

Facile synthesis of novel hierarchical hollow ZnO microspheres†

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Novel hierarchical hollow ZnO microspheres, composed of large ZnO crystals on the outer surfaces and small ZnO crystals on the inner surfaces, were synthesized by a chemically induced self-transformation process, employing the ester elimination between zinc formate dihydrate and ethanol.

ZnO is a typical n-type semiconductor with a wide band gap and high excitation binding energy of ~60 meV, which has been extensively applied in optoelectronic devices, catalysis, chemical sensors, drug delivery, and energy conversions.^{1–5} Though considerable ZnO structures have been developed by various methods, hierarchical hollow ZnO structures have attracted great attention recently.^{1,6}

Hierarchical micro-/nanostructures are mentioned as the higher dimension structures composed of low dimensional nano-building blocks.^{7,8} As an important category of micro-/nanostructures, hollow micro-/nanostructures have the advantage of refractive index tunability, lower density, large active area for catalysis and ability to withstand cyclic changes in volume. The templates or other additives, which were employed to facilitate the formation of the hollow structures in these methods, caused impure products and increased costs. Ideally, a one-step template-free method is preferred for controlled preparation of hollow structures. In this sense, it is highly desirable to develop a simpler and more efficient synthetic strategy for hierarchical hollow structures.

Actually, from the methodological point of view, the key point for the fabrication of hollow micro-/nanostructures is to create the interior cavity. Recently, the interior cavity was spontaneously formed by the Kirkendall effect, Ostwald ripening mechanism or chemically induced self-transformation process,⁹ which inspired us to fabricate the hollow structure

directly through solid intermediates rather than through template methods. However, the Kirkendall effect can only be applied in a small number of well-defined systems¹⁰ and the ability to construct hollow structures with complex internal textures is often limited through the Oswald ripening mechanism. Fortunately, this can be circumvented to some extent by the use of a chemically induced self-transformation process involving metastable solid microparticles that undergo localized transformations without gross morphological change.¹¹

Herein, it is reported that a process of chemically induced self-transformation is used to prepare hierarchical ZnO hollow microspheres through zinc formate. Although ZnO hollow spheres composed of internal microparticles have been described, to our knowledge, there is no report concerning the fabrication of ZnO hollow microspheres with hierarchical bilayer structures using a single-step process.

The present single-step method is based on sequential self-transformations occurring under mild solvothermal conditions in an ethanol system containing zinc formate dihydrate (ZFD) formed by formic acid (FA) and zinc acetate dihydrate (ZAD). Fig. 1 shows the XRD calculation pattern of ZFD (Fig. 1a) and XRD patterns of the samples prepared at various times (Fig. 1b–e). The crystal structure data of ZFD for the calculation are obtained from Lipton.¹² All of the diffraction peaks of the samples prepared for 0 h and 1 h are in good agreement with the calculation pattern of ZFD (Fig. 1a–c), indicating that the crystal phase of these samples belongs to the zinc formate hydrate (JCPDS no. 14-0761). The crystal phase of the sample prepared for 6 h (Fig. 1e) belongs to zinc oxide (JCPDS no. 70-2551). According to Fig. 1c, the (10 $\bar{1}$ 3) peak of ZnO appears, suggesting that the decomposition of ZFD starts within 1 h. The drastic reaction occurs between 1 h and 2 h since the content of ZFD phase decreases rapidly during this period. Therefore, ZnO is precipitated by the gradual decomposition of ZFD.

FE-SEM images of the samples prepared for various times are shown in Fig. 2. In Fig. 2a, the particles prepared without solvothermal treatment are 0.9 μ m in average size and the

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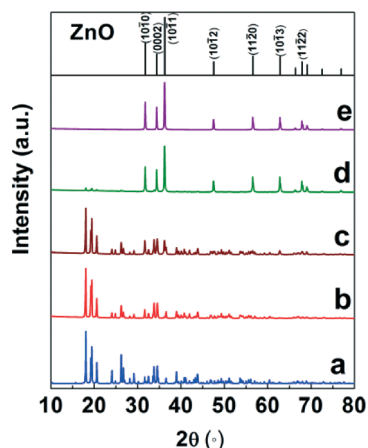


Fig. 1 (a) XRD calculation pattern of zinc formate dihydrate; XRD patterns of the samples prepared for (b) 0 h, (c) 1 h, (d) 2 h, and (e) 6 h. (ZnO from JCPDS 70-2551; zinc formate dihydrate from ref. 12.)

