Fabrication of Hourglass-Like ZnO Particles with Enhanced Blue Emission

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Hourglass-like ZnO microcrystals with circular cross sections have been synthesized through a solvothermal method. Two kinds of morphologies have been observed: glabrous hourglasses with relatively smooth surface which show single-crystalline diffraction behavior; and crinite ones covered by irregular ZnO nanowires with diameters of about 20–30 nm and lengths up to 200 nm which show polycrystalline diffraction behavior. Time-dependent experiment is introduced to reveal the growth mechanism. Moreover, it was found that both the reaction temperature and the solution environment play a key role in the fabrication of ZnO hourglasses. The ZnO hourglasses have reduced ultraviolet emission and enhanced blue emission with a dominant peak at 467.2 nm and three weak peaks at 451, 481, and 492 nm.

Keywords: ZnO, Hourglasses, Microcrystals, Solvothermal.

1. INTRODUCTION

ZnO is one of the most promising materials for electronic and optoelectronic applications. It can be used in solar cells, ultraviolet lasers, blue-light-emitting diodes, field-effect transistors and sensors.\textsuperscript{1–3} The properties of ZnO are affected by their sizes and morphologies, thus much effort has been devoted to fabricating ZnO nano- or microstructures.\textsuperscript{4–6} Vapor-phase and solution-phase methods are two widely adopted approaches, but considering the cost and the simplicity, the latter may be more promising. Through solution routes, various ZnO crystals have been synthesized.\textsuperscript{5,6} In addition, the ZnO crystals prepared in solution usually have many intrinsic defects, which bring them some interesting optical properties. ZnO usually exhibits two kinds of photoluminescence (PL) emissions: one is a near-band-edge ultraviolet (UV) emission and the other is a group of visible deep-level emissions related to intrinsic defects. In the visible range, blue emission is demanded for full-color display,\textsuperscript{3} but it is either not widely observed or usually rather weak.\textsuperscript{7,8} In this paper, we report hourglass-like ZnO microcrystals fabricated via a simple solution route using water–ethanol mixed solvent. The ZnO hourglasses are distinctively different from the previously reported ZnO dumbbell-like and hourglass-like microcrystals.\textsuperscript{9–11} Hexagonal edges and corners, which are the features of those microcrystals, are seldom observed in our ZnO hourglasses. The ZnO hourglasses are similar to the spindle-like ZnO twin-cones synthesized by solvothermal method.\textsuperscript{6} The twin-cones also have circular cross sections, but they are united by the bottoms of two cones. We observed the secondary nucleation and growth on the surface of ZnO hourglasses. The hierarchical growth of crinite ZnO hourglasses in one-pot process is an interesting phenomenon. Usually the fabrication of hierarchical ZnO nanostructures via solution routes need the assistance of surfactants or polymers,\textsuperscript{6,12} but our experiment did not use any additives. It is worthy to note that water plays an important role in the formation of the ZnO hourglasses, without water irregular ZnO nanoparticles would be obtained in the experiment. Reduced ultraviolet emission and enhanced blue emission have been observed for these ZnO hourglasses. Condition-dependent comparison experiments were performed, and the solution environment has been considered in our research.

2. EXPERIMENTAL DETAILS

In a typical synthesis, 0.2195 g zinc acetate (Zn(Ac)\textsubscript{2} \cdot 2H\textsubscript{2}O) and 0.1402 g hexamethylenetetramine (HMT) were dissolved into 38 mL ethanol with stirring at room temperature. 2 mL deionized water was then added into the solution. The mixture was transferred into a Teflon-lined stainless steel autoclave and kept inside an electric oven at 120 °C for 30 min. After reaction, the
autoclave was cooled through tap water, and the white products were centrifuged, washed and finally dried at 80 °C in air. In the condition-dependent comparison experiment, the reaction temperature has been controlled in range of 100 °C~150 °C with the reaction time from 20 min to 2 h. In addition, the solution environment has been discussed in our research. The structure and morphology of the products were characterized using X-ray diffraction (XRD, Bruker D8, Cu Kα), scanning electron microscopy (SEM, SIRION TMP), and transmission electron microscopy (TEM, JEM-2010FEF, 200 KV) equipped with selected area electron diffraction (SAED). PL measurements were carried out at room temperature (150 W Xe lamp, λex = 325 nm) with a spectrofluorometer (Shimadzu, RF-5301).

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the as-prepared products. The diffraction peaks can be indexed to the wurtzite ZnO structure (JCPDS No. 36-1451). The lattice parameters calculated from XRD spectra were a = 0.32514 nm and c = 0.52081 nm, which slightly bigger than the standard values with a = 0.32498 nm and c = 0.52066 nm (according to JCPDS No. 36-1451). The difference of lattice parameters should indicate that more intrinsic defects excited in the ZnO samples. Moreover, the XRD pattern shows noticeably stronger (002) peak compared to the standard card. For randomly oriented ZnO powders, (101) should be the dominant diffraction peak. Figure 2(a) shows the SEM images of the ZnO products. Hourglass-like ZnO particles combined by two cones can be observed. The two cones are slightly different in size; usually one is larger than the other. The diameters of the round bottoms are about 1–2 μm, and the lengths of the hourglasses are ∼1.8 μm. Two typical ZnO hourglasses can be identified in the products as shown in Figures 2(b and c). The surface of the glabrous ZnO hourglass shown in Figure 2(b) is relatively smooth, but that of the crinite ZnO hourglass shown in Figure 2(c) is covered with dense nanowires. The glabrous and crinite particles were two different stages in the whole reaction process, which will be discussed later in time-dependent experiments. Figure 3(a) shows the TEM image of an individual glabrous ZnO hourglass, and the inset is the corresponding SAED pattern. No nanoparticle building units or pores can be recognized in the glabrous hourglass and single-crystal diffraction behavior from the [001] zone axis can be observed from the SAED pattern, though some misalignments are also visible. The crinite ZnO hourglass shown in Figure 3(b) has a distinctively different structure. The surface is covered by many nanowires, and the individual hourglass shows polycrystalline diffraction behavior (inset of Fig. 3(b)). Figures 3(c) and (d) are the enlarged TEM images of the glabrous and crinite ZnO hourglasses, respectively. The surface of the
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The reaction time is (a) 20 min, (b) 45 min, (c) 1 h, (d) 2 h, respectively.

