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Twinned tabour-like ZnO: Surfactant-, template-free synthesis and gas sensing behaviors

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ABSTRACT

The twinned tabour-like ZnO microstructures have been successfully synthesized via a solvothermal method without the assistant of any additive and template. The as-prepared products are characterized by X-ray diffraction, field emission scanning electron microscope, and high-resolution transmission electron microscope. The ZnO microcrystals grow symmetrically, and are wurtzite structure. The tabour, with a diameter of about 8.5 μm, grows along the c axis. The time-dependent morphology evolution of the ZnO microcrystal presents every single ZnO tabour is composed by many single crystal units. A possible formation mechanism of these complex hierarchical structures is investigated by adjusting the reaction time. In addition, the twinned ZnO tabours exhibit excellent ethanol-sensing properties at 250 °C. The highest response is 6.4–20 ppm ethanol. The response of the sensor rapidly increases with the increasing concentration of ethanol, until the ethanol reaching 200 ppm. The response of the sensor to 200 ppm ethanol is about 24.64 with the response time of 3 s.

1. Introduction

Over the past decades, inorganic materials have attracted intensive attention because of their wide application in many fields. In particular, metal oxide semiconducting materials have several advantages owing to their various physical and chemical properties. Due to their unique conductance properties, metal oxide semiconductors, ZnO, TiO_2, SnO_2, Fe_2O_3, CuO and so on [1–6], have been used as the sensitive materials toward various gases. Considering the selectivity and sensitivity of the sensors, various approaches have been introduced to improve these problems in the previous research, including adjustment of the microstructure, change of the preparation method, and the addition of catalysts/dopants [7–9].

ZnO, an important n-type semiconductor with particular physical and chemical properties, presents multiformity on their morphologies and structures, which are crucial for their potential applications [10–12]. To date, ZnO nano/microstructures with different morphologies [13–20] have been synthesized by various approaches [21–24]. Although the intrinsic structure of ZnO determines its growth habit, the size and shape of ZnO crystals could be successfully controlled by many capping agents. In liquid medium, the capping molecules can tailor the surface energy according to capping the surface of nuclei and thus control the shapes of microcrystals. However, the addition of surfactants or polymers to the reaction systems could increase experiment cost and introduce some impurities, as these additions are generally bonded to the surface of ZnO. Furthermore, high temperature treatments are needed in order to remove these adsorbed species. The heating process may alter the ZnO morphology and their properties. Therefore, developing a low-cost facile method for the synthesis of ZnO nano/microstructures is in expectation.

Recently, our group has prepared many twinned ZnO nano/microstructures [17,25–28], but the morphologies are always controlled by additives or templates. As we know, any additive and template will increase the cost. Normally, organic additive would make pollution into our environment. Herein, we present a tractable and green synthetic route for novel twinned tabour-like ZnO microcrystals without any additive or template assisting. The crystallinity, morphology, and structure of the twinned tabour-like ZnO microcrystals are examined, effects of the reaction time on the shapes of the ZnO products are analyzed, and the formation mechanism of these ZnO microcrystals is discussed from the angle of nucleation and morphology. Furthermore, the ethanol gas sensing properties of the tabour-like ZnO microcrystals have also been investigated.

2. Experimental

All regents were analytical grade and used without any further purification. In a typical experiment, the precursor solution was prepared by dissolving 0.003 mol zinc nitrate hexahydrate

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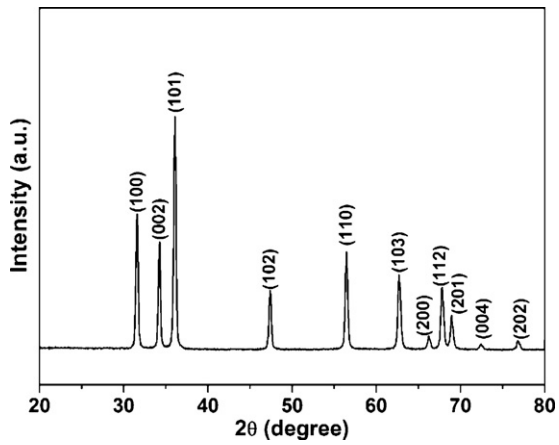

Fig. 1. XRD patterns of the twinned ZnO microcrystals.

($Zn(NO_3)_2{\cdot}6H_2O$) in 35 ml absolute ethanol under vigorous magnetic stirring at room temperature to form a transparent solution. Then the solution was transferred into the Teflon-lined stainless steel autoclave which was sealed tightly. The autoclave was maintained at 160 °C for 4 h and then naturally cooled down to room temperature. Finally, the white solid products were collected by centrifugation and cleaned with distilled water for several times, and dried in air at 90 °C for further characterization.

The identification of the phase was tested by X-ray diffraction (XRD) using a Rigaku D/max-2500 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). The morphology and particle size were studied on a field emission scanning electron microscope (SEM, JEOL JEM-6700F) operating at 5 kV. The structures of the products were investigated by high-resolution transmission electron microscope (HRTEM, JEOL JEM-3010). The acceleration voltage of HRTEM is 200 kV, the cathode is LaB_6 and the point resolution is 0.17 nm.

