Research Article

Controlled Synthesis of Hollow Hemispheric ZnO Shells/Cages on Graphite Fiber

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Hollow hemispheric ZnO shells/cages are synthesized on graphite fiber via simple thermal evaporation process. The cage-like ZnO structures exhibit micron or submicron size and hollow hemispheric shape with polycrystalline shell made of the ZnO nanocrystals. Controlled time-sequenced growth experiment is conducted to interpret the growth process, which indicates that the growth mechanism of the hollow hemispheric ZnO shells/cages involves formation of Zn particles firstly, followed by oxidation of the outer surface of Zn droplets and meantime sublimation of the core Zn.

1. Introduction

Zinc oxide (ZnO) is a good candidate optoelectronic material owing to its direct bandgap and the large exciton energy [1]. Noncentrosymmetric structure-induced piezoelectric behavior makes it possible for electromechanical devices [2]. In addition, ZnO is biocompatible and biosafe which makes it suitable for biomedical applications [3]. In the past decades, ZnO nanostructures have been widely studied for electronic, optoelectronic, electrochemical, and electromechanical applications, such as UV lasers [4], light-emitting diodes (LEDs) [5], solar cells [6], sensors [7], and piezoelectric nanogenerators [8]. Significant efforts have been made to obtain desirable morphological nanostructures through various synthesis methods, mainly including thermal evaporation method [9–11], metal-organic chemical vapor deposition (MOCVD) [12, 13], pulsed laser deposition (PLD) [14], and aqueous solution methods [15].

Among all available morphologies, hollow cage-like ZnO structures represent an important category, which may exhibit particular applications for catalyst, sensor, and optoelectronic component owing to their lower densities and higher surface area. However, up to now, synthesis of hollow cage-like ZnO structures is still a challenge. Recently, cage-like ZnO structures have also been achieved by different

researchers [16–18]. However, the growth mechanism for the cage-like ZnO structures is still controversial and further investigation is necessary. In this paper, we report the successful synthesis of hollow hemispheric ZnO shells/cages on graphite fiber using mixtures of ZnO and graphite powder at 750°C in a low pressure. The structures of the hollow ZnO shells/cages exhibit with rough surface rather than polyhedral profile (as the reports [16–18]). Meanwhile, a detail discussion of the growth mechanism is presented based on a time-sequenced growth experiment.

2. Experimental Section

The synthesis of ZnO shells/cages was carried out in a conventional tube furnace system which we have reported previously [19]. ZnO powder (99.9%) and graphite powder (99.9%) with 1:1 mole ratio were mixed and loaded into an alumina boat. The mixture was placed at the center of the quartz tube. A bundle of graphite fibers with average diameter of 7 μm was put on a silicon substrate and loaded downstream (16–18 cm) from the centre, where the temperature is ~750°C. The tube was heated to 1100°C and kept for special times. The furnace pressure is 2.5×10^{-2} Torr with constant Ar flow at 50 sccm and O₂ flow at 1 sccm. After

FIGURE 1: (a) A typical low-magnification SEM image of the as-grown honeycomb-like ZnO cages covered around the graphite fiber. (b) High-magnification SEM image of the hemispherical ZnO shells/cages with average diameter $2\ \mu\text{m}$ stacked together around the graphite fiber.

FIGURE 2: XRD pattern of the as-made hemispherical ZnO shells/cages.

that, the furnace was turned off and we let it cool down to room temperature under Ar flow.

Then scanning electron microscopy (SEM, Hitachi S-3500N) was employed to examine the morphology of the as-made product. The crystal structure of the sample was characterized by X-ray diffraction (XRD) using copper $K_{\alpha 1}$ radiation. High-resolution transmission electron microscope (HRTEM) and electron diffraction patterns were obtained on a JEOL JEM-2010 instrument with operation voltage at 200 kV.