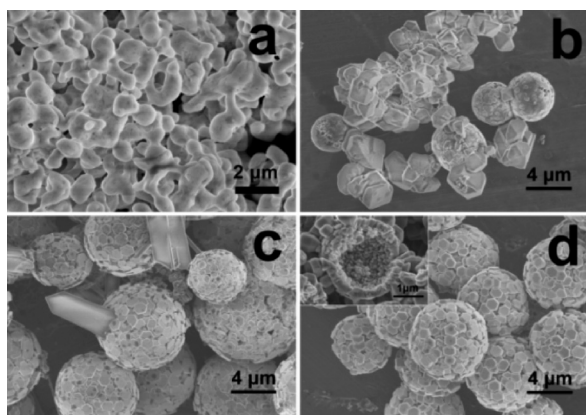


Fig. 2 FE-SEM images of the samples prepared for (a) 0 h, (b) 1 h, (c) 2 h, (d) 6 h.

morphology is extremely different from the morphologies of any other samples. In Fig. 2b, the particles exhibiting a crystallographic symmetry and the spherical particles appear in the sample prepared for 1 h. In Fig. 2c, a large number of microspheres are found in the sample prepared for 2 h. A small amount of the species exhibiting a crystallographic symmetry is observed within the microspheres, suggesting that the microspheres prepared for 2 h have a core/shell structure. The core/shell structure is also observed in the sample prepared with 0.07 M zinc acetate dihydrate as shown in Fig. S1a.† In Fig. 2d, well-dispersed microspheres are observed in the sample prepared for 6 h. In the inset of Fig. 2d, the microspheres are hollow and consist of bilayer hierarchical structures. The outer layer is composed of large crystals about several hundred nanometers with hexagonal morphology, and the inner layer is composed of small crystals about 100 nm. FE-SEM images of the sample prepared for 18 h and 36 h are shown in Fig. S2.† In Fig. S2a,† some aggregated microspheres are found in the sample prepared for 18 h. As shown in Fig. S2b,† the microspheres are hollow

and the large crystals on the outer layer have a truncated pyramid morphology. In Fig. S2c,† the microspheres prepared for 36 h have rough surfaces and the large crystals on the outer layer have a conical shape. According to Fig. S2d,† it is confirmed that the microspheres have hollow structures and hierarchical bilayer structures.

TEM images of the samples prepared for 1 h are shown in Fig. S3.† The solid spherical particles and the particles exhibiting a crystallographic symmetry are found, which is consistent with the SEM result shown in Fig. 2b. TEM images of the samples prepared for 6 h and 36 h are shown in Fig. 3a and b, respectively. In Fig. 3a, the angle between the surfaces of the large crystals is about 61° , which is close to the theoretical angle between the (000 $\bar{1}$) and (0 $\bar{1}1\bar{1}$). The TEM image of a thin section of resin holding sliced microspheres obtained with a microtome is shown in the inset of Fig. 3a. In the inset of Fig. 3a, the microsphere is hollow and composed of hierarchical bilayer structures which have large crystals on the outer layer and small crystals on the inner layer. In Fig. 3b, two sizes of ZnO crystals are also observed. The aspect ratio of the large ZnO crystals is larger than that of the large crystals prepared for 6 h, suggesting that there is a continued slow growth of the large ZnO crystals as the reaction time increases. According to the SEAD pattern indexed as [12 $\bar{3}0$] zone axis, the large crystals have the [0001] growth direction (see the inset of Fig. 3b).

According to the SEM and TEM results, schematic diagrams of the hierarchical hollow ZnO microsphere and large crystal are shown in Fig. 3c and d, respectively. As depicted in Fig. 3c, ZnO microspheres are hollow and composed of hierarchical bilayer structures. The large crystals are on the outer layer and the small crystals are on the inner layer. As depicted in Fig. 3d, the hexagonal facet exposed on the surfaces of the microspheres is assigned to (000 $\bar{1}$). The

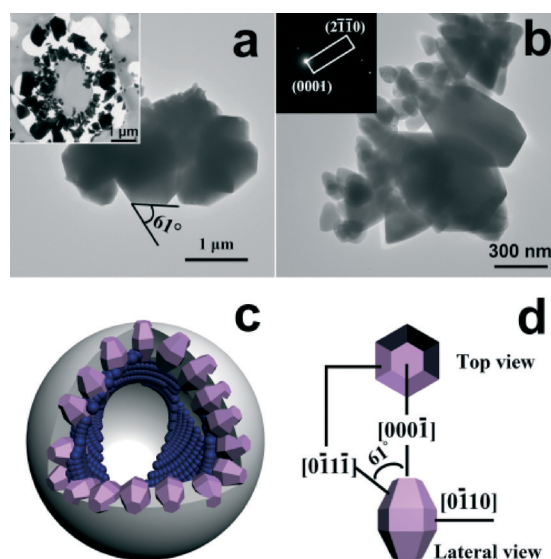


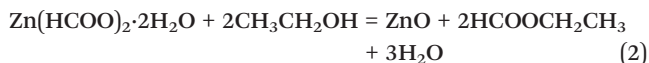
Fig. 3 TEM images of the samples prepared for (a) 6 h and (b) 36 h; schematic diagrams of (c) the hierarchical hollow ZnO microsphere and (d) large crystal.

