

# Single-crystal ZnO flocky sphere formed by three-dimensional oriented attachment of nanoparticles

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## Abstract

The nanostructure of a single-crystal ZnO flocky sphere was synthesized by using a simple chemical route in the Zn<sup>2+</sup>–triethanolamine system. Formation of such quasi-single-crystal nanostructures was achieved through oriented attachment of a large number of ZnO nanoparticles in three dimensions. It is suggested that the adsorption of triethanolamine molecules on the surface of ZnO particles plays an important role in their oriented attachment, leading to the formation of flocky spheres with single-crystal structure.

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## 1. Introduction

The control of size and shape of nanoparticles is essential for the application and development of nanodevices. Therefore, understanding how nucleation, growth coarsening and aggregation processes affect the final shape has always been of constant interest in nanoresearch.

The formation of nanocrystals in solution typically involves fast nucleation of primary particles followed by subsequent growth through two mechanisms: coarsening and aggregation [1–7]. Coarsening, also known as Ostwald ripening, can be described as a diffusion-limited growth of nanoparticles at the expense of smaller ones [1], whereas aggregation can occur via various mechanisms. One of such mechanisms is oriented attachment (OA), which involves spontaneous aggregation of nanoparticles and their further transition into bulk single crystal [2]. This process seems very promising as a route for the preparation of anisotropic nanostructures, such as nanowires, nanorods, nanoprisms and so on [3–7]. However, as compared with the great progress achieved with anisotropic nanostructures, very little attention has been paid to the

nanostructures with isotropic shape via controlled organization of primary building units. As so far, the isotropic growth of nanostructures has never been realized through OA [8–10].

Crystal morphology is known to be determined by the relative growth rates of various crystal planes, which differ greatly in surface free energies. Organic ligands can bind to crystal surfaces and thus alter the surface properties of particles. Therefore, surface-attached molecules are expected to have a significant effect on the control of the final shape and size of nanostructures [11], e.g. Li et al. obtained microparticles with rice-like shapes through Ostwald ripening by using organic additives [12]. In this work, by using zinc nitrate and triethanolamine (TEA) as starting materials, we prepare isotropic nanostructured ZnO flocky-spheres with single-crystalline orientation. The structures grow through three-dimensional OA of small primary ZnO nanoparticles. The role of organic ligands of TEA and the growth mechanism are discussed.

## 2. Experimental procedure

All reagents used in the experiment were analytical grade. Based on pilot experiments, the concentrations of

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zinc nitrate and TEA were chosen as 0.02 and 0.1 M, respectively. In a typical experiment, 40 mL of 0.02 M zinc nitrate aqueous solution was added to 40 mL of isopropyl alcohol (IPA) at room temperature, the mixture was vigorously stirred, and, synchronously, the temperature was elevated to 50 °C. Then, 40 mL of 0.1 M aqueous TEA solution was added slowly into the above well stirred mixtures. The temperature was continuously elevated to 80 °C. The stirring was continued for 1 h. At the end of the aging time, the system was quenched in cold water, giving rise to milk white suspension. The white precipitate was separated by centrifugation and washed with absolute alcohol and distilled water several times. The final white powder was obtained by drying the precipitate at 60 °C in air.

The crystal structure of the product was characterized by X-ray diffractometry (XRD, Rigaku D/max 2500v/pc) at a scanning rate of 4 °/min in the  $2\theta$  range from 20° to 80° at room temperature. The morphology of the products was investigated by a scanning electron microscope (SEM, JEOL-6700F). Transmission electron microscopy (TEM, FEI Tecnai G2F20) was employed to obtain the low-magnification images, high-resolution TEM (HRTEM) images and selected area electron diffraction (SAED) patterns. Fourier transform infrared spectroscopy (FTIR) spectrum of obtained products after 1 h reaction was recorded using an attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) spectro-

meter (Nicolet 470) over a wave number range from 600 to 4000  $\text{cm}^{-1}$ .

### 3. Results and discussion

Low-magnification images of the product, as revealed by SEM and TEM, are shown in Fig. 1a and b. The particles have a quite uniform sphere shape with somewhat rough surface. The size distribution is shown in Fig. 1c, which indicates that the average size of these flocky spheres is around 200 nm. A typical XRD pattern of the product is provided in Fig. 1d. The pattern fits well with ZnO with wurtzite structure (JCPDS card no. 89-1397).

