Materials Research Bulletin 74 (2016) 21–26

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Sheet-tube-rod transformation for ZnO nanorods prepared by a simple reflux route

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ARTICLE INFO

Article history:
Received 12 February 2015
Received in revised form 7 September 2015
Accepted 6 October 2015
Available online xxx

Keywords:
A. Oxides
A. Nanostructures
A. Semiconductors
C. Electron diffraction
C. Electron microscopy

ABSTRACT

As an important semiconductor material, ZnO nanocrystals with various morphologies have been extensively investigated in the literature. In this paper, we designed a simple reflux route to prepare ZnO nanorods, employing $Zn(NO_3)_2 \cdot 6H_2O$ and urea as the original reactants. Our interest mainly focused on the formation process of ZnO nanorods. The reaction was carried out at 120 °C. XRD analyses showed that the final product underwent a conversion from $Zn_4(OH)_6CO_3 \cdot H_2O$ to ZnO with the prolonging of the reaction duration from 10 to 120 min. SEM observations discovered that during the above conversion the final product comprised of nanosheets, nanotubes and nanorods, respectively. Simultaneously, nanosheets, nanotubes or/and nanorods were found to coexist in certain periods. A possible mechanism was suggested for explaining the formation of ZnO nanorods.

1. Introduction

Since the properties of materials depend on their sizes and morphologies, the controlled syntheses of materials are drawing increasing interest in chemistry and materials science. Much attention is paid to ZnO, an important semiconductor with a band gap of 3.37 eV, due to its special physicochemical properties and wide applications in photocatalysis [1], gas sensing [2], solar cells [3], light-emitting devices [4], laser emission [5], and so on. To date, ZnO nanostructures with various morphologies have been successfully prepared, including nanoparticles [6], nanorods [7], nanowires [8], nanotubes [9], nanoplates [10] and nanocubes [11]; simultaneously, their properties are also investigated.

Among anisotropic structures, nanorods are quantum confined in two dimensions, which show enhanced performances against their bulk states. To prepare one-dimensional ZnO nanorod, many methods have been developed, including the microemulsion method [12], the hydrothermal process [13], the low-temperature liquid-phase route [14], the thermal evaporation [15] and the CVD technology [16]. Compared with the widely reported synthetic strategies, however, only few studies are focused on the formation process of ZnO nanorods. In 2002, for instance, Pacholski et al. [17] experimentally proved the oriented attachment mechanism of the formation of ZnO nanorods. Ethayaraja and Bandyopadhyaya [18] theoretically proposed that ZnO and ZnS nanorods were formed by the mechanism of the oriented attachment and coalescence of nanodots. However, the above mechanisms were mainly involved in the colloidal chemistry.

In the current work, we designed a simple reflux route to synthesize ZnO nanorods, using zinc nitrate and urea as starting materials. To ascertain the formation process of ZnO nanorods, XRD, SEM and TEM technologies were employed for the phase and morphology analyses of the final product. According to SEM/TEM observations, the formation of ZnO nanorods underwent a process from nanosheets, to nanotubes, and finally to nanorods. It was found that the nanotube was an inevitable intermediate product during the above morphology transformation process. Based on the experimental results, a mechanism called as the sheet-collapse and Ostwald ripening cooperative mechanism was proposed.

2. Experimental

2.1. Materials

All reagents and chemicals were analytically pure, purchased from the Shanghai Chemical Company and used without further purification. Distilled water was used throughout the experiments.

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http://dx.doi.org/10.1016/j.materresbull.2015.10.012

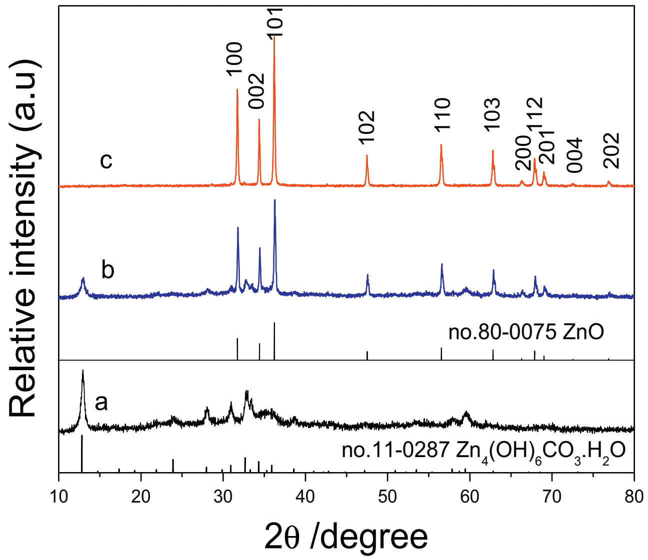

Fig. 1. XRD patterns of the products prepared at 120 °C for different reaction durations: (a) 30, (b) 90 and (c) 120 min.

