

Microwave-Assisted Preparation and Optical Property of Reddish-Brown N-Containing ZnO Nanorods

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Reddish-brown N-containing semiconductor ZnO nanorods have been prepared by microwave-assisted aqueous chemical reaction and subsequent heat treatment process. The as-prepared products have been characterized by X-ray diffraction, field-emission scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and photoluminescence spectrum. The diameter and length of ZnO nanorods are estimated to be 40-60 and 300-500 nm, respectively and the long-radius ratio is about 10:1. According to XPS analysis, the concentration of N in ZnO is calculated to be 9.92 %. Room temperature photoluminescence spectrum shows a strong UV peak at 383 nm and a weak broad orange-red band emission centered at 603 nm. As a multi-functional material, this high N-containing ZnO nanorods may be applied in solar cell, photo-electron device and photocatalyst, *etc.*

Keywords: Semiconductor, N-Doped ZnO, Nanorods, Optical property.

INTRODUCTION

Zinc oxide (ZnO), as a direct wide band (3.37 eV) multi-functional semiconductor, has a large exciton binding energy (60 meV) at room temperature, which has aroused considerable attention due to its potential applications in solar cells, pi-ezoelectric transducers, gas sensors, photocatalysts, *etc.*¹⁻⁴. Various pure ZnO nanostructures have been reported, such as nanowires and nanobelts⁵, nanotubes⁶, nanobridges and nanoanils⁷, nanocombs and nanobelts⁸, nanoflowers⁹ and nanospheres¹⁰, *etc.* Recently, great efforts have been devoted to synthesize doped ZnO nanocrystallites by using various dopants such as Al, Co, Cr, N, P, Sb in order to improve the electrical, optical and catalytic properties of materials. Among them, nitrogen doping is found to be very effective on improving photoactivity of ZnO, creating *p*-type semiconductor. Experimentally, the incorporation of N into ZnO is not very simple to come true employed by some traditional wet-chemical methods. Up to now, some methods including physical and chemical techniques have been tried to synthesize N-containing ZnO nanocrystals with particular morphologies, such as nanoparticles¹¹, nanorods¹², nanowires¹³, nanowire arrays¹⁴, nanotetrapods^{15,16}, *etc.* Nevertheless, a feasible and environmental-friendly method for controllable synthesis of high N-containing ZnO nanomaterials still remains a long-term challenge. In this work, reddish-brown high N-containing ZnO nanorods with diameters of 40-60 nm and lengths of 300-500 nm have been

successfully prepared through a simple microwave-assisted wet-chemical reaction and subsequence heat treatment process.

EXPERIMENTAL

Preparation of precursor: In a typical procedure, 10 mmol organic base hexamethylenetetraamine (C₆H₁₂N₄) was dissolved in 60 mL deionized water in a 100 mL beaker under stirring. 2 mmol self-prepared Zn(N₂H₄)₂-Cl₂ was added into the above solution and continue stirring for 20 min. Then, the reaction mixture was subsequently transferred into a sonication bath. After 5 min ultrasound radiation at ambient conditions, the beaker containing the reaction mixture was covered with a piece of PE film, then put into a domestic microwave oven and irradiated by 18 % output power for 10 min. After cooling down to room temperature, the white precipitation was washed with anhydrous ethanol and deionized water for several times and then finally dried in a vacuum at 60 °C for 6 h.

Preparation of reddish-brown N-doped ZnO nanorods: 0.2 g precursors was put into a 60 mL crucible and then transferred into a resistance furnace and heated to 400 °C in air with a ramping rate of 5 °C /min, then calcined at 400 °C for 1 h under the ambient pressure. Finally, the reddish-brown powders were collected for characterization.

Instrument and characterization: Microwave-heating was performed by a domestic microwave oven (Galanz D80D23N1P-T7, 2.45 GHz, maximum power 800 W). Ultrasonic dispersion

was conducted on a locally supplied ultrasonicator (KQ-50, 40 kHz, 50 W). The phase purity of as-prepared products was examined by X-ray diffraction (XRD) using a Philips X'Pert PRO X-ray diffractometer equipped with graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Field-emission scanning electron microscope (FESEM) images of the sample were taken on a field-emission microscope (FEI Sirion 200, 15kV). Analysis of element content was done with Thermo ESCALAB 250 XPS instrument (America) using $\text{AlK}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). Photoluminescence spectrum was recorded on a Laser Micro Raman Spectrometer (JYLABRAM-HR) using the 325 nm exciton of the He-Cd laser at room temperature.