3. Results and Discussion

After thermal evaporation, it was found that some white products were deposited around the graphite fibers. The

FIGURE 3: (a) TEM image of the carapace-like ZnO nanoshell broken from the shell of the hollow ZnO cages. (b) HRTEM image of the red dashed frame marked in Figure 3(a), the upleft inset is the enlarging image corresponding to the white dashed frame in Figure 3(b), and the upright inset is the SAED pattern on the ZnO nanoshell.

morphology of the as-synthesized product obtained after thermal evaporation for 40 min is shown in Figure 1. Figure 1(a) is a low-magnification SEM image which clearly shows that the graphite fiber is covered with honeycomb-like products. A high-magnification SEM image is shown in Figure 1(b); it clearly indicates that the honeycomb-like products are made of numerous uniform microsize hemispherical ZnO shells/cages, which stacked together around the graphite fiber. It shows that the hollow ZnO microcages are almost hemispherical open with average diameter of about $2\ \mu\text{m}$. One point to emphasize is that the above cage-like products are stacked one by one separately, and

(a)

(b)

(c)

(d)

FIGURE 4: SEM images representing the growth progress of the hemispherical ZnO shells/cages. (a) Sample growth less than 1 min. (b) Sample after 3 min growth. (c) Sample after 5 min growth. (d) Sample after 10 min growth.

FIGURE 5: EDS spectrum taken from (a) individual enclosed Zn particles in Figures 4(a) and 4(b) individual hollow ZnO cages.

almost not hinge joint, which suggests that they nucleated and grew independently to form individual spherical-shaped Zinc liquid droplets [16].

The XRD pattern is illustrated in Figure 2. As indicated in the figure, all diffraction peaks match the wurtzite structural ZnO (JCPDS card no. 36-1451) with lattice constants $a = 3.250 \text{ \AA}$ and $c = 5.207 \text{ \AA}$. The characteristic diffraction peaks of the as-made ZnO micro- and nanocages are located at 32.3° , 34.9° , 36.8° , and 63.4° which correspond to $(10\bar{1}0)$, (0002) , $(10\bar{1}1)$, and $(10\bar{1}3)$ planes of the wurtzite ZnO, respectively. The result of XRD spectrum indicates that the as-made products are composed of wurtzite ZnO with good crystallinity.

Further examination of the crystallography and structure of the hollow cage-like structures was carried out by transmission electron microscopy (TEM) as shown in Figure 3. A low-magnification TEM image of a fragment broken from the shell of the hollow ZnO cages is given in Figure 3(a), which clearly shows that the carapace-like shell of the ZnO cages is polycrystalline and composed of plentiful nanocrystalline ZnO slices. Figure 3(b) is HRTEM image recorded from the red dashed frame of the nanoparticle in Figure 3(a). From the upper-left enlargement image shown in Figure 3(b), it can be clearly seen that the atoms arrange regularly to form a sixfold quasisymmetric projected structure. The distances between the lattice fringes are 0.245 nm and 0.192 nm , corresponding to the $\{10\bar{1}1\}$ and $\{10\bar{1}2\}$ planes, respectively. Moreover, the selected area electron diffraction (SAED) pattern is also presented in the upper-right inset in Figure 3(b). The distance of the diffraction patterns is measured: $R_1/R_2 = 0.99 \approx 1$, $R_3/R_1 = 1.31$, and the included angle between R_3 and R_2 is 49.2° , which indicates that the zone axis is $[2\bar{1}31]$ and the nearest diffraction planes are marked on the SAED pattern (which is consistent with our aforementioned HRTEM results). Herein, it is worth mentioning that the free-standing plane of the ZnO nanocrystal is $(2\bar{1}31)$, not as normally reported [16] equilibrium planes (0001) , $(01\bar{1}0)$, or $(2\bar{1}10)$, which

FIGURE 6: Schematic diagram of the growth process of the hemispheric ZnO shells/cages. (a) Vapor ZnO_x reduced into vapor Zn, and Zn droplets/particles are precipitated on the graphite surface. (b) Zn particles transforming into ZnO from the outside surface to the core, and meantime Zn in the core is ready to vaporize at elevated temperature, leaving behind a hollow cage-like ZnO crust. (c) Precipitation, oxidation, and vaporization are undergoing simultaneously during the experiment, and more hollow hemispheric ZnO shells/cages are formed and stacked together around the graphite fiber.

indicates that the formation process of the hemispheric ZnO shells/cages is probably nonequilibrium. In our experiment, the hemispheric ZnO shells/cages were synthesized at 750°C , which is much higher than the melting point of Zn (419°C). Hence, the solidification and oxidation are in the nonequilibrium level and tend to preserve its droplet spherical-shaped [16].