The high-magnification image of a flocky sphere in Fig. 2a shows its detailed microstructure. The sphere seems to be composed of numerous small nanoparticles of about 4–6 nm in size. Such primary nanoparticles pile up to form larger flocky-sphere architectures with recognizable boundaries or voids between them.

Surprisingly, the SAED pattern of one flocky sphere, shown as the inset in Fig. 2a, demonstrates that a flocky sphere composed of many nanoparticles and with many defects exhibits a single-crystal diffraction pattern. The SAED pattern can be indexed as the [011] axis of a hexagonal structure of ZnO with a high phase purity.

The HRTEM image (Fig. 2b) shows the stacking of nanoparticles. The classical crystal growth of ZnO is along [001] direction; however, to form the flocky spheres, the

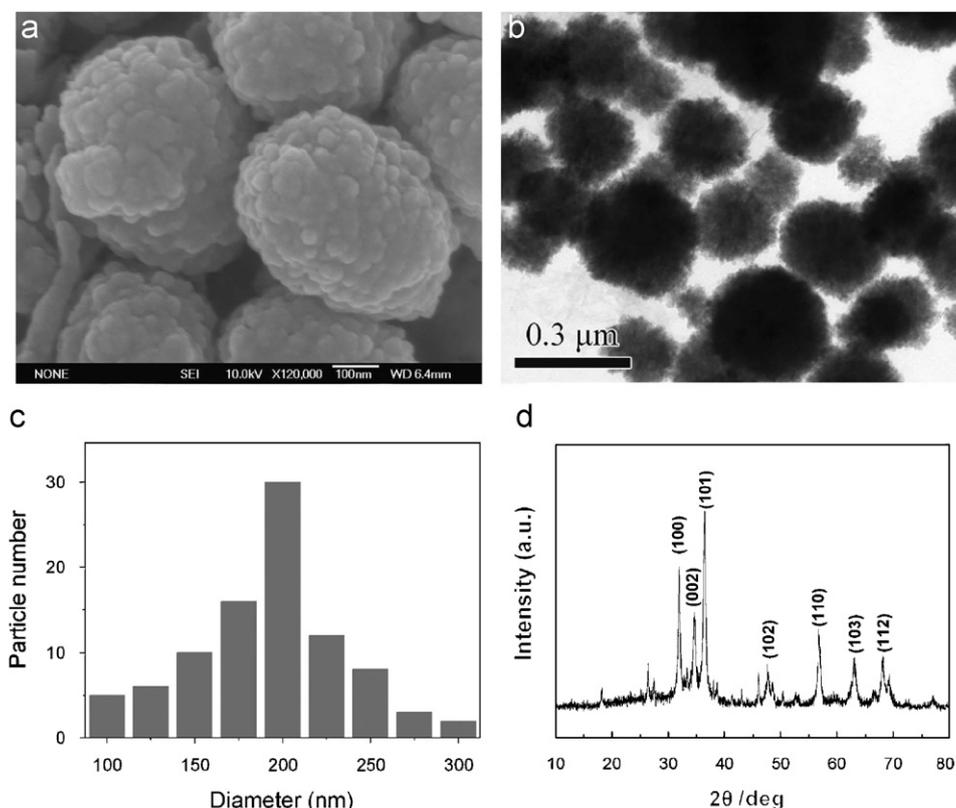


Fig. 1. Morphology and phase structure of ZnO flocky spheres. (a) SEM image; (b) TEM image; (c) size distribution; and (d) XRD pattern.