RESULTS AND DISCUSSION

The crystal phases of the products were detected by X-ray diffraction (XRD). Fig. 1 shows the typical XRD patterns of precursor and calcined product. From the XRD pattern of precursor [marked as (a) in Fig. 1], though these diffraction peaks are not accurately indexed to a certain material, one can see that the precursor has good crystallinity and can be assigned to ZnO-containing precursor. The peaks marked by (*) are indicated to ZnO. From the XRD pattern of calcined product [labeled as (b) in Fig. 1], Nine prominent XRD peaks can be indexed to the pure ZnO crystal planes of (100), (002), (101), (102), (110), (103), (200), (112) and (201), in good agreement with the reported data for ZnO (JCPDS card No. 5-664). No characteristic peaks belonging to other impurities were detected. The sharp diffraction peaks indicate the good crystallinity of as-prepared ZnO products.

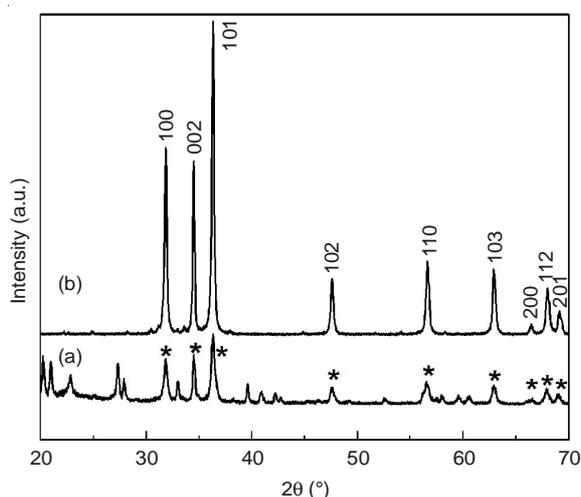


Fig. 1. Typical XRD patterns of samples: (a) precursor; (b) calcined product

Field-emission scanning electron microscopy and transmission electron microscopy are employed to further examine the morphologies of precursor and N-containing ZnO products, as shown in Fig. 2. Fig. 2(a) and 2(b) give the pictures of precursor obtained through a microwave-assisted wet chemical reaction using $\text{C}_6\text{H}_{12}\text{N}_4$ and $\text{Zn}(\text{N}_2\text{H}_4)_2 \cdot \text{Cl}_2$ as starting raw material, which indicates that the pre-obtained precursor are mainly composed of nanosheet with the thickness of about 30 nm. These nanosheets interconnect with each other to form porous network-like architectures. Fig. 2(c) and 2(d) show the

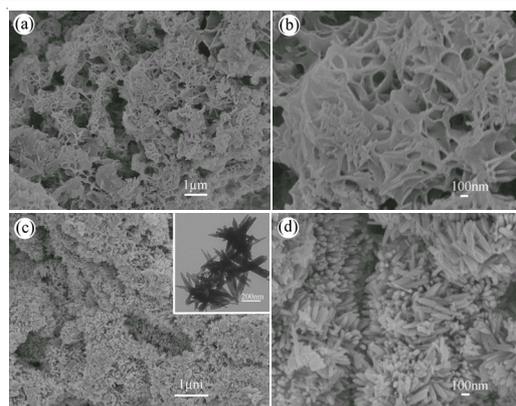


Fig. 2. FESEM images and transmission electron microscopy image of samples: (a, b) precursor; (c, d) reddish-brown N-containing ZnO products

morphologies of reddish-brown N-containing ZnO products obtained by calcinating precursors, which display that the calcined products do not maintain the morphologies of precursors. A good deal of nanorods is observed in as-obtained reddish-brown ZnO products. These nanorods aggregated together to form the appearance of woodpile. A closer examination reveals that the diameter and length of the nanorods are estimated to be 40-60 and 300-500 nm, respectively and the long-radius ratio is about 10:1.

Fig. 3 shows X-ray photoelectron spectra of as-synthesized reddish-brown ZnO products. As depicted in Fig. 3(a), no impurities were detected in the XPS survey spectrum of ZnO