To better interpret the growth mechanism of the cage-like ZnO, time-sequenced growth experiments were carried out. Vapor-liquid-solid (VLS) [20] mechanism and vapor-solid (VS) [21] mechanism have been proposed to be dominant theory for synthesizing ZnO 1D nanostructures via thermal evaporation or vapor transport method. In VLS mechanism, metal catalysts are always used to promote the growth of the nanostructures. Since no metal catalyst has been used in our experiment, the growth process does not follow the VLS mechanism but VS mechanism. Figure 4 shows the SEM results after growth under the same conditions ($T_{\text{source}} = 1100^\circ\text{C}$, $T_{\text{sub}} = 750^\circ\text{C}$) but different growth times, which clearly exhibits the whole progress during the first growth stage. Figure 4(a) presents the result after <1 min growth, that is, the furnace was shut off immediately when the temperature reached (1100°C). Only a few closed particles with diameter less than $1\ \mu\text{m}$ were found, while the energy dispersive X-ray spectrometer (EDS) spectrum reveals that the chemical composition of the enclosed particles is mainly composed of element Zn and a little element O (Figure 5(a)). To clearly illuminate the growth mechanism, the schematic diagram of the growth process is proposed in Figure 6. In the beginning of the growth, vapor ZnO_x passing through the substrate, was reduced into vapor Zn by the graphite fiber firstly and precipitated into Zn particles once vapor Zn is supersaturated (see Figure 6(a)).

After several minutes growth (Figures 4(b)–4(d)), we can see that (1) all the individual hollow ZnO cages are verified to be ZnO (Figure 5(b)). (2) All of the particles become hollow ZnO cages or vacant shells with less than $1\ \mu\text{m}$ diameter and tens to hundred nanometers thickness, and almost no closed. (3) The quantity is increased nearly exponentially with growth time increasing. Therefore, it is believed that the precipitated Zn particles is not stable, which are ready to

be oxidized into ZnO from the outer surface to the center. And at this temperature, the core Zn also cannot be survived but sublimated, leaving behind hollow cage-like ZnO crust (Figure 6(b)). During the experiment, precipitation, oxidation, and sublimation are undergoing almost simultaneously and ceaselessly (i.e., in nonequilibrium level), hence more and more hemispheric ZnO shells/cages are stacked around the graphite fiber (Figure 6(c)). It is necessary to note that a low oxygen partial pressure ($2\text{--}5 \times 10^{-2}$ Torr in our experiment) is a crucial factor to obtain such hollow cage-like ZnO structures, which is consistent with Fan's report [17]. We have synthesized wirelike ZnO nanostructures around graphite fiber at higher pressure [22]. In addition, carbon form graphite fiber may be acted as a significant stabilizer [18] besides its reducing effect, which can be attributed to another ingredient for formation of such cage-like ZnO structures. From the above results, we propose that reductive atmosphere (low pressure or C stabilizer) to form Zn or Zn-rich particles firstly is responsible for synthesis of hollow cage-like ZnO structure.

4. Conclusions

Hollow hemispheric ZnO shells/cages have been synthesized on graphite fiber by simple thermal evaporation process. Through the controlled time-sequenced growth study, a possible growth mechanism of such hemispheric ZnO shells/cages is proposed as follow: formation of Zn particles firstly, followed by oxidation of the outer surface of Zn droplets and meantime sublimation of the core Zn. In summary, formation of Zn or Zn-rich particles is an indispensable step for successful synthesis of hollow cage-like ZnO structure.

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