ZnO Microspheres Self-assembled by Hexagonal Nanoplates

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Because of the polar growth manner ZnO of different shapes has been synthesized. However, the isotropic shapes of ZnO have not reported yet. In this paper, the novel ZnO microspheres were synthesized by the complex system in which starting reagents, $Zn(AC)_2$, H_2O, and HMT, were kept in methanol solution at 60 °C for 12 h. The FE-SEM images and XRD pattern results show that the microspheres are formed by ZnO nanoplates that align in a regular periodicity via self-assembly. The formation mechanism of this nanostructure was discussed briefly.

Recently, controlled growth of ZnO has stimulated wide interest in materials research because the unique optical, chemical, electrical properties of ZnO rely heavily on its size, shape and so on.[1–4] More and more attention has given to develop simple and effective kinds of synthetic methods to prepare size- and shape-controlled ZnO crystals. Self-assembly, as a "bottom-up" technology, is a promising method to control crystal growth. Up to now, different structures with size- and shape-controlled crystals, including rods,[5] cages and shells,[6] ribbons,[7] and so forth, have been prepared. We report here a novel self-assembled nanostructure: uniform microspheres formed by alignment of hexagonal nanosized crystals via self-assembly of ZnO, which shows the similarity to nanocolumns made of nanoplates reported by Tian et al. and might find application in photodecomposition of volatile organic compounds.[8] The structures of microspheres and the formation mechanisms were studied briefly.

All the reagents used in our experiment are analytical grade. In the 50-mL conical flask, 0.6586 g of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, with 99.9% purity) and 0.2100 g of HMT (hexamethylenetetramine) was dissolved in 50 mL of methanol solution under vigorous stirring at room temperature, then ultrasonicated for 10 min, and a transparent solution was obtained. Then 4 mL of distilled water was added into the conical flask. After that, the conical flask was put into the water tank at constant temperature 60 °C for different hours, and then taken out, cooled to the room temperature. In the bottom of conical flask, there were white precipitates deposited from the mixed solution. These precipitates were washed several times with ethanol, then dried at 60 °C for the examination.

Morphology of the as-prepared precipitates was identified by a Sirion II type field emission scanning electron microscope. The XRD patterns of the products were obtained by using a Philips X'pert X-ray diffractormeter with Cu Kα_1 radiation in the 2θ range from 20 to 80. TEM images were recorded by Tecnai G2 20 instrument with an accelerating voltage 200 kV.

Figure 1. shows the XRD pattern of as-prepared ZnO at 60 °C for 12 h. All the diffraction peaks can be indexed as the hexagonal wurtzite ZnO with lattice constants in agreement with the values in the standard card (JCPDS 36-1451). No other diffraction peaks were detected.

The morphology of as-prepared ZnO is shown in Figure 2. From Figure 2a, we could see that the average size of the uniform spheres is 1–2 μm. These spheres are not really ball-like, but each sphere has a cave on its surface (see Figure 2b). Because of the polarity of ZnO, many strange shapes, including nanoneedle,[9] nanoring,[10] nanowall,[11] and so forth, have been obtarmed. However, there was no report about the ball-like microspheres, as the best of our knowledge. The surface characteristic and internal structure of spheres are clearly shown in Figures 2b–2d, respectively. It can be found that each sphere has its unique nanostructure that no previous literature has re-

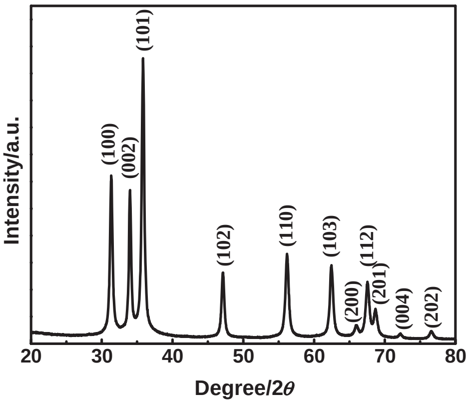

Figure 1. XRD pattern of ZnO prepared at 60 °C for 12 h.

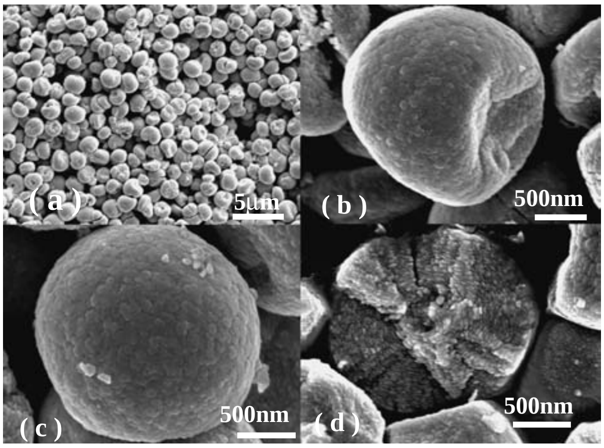

Figure 2. FE-SEM images of as-prepared ZnO at 60 °C for 12 h. (a) low magnification image. (b) and (c) high magnification images. (d) cross section image of sphere.

ported. The microspheres are made of regular hexagonal plate-like ZnO with average size 30–40 nm, which stack very compactly and align regularly.

