the (0002) planes in the ZnO crystal lattice. However, the lattices of the adjacent crystallites exhibit a little misalignment, as indicated by the white lines in Figure 3c.

It is well-known that ZnO can form various twinned crystal-line structures by incorporate the growth units on its identical \{0001\} surfaces, and it is supposed that the combining of the polar surfaces with higher energy may lower the system energy in the solution conditions.\(^{9,10}\) However, considering the various multispherical structures here, new contents should be added to understand the nature of the ZnO twinning mechanism. It is noteworthy that the products are rather stable, without morphology destruction after ultrasonic or annealing treatment, as shown in Figure 4. The products maintain their spherical morphology, and twinning spheres and multispherical structures still exist, as indicated by the white arrows.

**Growth Mechanism.** To understand the growth kinetics, the growth process was studied by time-dependent observation. Figure 5 depicts the morphology of products obtained for 2.5, 5, 7.5, and 10 h. Hexagonal prism clusters and grenade-like hexagonal prisms with two subunits were obtained at the initial reaction stage as shown in Figure 5a. The prisms in the clusters
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Figure 4. SEM images of (a) the ultrasonic treated sample and (b) the annealed sample.

Figure 5. SEM images of the as-prepared products for different times: (a–c) 2.5 h, (d, e) 5 h, (f, g) 7.5 h, (h, i) 10 h.

Figure 6. Schematic illustration of the possible formation process for typical ZnO spheres and twinning spheres: (1) the formation of hexagonal prism clusters and grenade-like hexagonal prisms; (2) the prism clusters and grenade-like prisms dissolved and reprecipitated into smaller hexagonal prisms; (3) the hexagonal prisms also dissolved and spheres formed; (4) granules nucleated on the surfaces; (5a) all the granules dissolved and evenly reprecipitated on the surfaces; (5b) one granule grew to form a twinning sphere while others dissolved.

were ~700–800 nm in width. The bottom subunit of the grenade-like hexagonal prisms was ~550–700 nm wide and ~900–1100 nm long, larger than the up subunit with a width of ~750–900 nm and a length of ~550–750 nm. The same twining ZnO structures have been reported in ref 10, which were also obtained in the initial stage of a solution reaction. However, when the reaction time extended to 5 h, both the prism clusters and the grenade-like prisms disappeared. Instead, hexagonal prisms with nearly equal width and length of ~350 nm appeared, as shown in Figure 5, panels d and e. Although the result is similar to that in ref 10, in which the smaller subunit of the twinning structure evolved to be equivalent to the big one and an integrated hexagonal prism was obtained, the process here should be rather different because the hexagonal prisms were much smaller than the former grenade-like hexagonal prisms. When the time extended to 7.5 h, spheres appeared as shown in Figure 5, panels f and g, although hexagonal prisms could still be seen. Then, after 2.5 h, all the prisms disappeared, and all the products are ZnO spheres (Figure 5h). Many spheres contained a disk-like adjunction, as shown in Figure 5i, and the surfaces were adhered by some granules.

On the basis of the experimental results, a proposed growth mechanism for the formation of typical ZnO spheres and twinning spheres is given in Figure 6. First, the HMT hydrolyzed according to the following equations.

\[
\begin{align*}
(\text{CH}_3)_2\text{NH}_2+6\text{H}_2\text{O} & \rightarrow 6\text{HCHO} + 4\text{NH}_3 & (1) \\
\text{NH}_3+\text{H}_2\text{O} & \rightarrow \text{NH}_4^++\text{OH}^- & (2)
\end{align*}
\]