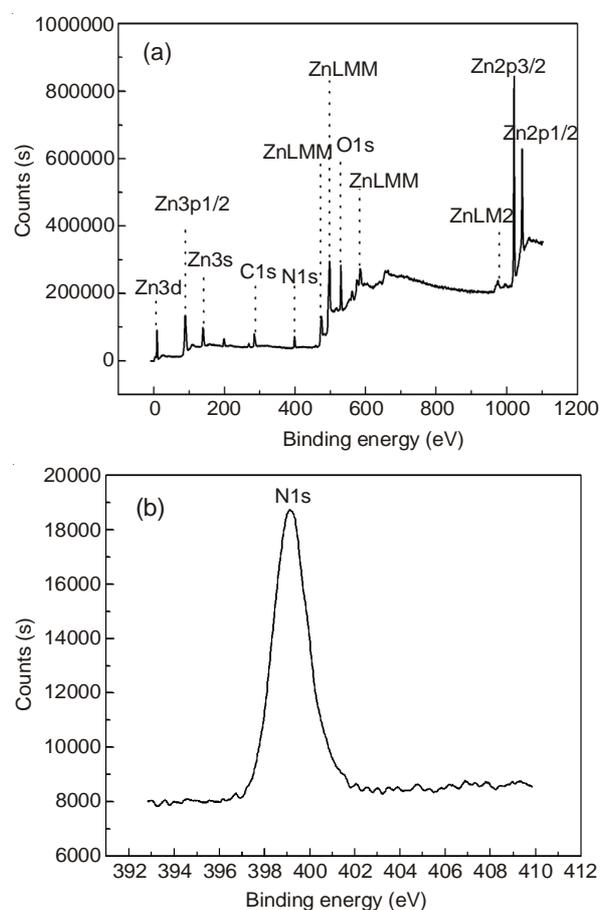


Fig. 3. X-ray photoelectron spectroscopy (XPS) spectra of the reddish-brown N-containing ZnO products: (a) survey spectrum; (b) N1s core level

products. The photoelectron spectrum of N1s core level is shown in Fig. 3(b). The peak intensity is very strong. The binding energy peak centered at 399 eV is assigned to the N1s, which is almost agreement with the reported value⁵ of N-doped ZnO. According to the XPS analysis, the concentration of N in ZnO is calculated to be 9.92 %. The results of XPS indicate that as-prepared reddish-brown product is actually high N-containing ZnO.

The optical property of the reddish-brown ZnO products was further investigated. Fig. 4 shows the room-temperature photoluminescence spectrum of as-synthesized N-containing ZnO products. An intense, sharp and dominated peak at 383 nm in the UV region and a suppressed and broad orange-red emission band centered at 603 nm in the visible region are observed. The UV peak of ZnO is attributed to the near band-edge excitonic emission¹⁷. The broad orange-red emission may be related to the incorporation of nitrogen in ZnO crystal lattice. This unique emission behaviour demonstrates that the high N-containing ZnO nanorods may be applied to many aspects as multi-functional materials, such as solar cell, photo-electron device and photo catalyst, *etc.*

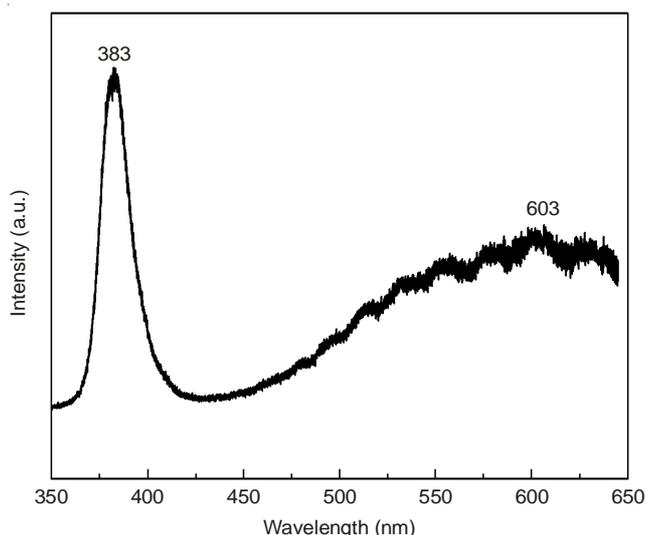


Fig. 4. Photoluminescence spectrum of the reddish-brown N-containing ZnO nanorods

Conclusion

A convenient environmental friendly two-step route is developed to prepare reddish-brown N-containing ZnO nanorods.

The sheet-like precursor is firstly synthesized by a microwave-assisted chemical reaction using $C_6H_{12}N_4$ and $Zn(N_2H_4)_2 \cdot Cl_2$ as starting raw materials. Then the pre-obtained precursor is calcined at 400 °C for 1h in air to obtain N-containing ZnO nanorods. The presence of nitrogen in ZnO products is indicated by XPS. Room temperature photoluminescence shows a strong UV peak at 383 nm and a weak broad orange-red band emission centered at 603 nm. The present work provides a new simple synthetic methodology to controllably prepare high-concentration N-doped ZnO crystals. It is observed that this high N-containing ZnO nanomaterials could have potential applications in many fields, such as solar cells, electrical and optical materials and photocatalysts, *etc.*

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