neighboring side surfaces of the (000 $\bar{1}$) facet are assigned to {0 $\bar{1}$ 1 $\bar{1}$ } and the facets exposed vertically to the (000 $\bar{1}$) facet and close to the {0 $\bar{1}$ 1 $\bar{1}$ } are assigned to {0 $\bar{1}$ 10}.¹³

Fig. 4a gives a schematic diagram of the formation of ZnO. The chemical reactions involved in the formation of ZnO are suggested to be as following. Firstly, ZFD particles, which have low solubility in ethanol, are formed by the reaction between ZAD and formic acid according to



As the solvothermal reaction proceeds, the ester elimination reaction^{14–16} between ZFD particles and ethanol occurs according to



There are two distinct sites of Zn ions in the ZFD: one containing four in-plane waters with two bridging formates, the other containing six bridging formates.¹² The same site of Zn ions are arrayed in sheets and a sandwich lattice structure is formed¹⁷ (see Fig. 4a). Due to the unusual crystal structure of ZFD, zinc formates with different alcoholysis rates are suggested to be produced during the reaction. The zinc formates possessing less formates may have a higher alcoholysis rate and the zinc formates possessing more formates may have a lower alcoholysis rate, leading to the formation of large and small ZnO crystals, respectively.

Many studies support an O-terminated (000 $\bar{1}$) polar surface being usually inert in comparison with the Zn-terminated ZnO (0001) polar surface.^{13,18} In the present work, the (0001) facet of the large ZnO crystals disappears for rapid growth along the [0001] and (000 $\bar{1}$) hexagonal facets appear on the surfaces of the microspheres. Moreover, the large ZnO crystals tend to maximize the exposed areas of the {0 $\bar{1}$ 10} nonpolar facets and minimize the exposed areas of the (000 $\bar{1}$) and {0 $\bar{1}$ 1 $\bar{1}$ } polar facets because {0 $\bar{1}$ 10} non-polar facets are the energetically most favorable surfaces. Therefore, large crystals with truncated pyramid morphology are formed. The surface energy of the large ZnO crystals can be further

reduced by decreasing the area of (000 $\bar{1}$) polar facet and increasing the area of the {0 $\bar{1}$ 10} nonpolar facets. As a result, the large crystals with the cone shape appear in the sample prepared for 36 h.

Fig. 4b shows the schematic diagram of the formation of the hierarchical hollow ZnO microspheres. Firstly, the ZFD crystals keep growing to several microns in the early stage (see Fig. 2b). In order to reduce the surface energy, some of the ZFD crystals turn into rounded matter (see Fig. 2b). Secondly, the decomposition of ZFD and precipitation of ZnO occur on the surface ZFD crystals. Thirdly, as the reaction proceeds, the structures are gradually hollowing and ZFD/ZnO core/shell structure intermediates are formed. The large ZnO crystals grow toward the centers of the microspheres, and the small ZnO crystals are gradually deposited on the as-formed shells which are composed of large crystals. Finally, the hierarchical hollow ZnO microspheres are formed when the ZFD cores are completely decomposed.

In summary, a facile solvothermal route is developed to synthesize novel hierarchical hollow ZnO microspheres by employing the ester elimination between zinc formate dihydrate and ethanol. In the microspheres, the large ZnO crystals locate on the outer surfaces and the small ZnO crystals locate on the inner surfaces. The microspheres are composed of two sizes of ZnO crystal which are suggested to be caused by the two distinct sites of zinc ions in zinc formate dihydrate.

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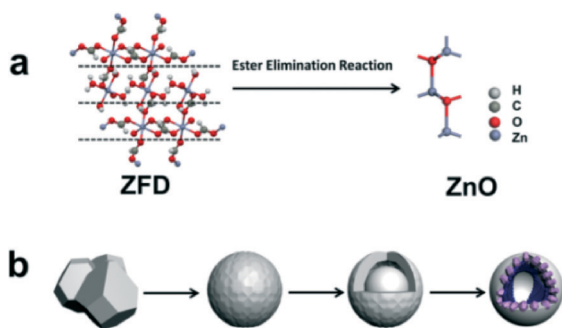


Fig. 4 Schematic diagrams of the formation of (a) ZnO and (b) the hierarchical hollow ZnO microspheres.

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