Fig. 4. SEM images of ZnO hourglasses in time-dependent experiment: the reaction time is (a) 20 min, (b) 45 min, (c) 1 h, (d) 2 h, respectively.

In Figure 5(a) many debris of ZnO could be observed. The small pieces of ZnO in Figure 5(a) are much more like the bowl-like debris as we mentioned at Figure 4(d) (2 h).

In addition, the relatively big particle in Figure 5(b) has a full structure of primary hourglasses. The right particle looks like the primary one in Figure 4(a) (20 min), and even a single crack could not be found in the left particle in Figure 5(b), which may indicate the reaction process is still at the initial step. In Figure 5(c) we observed the same structure which we called an abloom flower in Figure 4(c) (45 min). Some of them even broke up into two pieces which indicate that higher water concentration in solution would definitely accelerate the reaction process.

Also, the particles in Figure 5(d) look like the original reagent in which hourglasses structure could hardly be observed. Based on all the observation discussed above we could come to the conclusion that both the higher reaction temperature and higher water concentration in the ethanol solution would accelerate the reaction process of the hourglasses ZnO particle.

The hourglass ZnO structures may be formed by two different growth mechanisms. The first hypothesis is that the hourglasses grow out along the [0001] direction (c-axis) in one certain particle. It is well known that the...
[0001] direction of ZnO often has the highest growth rate. And this phenomenon could also be proved by other shapes of ZnO structure such as twin-cones. The other hypothesis is that the hourglass is combined by two different smaller ZnO particles. If the former hypothesis is true, the two sides of hourglasses should exhibit the same SAED pattern. Otherwise, they will not show the same SAED pattern. Figure 6 shows the SAED patterns from the both sides of an hourglass particle. Obviously they show the same SAED pattern. So we could draw the conclusion that this kind of ZnO hourglasses is grown from [0001] direction, and they are single crystals at both sides of hourglasses. Besides, we should point out that these two SAED patterns obtained are at a same inclination angle. And the particle in Figure 6 (with a length less than 1 μm) looks smaller than ordinary hourglasses (with a length ~2 μm). Because the electron beam cannot penetrate thick samples, we choose a relatively small one to get the SAED patterns.

PL spectrum of the as-prepared ZnO hourglasses is shown in Figure 7. A strong blue emission at 467.2 nm and three relatively weak blue emissions at about 451, 481 and 492 nm can be observed. The near band-edge emission at ~390 nm in the PL spectrum is rather weak and could hardly be identified. Some researches showed that blue emission for ZnO quantum dots could come from the formation of surface-bonded organic molecules. However, after annealing the as-prepared ZnO hourglasses at 500 °C for 2 h in air, the four blue emissions still exist as shown in Figure 7, and the relative intensities are even increased, indicating that these emissions are related to intrinsic defects. In fact, the four emissions have been also observed in ZnO nanowires, nanorods, nanorings and complex structures prepared by different methods, although these emissions are rather weak compared with their UV emissions. Especially, the ZnO nanowires were synthesized by direct evaporation of zinc powders which largely excluded the existence of impurities. Recent studies have assigned the 451 nm (2.75 eV) emission to interstitial zinc (Zni), the 467.2 nm (2.65 eV) to singly negatively charged Zn vacancy (VZn−), the 492 nm (2.52 eV) and 481 nm (2.58 eV) emissions to oxygen vacancy (VO) related defects. Moreover, the intensity ratio of the 481 and 492 nm emissions is nearly unchanged after the annealing, further confirming that they are correlative.

4. CONCLUSIONS
In summary, ZnO hourglasses have been solvothermally synthesized using mixed solvent of water and ethanol. Two kinds of morphologies have been observed: glabrous hourglasses with relatively smooth surface which show single-crystalline diffraction behavior; and crinite ones covered by irregular ZnO nanowires with diameters of about 20–30 nm and lengths up to 200 nm which show polycrystalline diffraction behavior. Time-condition experiment could reveal the growth mechanism of ZnO hourglasses. Both the higher reaction temperature and higher water concentration in the ethanol solution would accelerate the reaction process of the hourglasses ZnO particle. The ZnO hourglasses show defect-relevant blue emissions with a dominant peak at 467.2 nm, thus can be used as blue-light-emitting materials. Further understanding of the secondary nucleation and growth mechanism of the ZnO nanowires would benefit the hierarchical synthesizes of ZnO nanostructures.

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References and Notes
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