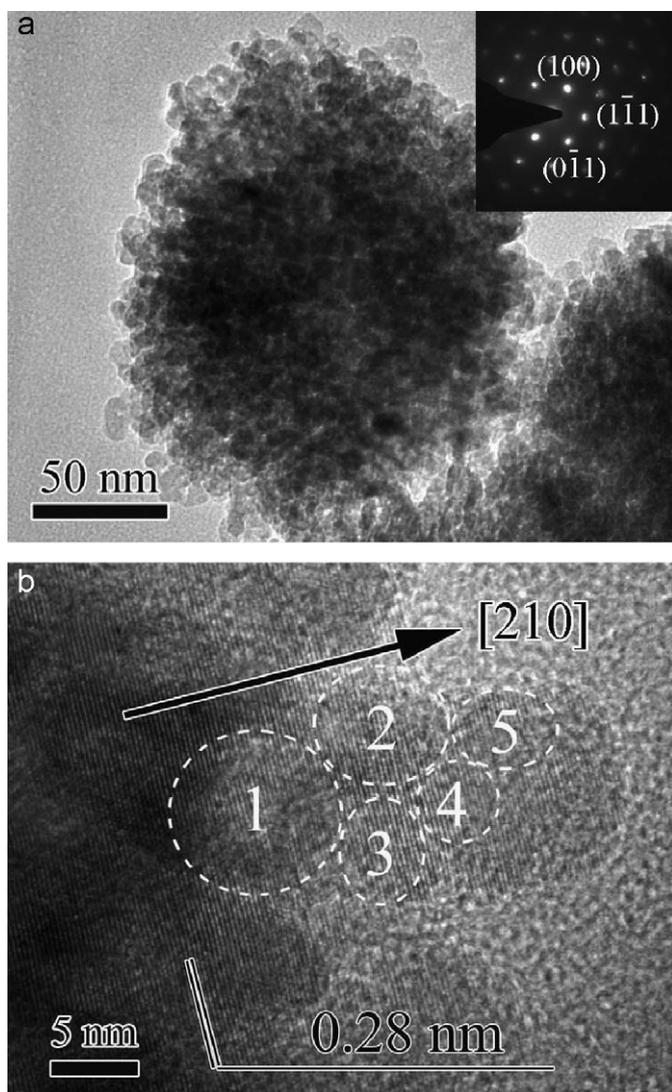


Fig. 2. TEM analysis on one ZnO flocky sphere. (a) High magnification image on one ZnO flocky sphere, the inset is SAED pattern; (b) HRTEM image on the edge of the ZnO flocky sphere, the numbers and circles indicate the positions and ranges of subunits.

orientation attachment of ZnO nanocrystals should occur in every direction, for example, the  $[210]$  direction as indexed in Fig. 2b. The stacking of nanoparticles in three dimensions strongly suggests that the architecture arises from particle-by-particle aggregation rather than from classical atom-by-atom growth, and a large number of ZnO nanoparticles in a flocky sphere adopt identical crystallographic directions in three dimensions.

Some nanoparticles were found to be dispersed randomly in the solution rather than attached to flocky spheres (Fig. 3a). Their size is also about 4–6 nm in diameter, which is consistent with that of the subunits in the flocky sphere in Fig. 2b.

A FTIR spectrum of the as-prepared product is shown in Fig. 3b. While the only vibration peak of surface-free ZnO should be expected at  $500\text{cm}^{-1}$ , several signals related most likely to TEA are observed in Fig. 3b. The peaks

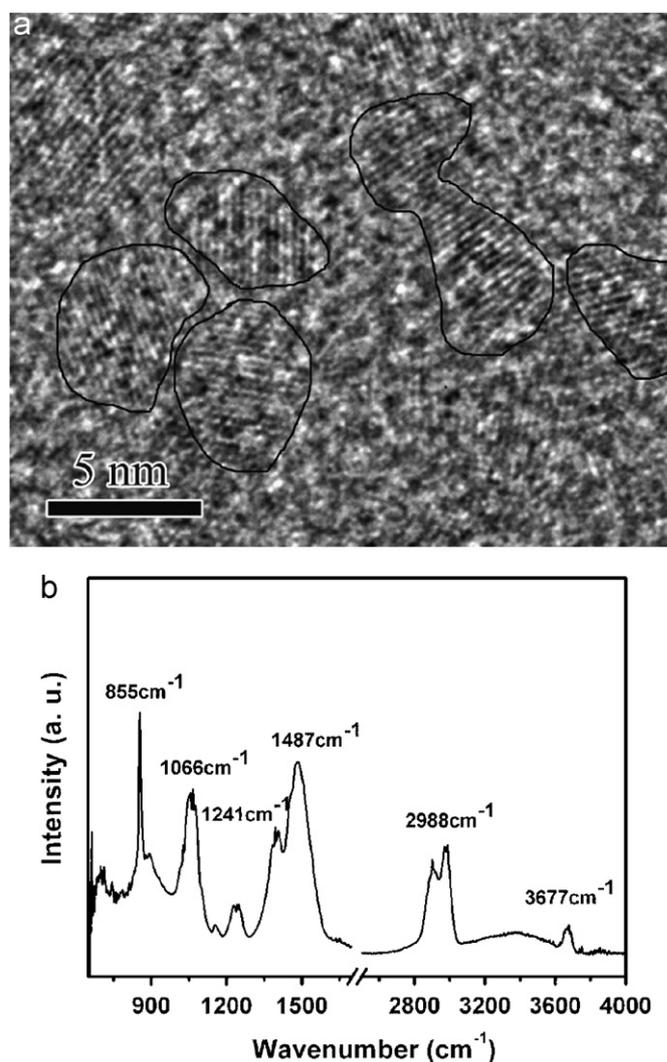


Fig. 3. The morphology and surface state of nanoparticles acting as subunits of flocky spheres. (a) HRTEM image; (b) FTIR spectrum.