The H_2O came from the crystal water of Zn(NO_3)_2·6H_2O. Soon, [Zn(OH)_6(NH_3)_n]^{2−n} formed, but this intermediate product then decomposed and grew into grenade-like ZnO twinning crystals and hexagonal prism clusters.10 As the HMT further hydrolyzed, twinning crystals dissolved and reprecipitated into smaller hexagonal prisms, but these hexagonal prisms also dissolved, and then ZnO spheres formed. Granular ZnO crystals nucleated on the surfaces of the spheres; one or more may have grown bigger and formed the twinning or multi-spherical structures while others dissolved and reprecipitated to form relatively smooth surfaces of the spherical structures. In the aging time, forced by the Gibbs free energy minimization, the dissolution/reprecipitation process reoccurred until the diameters of the spheres were relatively uniform.17 The ethanol plays an important role in the formation of the ZnO spheres and pseudospherical structures. The ZnO crystal grows faster along the [0001] direction in aqueous solution because Zn(OH)_2 ions, the growing unit in the solution, are likely adsorbed on the positive polar face of the (0001) surface. Thus, ZnO nanowires can be obtained using aqueous solution of zinc acetate dihydrate (Zn(CH_3COO)_2·2H_2O) and HMT.18 When water was used as solvent in our experiment, ZnO prisms, instead of spheres, were obtained. Noting that water has a stronger polarity than ethanol, the relatively weak polarity of ethanol may limit ZnO growth along the c-axis and favor the isotropic growth. It is worthy to note that when adding a little amount of water to the ethanol solution, for example, adding 2 mL of water to 40 mL of ethanol, layered basic zinc nitrate would be obtained.

Magnetic Properties. The magnetic properties of the ZnO spheres were investigated. Figure 7 presents the magnetic hysteresis (M−H) curves of the as-prepared and post-treated products measured at 300 K. The as-prepared products exhibited RT ferromagnetism with coercivity of about 120 Oe and the saturation magnetization (M_s) of ~0.0016 emu/g. It is interesting to observe that the M_s was weakened not only by annealing but also by ultrasonic treatment. The RT ferromagnetism in pure ZnO is generally believed to be related to intrinsic point defects,7,8 and the defects can be adjusted by annealing;8 it can also be affected by ultrasonic treatment.19 It has been found that ZnO film treated by ultrasonic can generate strong green photoluminescence (PL) emission (508 nm), which was attributed to oxygen vacancies produced by the enhancement of lattice vibration during the ultrasonic treatment.19 However, in our study the annealing treatment was supposed to reduce the oxygen vacancies, but the M_s was also weakened. Thus, the ferromagnetism may relate to other defects.

Optical Properties. To investigate the point defects in the as-prepared products and the concentration change of the defects...
by post-treatment, PL measurements were employed at RT. As shown in Figure 8, the PL spectrum of the as-prepared products consisted of four main emissions: an ultraviolet emission at around 400 nm, which can be attributed to the red band-edge excitonic emission; two blue emissions at $\sim$452 nm and $\sim$469 nm, and a broad green emission at $\sim$550 nm. Recent research has assigned the 452 nm (2.74 eV) emission to interstitial zinc and the green emission to oxygen vacancy. However, the 469 nm (2.64 eV) emission is not widely observed, although it is usually considered to be related to intrinsic defects generated during the preparation and post-treatment, such as the singly negative charged zinc vacancy; the origin is still not very clear. It can be seen from Figure 7 that the annealed and ultrasonic treated products exhibited different PL spectra. After annealing treatment, the green emission almost disappeared, and the relative intensity of the 469 nm emission decreased while that of the 452 nm emission nearly unchanged. However, after ultrasonic treatment, the relative intensity of green emission increased while both blue emissions were weakened. Because the magnetization of the as-prepared products decreased after annealing and ultrasonic treatment, the ferromagnetism in the as-prepared ZnO spheres should not originate from the defects that caused the 452 and 550 nm emissions, but it relates to the defects that caused the 469 nm emission. It is worthy to note that the $M_s$ values of the annealed and ultrasonic treated products were almost equal, as shown in Figure 6, and relative intensities of the 469 nm emission were also nearly equal. Although recent studies have shown that Zn vacancy can induce RT ferromagnetism in Mn-doped ZnO, the exact origin of the 469 nm emission still needs further theoretical and experimental investigation, and the nature of ferromagnetism in the ZnO spheres is still not clear.

Conclusions

We have demonstrated that non-centrosymmetric ZnO can be fabricated into symmetric spheres via a surfactant-free wet chemical method. The spheres and pseudospherical structures were formed by a dissolution/reprecipitation mechanism. The products showed RT ferromagnetism, which may relate to the defects that caused the 469 nm PL emission. Both the ultrasonic and the annealing treatments can weaken the ferromagnetism, and the annealing treatment can cause the products to mainly show a blue emission in the visible band. The synthesis process is facile and low-cost and gives a large-scale yield, indicating the products may be useful materials for optoelectronic and spintronic devices.

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References and Notes