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Controlling the morphology of ZnO structures via low temperature hydrothermal method and their optoelectronic application

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ABSTRACT

Here, zinc oxide (ZnO) with various morphologies were synthesized via a simple hydrothermal method at low temperature of 70 °C. Field emission scanning electron microscopy (FESEM) characterization exhibited that the block and flower-like samples could controllable grow on graphite and graphene substrate, respectively. In comparison, rod-like sample was fabricated in the absence of substrate. X-ray diffraction (XRD) indicated that the rod and flower-like samples were the well-crystallized wurtzite ZnO structure, and the block-like sample was a hybrid of ZnO and $Zn(OH)_2$. Graphite and graphene substrate were the reason that affects the formation of block hybrid of ZnO and $Zn(OH)_2$ crystal and flower-like ZnO, respectively. The results indicated that the substrate plays a crucial role in synthesizing ZnO sample with various morphologies and types. Additionally, the property characterization demonstrated that the flower-like ZnO exhibited the best optoelectronic performance compared with the other two structures.

1. Introduction

ZnO is an important semiconductor material with large direct band gap (3.37 eV) and high exciton binding energy (60 meV), and can be applied in many important fields, such as solar cells [1], gas sensors [2], light-emitting diodes [3], field-effect transistors [4] and photocatalysis [5]. The physico-chemical properties of ZnO are highly dependent on their structures. Up to now, synthesis methods including solo-chemical process [6], precipitation [7], combustion [8], chemical vapor deposition (CVD) [9], spray pyrolysis [10] and pulse laser deposition (PLD) [11,12] have been developed and various ZnO structures (e.g. rod-likes, sheets, needles, tubes and flower-likes) have been obtained [13–17]. Additionally, some additives were added in order to control the morphology of ZnO. Wang et al. [18] used the hexadecyltrimethylammonium bromide (CTAB) as the additives, which can be acted as a cationic surfactant and interacted with growth units of ZnO to generate active sites on the surface of ZnO nuclei, resulting in the formation of the flower-like ZnO. Zeng et al. [19] reported the synthesis of nut-like ZnO by triethanolamine (TEA) assisted hydrothermal method, which TEA is also a cationic surfactant and can form TEA ligands to restrain the anisotropic growth of ZnO under the coulomb force. However, the above methods need harsh synthesis conditions and complex procedures and most of additives are expensive and toxic.

In this paper, a facile and cost-effective low-temperature hydrothermal route has been adopted to synthesize ZnO with controllable morphology. The substrate plays a crucial role in controlling morphologies and types of ZnO sample. Block-like hybrid of ZnO and $Zn(OH)_2$ and flower-like ZnO were prepared on graphite and graphene substrate respectively, while rod-like ZnO was obtained in the absence of substrate. It was considered that the growth direction of c-axis [001] faster than that along other directions lead to the formation of rod-like ZnO. Van der Waals surfaces covered with anti-bonding π-electrons of sp^2-carbon on graphite surface, resulting in crystal growth along vertical and lateral direction. The lower temperature on graphite surface make product with lower energy and poorer mobility, which damaged the quality of the crystal. The formation of flower-like ZnO on graphene may be brought about by the epoxide groups of graphene oxide surface reacting with H_2O to produce CO_2, making alkalinity of solution weaker and residual Zn^{2+} ions act as binders. Finally, ZnO rods aggregated to form ZnO flowers under the action of driving force. In addition, the performance characterization of the three samples demonstrated that the flower-like ZnO exhibited the best optoelectronic performance.

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2. Materials and methods

All the chemicals (analytic grade reagents) were purchased from Sinopharm Chemical Reagent company and used without further purification. In a typical procedure to synthesize ZnO structures, 0.72 g sodium hydroxide (NaOH) and 0.31 g zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) were dissolved in 40 ML deionized water. The solution was stirred until the chemicals were completely dissolved. Then the solution was poured into a Teflon-lined stainless steel autoclave and graphite sheet ($1 \times 1\ cm^2$) and graphene were immersed into the solution, respectively. The autoclaves were sealed and heated at 70 ℃ for 20 h. After that, the white product was cleaned with ethanol and deionized water. The obtained precipitate was dried at the same reaction condition for the next characterization. Additionally, the influence of drying temperature on the structures of the sample was studied.

The structures of the samples were characterized by Philips 1730 powder X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å). Raman measurements of the ZnO were carried out using laser Raman spectrometer, and a 532 nm line of an Ar^+ laser was used as excitation source. The morphologies of the sample were investigated by field emission scanning electron microscopy (JEOL JSM-7800F) with the energy dispersive X-ray spectrometry (EDS) attached. The photo-responses were measured using a 300 W Xe lamp irradiation. The UV–vis absorption spectra were recorded in the range of 200–800 nm by the Japan Shimadzu Corporation (UV-3600 Plus).

