Preparation and characterization of ZnO/TiO₂ nanocomposite by Anodization and hydrothermal synthesis

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ABSTRACT:

ZnO nanorod arrays were deposited by hydrothermal process via an aqueous solution with ammonia and Zinc nitrate as inorganic precursors, using TiO₂ nanotube templates formed in HF solution by anodization method. The effect of NH₃.H₂O and Zn(NO₃)₂ concentration on ZnO nanorods morphology and crystallinity were investigated. XRD demonstrates that ZnO nanorods are wurtzite crystal structure preferentially oriented in c-axis direction. The length and the diameter of the ZnO nanorod range from 1,1 µm to 3,4 µm and from 250 to 500 nm respectively.

1. INTRODUCTION

One-dimensional (1D) nanostructures, including nanowires, nanotubes and nanorods have attracted significant interests owing to their unique geometries. [1] As a kind of 1D oxide material, ZnO nanorod arrays are considered as important functional oxide nanostructures in a wide area of high-technology applications such as a surface acoustic wave filters [2], ultraviolet laser devices [3], photonic crystals [4], photo detectors [5], field-emitting devices [6], sensors [7], piezoelectric materials [8], and solar cell electrodes [9].

Various physical, chemical, or electrochemical methods [10–13] have been developed to prepare 1D ZnO. Among these fabrication methods, ZnO nanorods are most commonly grown by vapor phase methods like vapor-liquid-solid (VLS), chemical vapor transport, and thermal evaporation [11–13]. These approaches can produce high quality and vertically aligned nanorods array with length of several microns. But, these fabrication procedures require higher temperature. The complex processes and high cost vacuum equipments are often involved in these technologies as well. Compared with those techniques, chemical solution method is attractive to synthesizing ZnO nanostructures because of the low cost equipments, lower growth temperatures, promising large-scale up, and controlled easily technology of growing high-density nanorods array [16].

A template-assisted approach has been proven to be effective for the growth of nanostructure oxides. A major advantage of using templates is that the dimension of the tubes or rods is set by the size of template and can be varied easily by adjusting preparation conditions. Few efforts have been made on the study of the use of ZnO nanorods as a template. Yang [17] and Kim [18], demonstrated that inorganic nanotubes can be obtained by using ZnO nanorods grown from the desired substrates as template. Their procedures involve the use of catalysts, high temperature, and a vacuum technique, leading to increase the cost. Seok et al [19] successfully fabricated aligned TiO₂ nanotube arrays by electrodeposition of ZnO nanorod as a template. In contrast, preparation of ZnO nanorods using TiO₂ nanotubes as templates remain largely unexplored although a few studies. Zhonghai et al [20] prepared ZnO nanorods embedded

in highly ordered TiO₂ nanotubes. Ning [21] has reported a strategy to prepare aligned ZnO nanorod films using TiO₂ nanotube array films as template.

Therefore, in the present study we would like to present a detailed investigation on the preparation and characterization of ZnO/TiO₂ nanocomposite film. The ZnO/TiO₂ nanostructured composite film was prepared using two steps: (1) Formation of TiO₂ nanotube arrays in HF solution by anodization method, which is a simple technique to control the structure parameters of TiO₂ NTs. (2) Deposition of ZnO nanorods by hydrothermal process with ammonia and Zinc nitrate as inorganic precursors.

2. EXPERIMENTAL

A. Materials and chemicals

Pieces of Titanium sheets (98% purity, 0.5 mm thickness), Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, AR), Hydrofluoric acid (HF), Acetone, Nitric acid, HNO₃, Ammonia solution NH₄OH. Distilled water was used in all aqueous solution preparations and washing.

B. Preparation of TiO₂ nanotubes

Anodic oxidation method was adopted to prepare TiO₂ nanotube (TNTs). Prior to anodization, titanium pieces were degreased in an ultrasonic with distilled water for 10 min, followed by eroding in a mixture of HF solution, nitric acid and distilled water for 1 min; then cleaned with acetone, rinsed with distilled water and dried in air. Anodization is performed in 2 wt % HF solution and distilled water with voltage of 20 Volts for 5 h. Finally, samples were rinsed and annealed at 450 °C for 1 h.

C. Characterization of resulting films samples

The surface morphology of the film samples was observed through scanning electron microscopy (SEM-JEOLJSM-7600 and JEOLJSM-7000 apparatus). The crystal phase composition of the samples were analyzed by X-ray diffraction (XRD, Bruker-Siemens D8- Advance, Cu.K α radiation $\lambda=1.5406$ Å).

3. RESULTS AND DISCUSSION

Figure 1 is the profiles of the TiO₂ nanotubes before and after annealing at 450 °C for 1 h. As shown in figure 1 b, peaks with 2θ value of 25.6° correspond to the crystal plan of anatase (101) phase. And other peaks are corresponding to the titanium substrate, which is similar to the results found in many literatures [21] and [22].

Figure 2 presents XRD patterns of ZnO/TiO₂ at different hydrothermal temperatures. Except for the peaks of titanium and titania, the diffraction peaks with 2θ value of: 32.1°, 34.7° and 36.3° agree well with the wurtzite hexagonal structure with the lattice constants of: $a=0.32$ nm and $c=0.26$ nm according to the standard JCPDS card (No. 36-1451). Based on the higher (002) XRD peak than (101) one, which is usually the highest in all XRD peaks of ZnO crystal.

XRD patterns in Figure 2 c show a disappearance of the peaks corresponding to titanium, at high temperature, the formation of ZnO increases with increasing of reaction rate into aqueous solution, and also the reaction rate between Ti and ZnO.

Figure 1. The XRD patterns of TiO_2 Nts (a) before and (b) after annealing.

Figure 2. The XRD patterns of ZnO/TiO_2 at different hydrothermal temperature: at 80 °C (a), at 100 °C (b) and at 160 °C.

No remarkable change in orientation of the films as the amount of ammonia was increased shown in Figure 3 but influenced the intensity of the preferred crystalline orientation.

Figure 3. The XRD patterns of ZnO/ TiO₂ with (a) 0.3 M of ammonia and (b) 0.4 of ammonia.

Figure 4. SEM images of (a) TiO_2 nanotube and (b) ZnO/TiO_2 nanocomposite .

The SEM image of the TiO_2 nanotube formed on the FTO substrate by anodization method shown in Figure 4 a, which reveals that high density, well ordered and uniform nanotubes array are formed.

The diameters of these nanotubes range from 60 nm to 95 nm and their length is about 1.7 μm detected by profilometry.

After ZnO deposition by hydrothermal process on the TiO_2 NTs as shown in Figure 4 b, the ZnO grows oriented through the TiO_2 NTs inner channels. The epitaxial growths of ZnO nanorods inside the TiO_2 nanotube channels are spilled over the TiO_2 , which is in good agreement with one reported by Z. Zhang et al [20] and K. Yu et al [23].

4. CONCLUSION

$\text{ZnO}/\text{titania}$ nanocomposites were fabricated via two step route. The TiO_2 nanotubes were fabricated by anodization method. The hydrothermal process was employed to form ZnO nanorods inside TiO_2 nanotubes. The obtained TiO_2 nanotubes and ZnO/TiO_2 nanocomposite are characterized by different techniques: XRD, and SEM. TiO_2 nanotubes are mainly anatase structure and well ordered. The diameter of these nanotubes ranges from 60 to 95 nm and the length is about 1.7 μm . The ZnO nanorods have high crystallinity of wurtzite hexagonal structure.

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