As we know, $Zn(CH_3COO)_2$ and HMT can disperse homogenously in the methanol solution because of the high dielectric constant of methanol. At the same time, parts of $Zn(CH_3COO)_2$ would be ionized. When 4 mL of distilled water was added into the mixed solution, CH_3COO^- ion begun to hydrolyze immediately. In our experiment, the solution became milky white in color several minutes later, revealing the hydrolyzing process started rapidly. The reaction process was as follows:

$$CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$$

$$Zn^{2+} + OH^- \rightarrow Zn(OH)_2 \rightarrow Zn(OH)_4^{2-} + 2H^+$$

After the growth unit $Zn(OH)_4^{2-}$ has been generated, the dehydration process between growth units resulted in the formation of cluster $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ owing to the ion diffusion. In the supersaturation solution, the cluster $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ will grow as the traditional coarsening mechanism by ion diffusion.

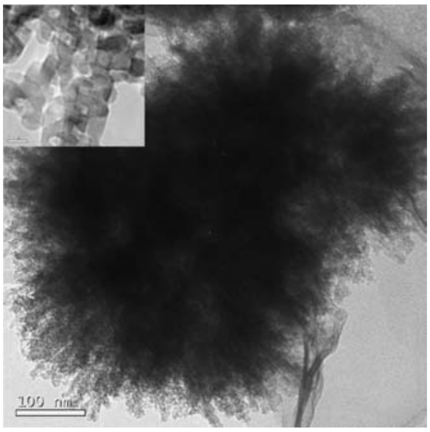

Figure 3. TEM image of aggregation particle at 60 °C for 2 h. (Inset is the magnified image of the edge of secondary particle.)

Figure 3 shows the secondary particle aggregated at 60 °C for 2 h in our experiment. It is observed that the average size of colloidal particle is about 5 nm from the insert picture. In classic colloid chemistry, Self-assembly of colloidal particles into secondary aggregate particles with particular micron size is well known. This process could be facilitated by the changes of chemical conditions of the solution, such as the increasing of ion concentration and pH values which caused the surface potential to approach the isoelectric point.[12] In our experiment, the reason may be that the added water had destroyed the double layers of particles that separate the surface of adjacent particle, thus accelerating the aggregation process. Comparing Figure 3 with Figures 2b and 2c, we can speculate that secondary particles that made of 5 nm particles on standing for 2 h changed into spheres that formed by regular 40-nm plate-like ZnO 12 h later. This phenomenon can be expressed by the crystal growth mechanism suggested by Penn and Banfield.[13,14] They found the adjacent 2- to 3-nanometer particles could aggregate and rotate so their structures adopt parallel orientations in three dimensions, thus leading to crystal growth. Penn also discussed the kinetics of orientation aggregation, which described the crystal growth that the traditional mechanism could not explain adequately.[15] In this case, the regular plate-like ZnO may be formed by the tiny particles. The driving force of this process was the reduction of surface energy by removal of pairs of surfaces. This phenomenon was also discussed in the paper of C. Pacholski et al. that ZnO nanodots self-assemble into nanorods.[16] However, this orientation attachment could not create the perfect hexagonal plate-like ZnO in that some spaces would exist between the constitution units (the nanocrystalline particles) inside the plates, which were discussed by Banfield et al. Then, the OH^- by the hydrolyzing process of HMT and Zn^{2+} that adsorbed on the active surfaces of ZnO particles would provide the ZnO source for the crystal growth through the diffusion of ion to fill the spaces that separate nanocrystalline units, thus form the perfect nanoplates. However, in the system without HMT, there were no perfect nanoplates formed in the obtained microspheres.

The microspheres that were made of plate-like ZnO crystal with average size 30–40 nm have been successfully prepared in a large scale by $Zn(CH_3COO)_2$ and HMT dissolved in methanol solution by adding distilled water into the solution at 60 °C for 12 h. This was the first report of ZnO microspheres that different from the other shapes formed because of the polar growth of ZnO. The possible formation mechanism was that small colloidal particles self-assemble into nanoplates which align in a regular periodicity.

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