located at 2988, 1487 and  $855\text{cm}^{-1}$  are assigned to the stretching vibration, deformation mode and scissoring vibration of  $-\text{CH}_2$  groups, respectively. The peaks at 1394, 1241 and  $1066\text{cm}^{-1}$  arise from the asymmetric stretching vibration mode of C–N bonds. The peak of  $3677\text{cm}^{-1}$  is assigned to the stretching vibration of  $-\text{OH}$  groups. All the above peaks clearly demonstrate that the ZnO nanostructures are covered by surface-absorbed TEA molecules.

Since ZnO flocky spheres are composed of ZnO nanoparticles, below, we discuss the formation mechanism of ZnO flocky spheres in two steps, e.g. the appearance of nanoparticles, and then the assembly of the nanoparticles into single-crystal ZnO flocky spheres.

In the first stage, the ZnO nanoparticles were prepared through the reaction between zinc nitrate and TEA. During this process, the surfaces of ZnO particles are believed to be covered with TEA ligands (Fig. 4a, inset), which is expected to slow down the growth speed of the particles. The fact of TEA bonding to the nanoparticles has been

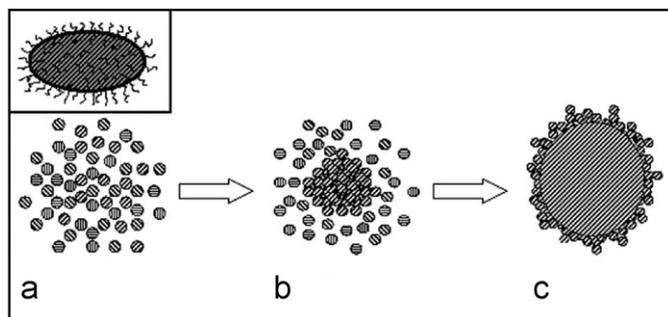


Fig. 4. Schematic map of the process of three-dimension-oriented attachment. (a) Nanoparticles dispersed in solution, the inset shows one nanoparticle with surface ligands; (b) the aggregation of nanoparticles by collision, rotation and oriented attachment; (c) the formation of a single-crystal sphere by further growth.

confirmed by the FTIR result. On the other hand, as a long chain alcohol, IPA might accelerate the nucleation and growth of the particles [13]. Above two factors should be beneficial for the formation of fine primary nanoparticles (e.g. similar to those in Fig. 3a).

Subsequently, the uniformly distributed primary particles aggregate together, forming a flocky sphere as shown in Fig. 4b. Two reasons can be responsible for the formation of such nanostructures. Firstly, the TEA ligands bonding to the nanoparticles change their surface energy and then slow down the anisotropic growth. Secondly, the observed sphere-like shape has the lowest surface area, thus being the primary choice for the aggregation.

As for the orientated attachment of the nanoparticles, TEA ligands appear to play an important role too. Firstly, TEA on the surface of the nanoparticles could decrease the effectiveness of the Ostwald ripening by suppressing the dissolution or growth of nanoparticles, and thus increase the probability of OA. On the other hand, the absorption of TEA on polar surface could decrease the polarity of nanoparticles and then electrostatic attraction among nanoparticles, which allows for the nanoparticles to keep on colliding, separating, and rotating easier. However, once identical atomic planes in two nanoparticles meet during the collision progress, they are unlikely to separate any more, since the system reaches the lowest total energy by eliminating the two surfaces and forming a bigger single crystal [14]. As the above description is applicable to different atomic planes with any indices, the attachment is expected to occur in three dimensions. This must lead to the formation and development of bigger single-crystal

spheres, which are thus built through the OA of small nanoblock particles (Fig. 4c).

#### 4. Conclusions

We have demonstrated the formation of a single-crystal flocky sphere of ZnO through the three-dimensional OA of a large number of nanoparticles. The growth occurs through collision, rotation, and conjunction of adjacent block nanoparticles. Selective adsorption of TEA molecules on crystallographic planes plays an important role in the isotropic growth of such ZnO flocky spheres. Understanding of the 3D-oriented attachment to an isotropic nanocrystal is helpful for controlling the aggregation-driven formation of ordered nanostructures and provides new insights into mineralization mechanisms.

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