2.2. Synthesis of ZnO nanorods

In a typical experimental procedure, ZnO nanorods were prepared as follows: 1 mmol $Zn(NO_3)_2{\cdot}6H_2O$ and 10 mmol urea were dissolved into 60 mL distilled water under vigorous stirring for 30 min at room temperature. Then, the transparent solution was transferred to a 100 mL round-bottom flask. The system was refluxed in oil bath at 120 °C for 10–120 min. The produced white precipitates were collected and washed with distilled water and absolute ethanol several times, then dried in vacuum at 60 °C for 5 h.

2.3. Characterization

The X-ray diffraction (XRD) patterns of the products were recorded on a Shimadzu XRD-6000 X-ray diffractometer (Cu Kα radiation, $\lambda = 0.154060$ nm), employing a scanning rate of $0.02^\circ\ s^{-1}$ and 2θ ranges from 10° to 80°. Field emission scanning electron microscopy (SEM) images of the final products were taken on a Hitachi S-4800 field emission scanning electron microscope, employing an accelerating voltage of 5 kV. High resolution transmission electron microscopy (HR/TEM) images were recorded on a JEOL 2010 transmission electron microscope, employing an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 1 shows the XRD patterns of the products prepared from the present reflux system at 120 °C for 30, 90 and 120 min, respectively. As seen from Fig. 1a, after refluxing for 30 min, the diffraction peaks of the product can be indexed as $Zn_4(OH)_6CO_3{\cdot}H_2O$ by comparison with the JCPDS card files no. 11-0287, which proves that zinc subcarbonate is first formed. Usually, urea can hydrolyze in an aqueous solution to produce $NH_3{\cdot}H_2O$ and CO_2 under the heating conditions (see Eqn.1). The produced $NH_3{\cdot}H_2O$ partially decomposes into NH_4^+ and OH^- ions (Eq. (2)). Meanwhile, $NH_3{\cdot}H_2O$ and CO_2 produced from Eq. (1) can rapidly react to form NH_4^+ and CO_3^{2-} ions (Eq. (3)). Thus, OH^- and CO_3^{2-} ions coexist in the solution. When metal ions are introduced, hydroxide, carbonate or basic carbonate will be obtained in the light of separate solubility. Since $Zn(OH)_2$ owns the close solubility to $ZnCO_3$, zinc subcarbonate is formed in the present work. The related reaction can be described as follows:

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_3{\cdot}H_2O + CO_2 \tag{1}$$

$$NH_3{\cdot}H_2O \rightarrow NH_4^+ + OH^- \tag{2}$$

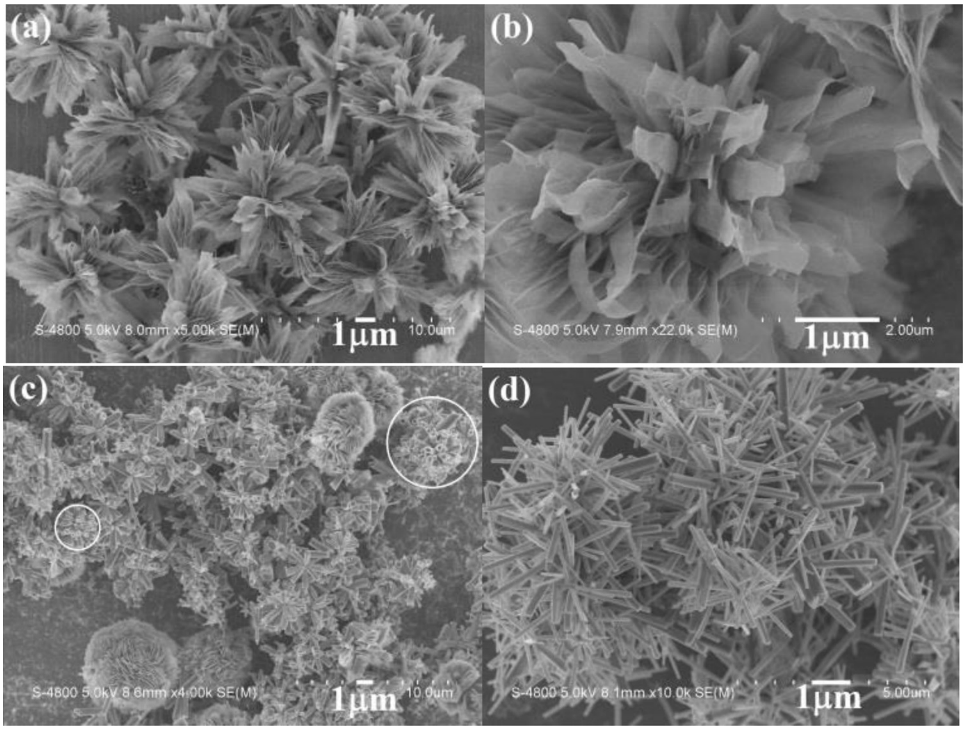

Fig. 2. SEM images of the products prepared from the present reflux system at 120 °C for different reaction durations: (a, b) 30, (c) 90 and (d) 120 min.