The gas sensing properties were measured by the gas sensing measurement system of RQ1 intelligent test meter (Qingdao, China). The details of the sensor fabrication were similar to those reported in other literatures [29]. The gas response of the sensor in this paper was defined as R_a/R_g, where R_a and R_g were the resistance in air and test gas, respectively. The operating temperature of the sensor was varied between 200 and 350 °C. The response or recovery time was expressed as the time taken for the sensor output to reach 90% of its total resistance change after applying or switching off the gas in a step function.

3. Results and discussion

The typical XRD patterns of ZnO products are presented in Fig. 1. The XRD analysis displays that all the diffraction peaks can be indexed as ZnO crystals with hexagonal wurtzite structure (JCPDS 36-1451) and with lattice constants of a = 0.325 nm and c = 0.52 nm. Because no diffraction peaks of other impurities were observed in the XRD patterns, it is concluded that pure hexagonal-phase ZnO structures were synthesized through this simple solvothermal method.

Fig. 2a shows a typical low-magnification SEM image of ZnO microstructures grown at 160 °C. The as-synthesized product is dominated by twinned tabours with the diameter of about 8.5 μm. The enlarged image (Fig. 2b) shows the detailed morphologies of the tabours. Apparently, the tabours are assembled by well-defined protuberant agglomerations, which may be assembled by many nanorods. It is also observed that there are the tips of the nanorods on the top of the tabours. The nanorods are served as building blocks to stack the rough surface of the tabours. It can be concluded that these nanorods are grown from the ZnO nanoparticles and further gather into bundles from the active sites in various directions. Then the nanorods share their outside face to form an agglomeration.

The detailed microstructure of ZnO tabour was characterized by TEM. Fig. 2c shows typical TEM image of ZnO tabours dispersed on a carbon film coated Cu grid. A compact standard symmetrical morphology of the individual ZnO sample could be observed, which is consistent with the result of the SEM. The representative HRTEM image marked by white square region in Fig. 2c is displayed in Fig. 2d, and the measured plane spacing is 0.26 nm, corresponding to the (0 0 0 2) plane spacing of the hexagonal wurtzite structure ZnO. Based on the details as shown in Fig. 2c and d, it is concluded that the two tabours are combined with each other of their [0 0 0 $\bar{1}$] direction and the tabour surfaces are on their [0 0 0 1] direction. The two-dimensional fast Fourier transform (FFT) pattern of the lattice-resolved image (inset of Fig. 2d) was indexed to a primitive hexagonal ZnO lattice. The FFT pattern further confirms that the ZnO grows along the [0 0 0 1] direction.

Comparison experiments with different temperatures also have been completed while keeping other synthesis parameter unchanged, which lead to failure in twinned tabours formation, as shown in Fig. 3. At lower temperature (130 °C), ZnO flower bundles consisting of rods with thin tops and thick bottoms were discovered in Fig. 3a. No twinned tabour was formed at this temperature. When the reaction temperature was increased to 160 °C, the typical twinned tabour structure dominates the products, which has discussed in Fig. 2. When the temperature is higher than 160 °C, the microcrystal keeps their twinned tabours in principle, although some small branches grow on its waist as shown in Fig. 3b. When the temperature is further increased to 210 °C, more branches on the tabour bodies resulted in it was far from the typical twinned tabours morphology. Multi-branches ZnO structure, as presented in Fig. 3c, replaces the twinned tabours. It is concluded that, higher temperature leads to the transition of the morphology from the symmetrical tabours to multi-branches asymmetrical structures. As the discussion above, the appropriate temperature for symmetrical twinned tabours is defined at 160 °C.

To study the formation process of twinned ZnO tabours and the possible growth mechanism, the morphology evolution of twinned ZnO tabours with different reaction times is examined thoroughly by SEM (Fig. 4a–d). The schematic of the possible growth process is shown in Fig. 4e. The overall reaction for the growth of ZnO crystals may be expressed by the following equations.

$$4CH_3CH_2OH + NO_3^- \rightarrow 4CH_3CHO + NH_3 + OH^- + 2H_2O \quad (1)$$

$$Zn^{2+} + 2OH \rightarrow Zn(OH)_2 \quad (2)$$

$$Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+} \quad (3)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (4)$$

$$[Zn(OH)_4]^{2-} \rightarrow ZnO + 2OH^- + H_2O \quad (5)$$

$$[Zn(NH_3)_4]^{2+} + 2OH^- \rightarrow ZnO + 4NH_3 + H_2O \quad (6)$$

In the solvothermal condition, the equilibrium in Eq. (1) shifts to right, and hence, a large number of OH^- are produced and induce reaction (2) in the solution. At the same time, a part of NH_3 can serve as the chelating agent to coalesce with Zn^{2+} to form the amine complex $[Zn(NH_3)_4]^{2+}$ according to Eq. (3), which benefits from the generation of growth units $[Zn(OH)_4]^{2-}$ [30]. When the concentrations of Zn^{2+} and OH^- ions exceed the critical value, large quantities of ZnO nuclei form [31] and a subsequent crystal growth process develops (Eqs. (4) and (5)). Additionally, a part of the Zn^{2+} amine complexes will react with OH^-, and ZnO can be formed as shown in Eq. (6).

To understand the observed behavior of ZnO, it is necessary to investigate its growth mechanism. It is well-known that ZnO is a polar crystal exhibiting a basal positive polar