3. Results and discussion

3.1. Structure and morphology characterizations

The XRD patterns of the samples prepared in the absence of substrate, graphite and graphene substrate are shown in Fig. 1. It was found that no diffraction peaks from any other impurities are detected for the sample of rod-like ZnO (PDF card No: 00-036-1451). Except the standard peak of ZnO phase, graphene peak in the flower-like ZnO XRD pattern attributed to the graphene substrate. However, XRD pattern of block-like sample shows that the crystal is mainly consisted of $Zn(OH)_2$ phase (PDF card No: 01-076-1778) and a fraction of ZnO phase [20,21]. Which indicated that the raw materials produce $Zn(OH)_2$ through the chemical reactions, resulting in hybrid of ZnO and $Zn(OH)_2$.

Fig. 2 shows the Raman spectra of the rod and flower-like ZnO, It was noted that the Raman spectra of the samples displayed similar spectral shapes with two main regions: one for ZnO region and the other for carbon-related components [22]. The phonon peak at 437 cm^{-1} corresponds to the E_2^{high} mode of the wurtzite structure ZnO,

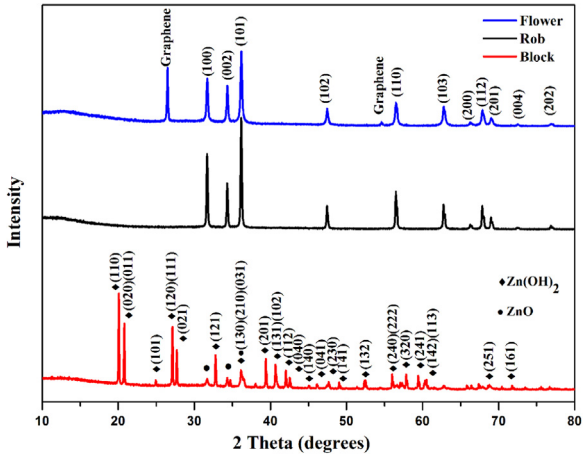

Fig. 1. XRD patterns of the samples synthesized in the absence of substrate, graphite and graphene substrate by hydrothermal method and dried at the same reaction condition.

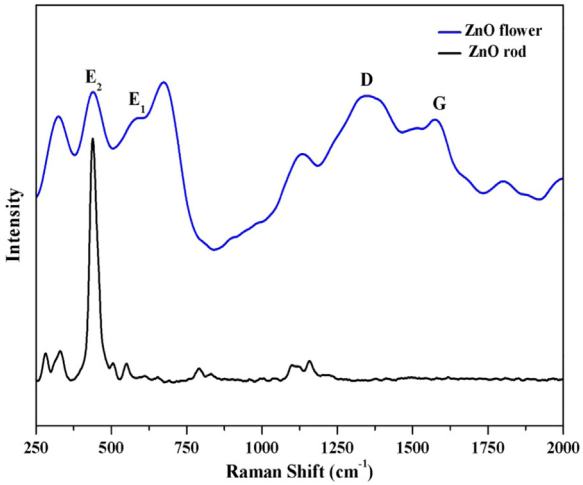

Fig. 2. Raman spectra of the rod and flower-like ZnO samples.

which is a Raman characteristic peak of ZnO. The peak at 582 cm^{-1} is assigned to E_1 (LO) mode associated with the structural defects in ZnO. The peaks located at near 330 and 1130 cm^{-1} are due to the multiple-phonon scattering processes [23]. So, the Raman and XRD analysis clearly confirmed the formation of ZnO phase with wurtzite. However, there have the two extra peaks for flower-like ZnO structure in Raman spectra, one is disordered (D) band around 1350 cm^{-1} present in carbon materials due to defects, while the other is graphitic (G) band at 1585 cm^{-1} for carbon materials due to the presence of sp^2 carbon atoms [24,25].

Fig. 3 shows the FESEM images of the samples prepared in the absence of substrate, graphite and graphene substrate respectively by hydrothermal method and dried at the same reaction condition. As shown in Fig. 3(a), it was found that there are almost ZnO rods and no other different shapes in these image and the average length and diameter of ZnO rods are about 1.46 μm and 0.13 μm, respectively. The block-like samples are shown in Fig. 3(b), the products mainly are $Zn(OH)_2$ and a small fraction of ZnO according to the XRD analysis. In spite of the phase is not unique, the appearance of the samples is block-like structure. Additionally, it could be found clearly from Fig. 3(c, d) that the ZnO prepared on graphene substrate is the flower-like structure.

In order to investigate the influence of drying temperature on the structure of the samples, the as-prepared white products were dried at 300 ℃ for 2 h while keeping other parameters constant. Fig. 4(a) and (b) show the images of the samples prepared in the absence of substrate and graphite substrate, respectively. The both rod and block crystals aggregate together and the size of corresponding samples reduced, but the structures of the samples have not considerable changed. It can be seen from Fig. 4(c, d) that the excellent ZnO flowers have been fabricated on graphene substrate and are consisted of many rods structures with average diameter of 1.2 μm. Which indicated that increasing the drying temperature is conducive to the growth of ZnO flowers. In addition, the EDS analysis (Fig. S1, Supporting information) of three samples indicates that the stronger C peak appears in the flower-like ZnO pattern due to the graphite substrate.

3.2. Mechanism analysis

The growth process of ZnO in the alkaline solution is generally accepted as the following chemical reactions:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (1)$$

$$Zn(OH)_2 \rightarrow ZnO + 2H_2O \quad (2)$$

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-} \quad (3)$$