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

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Keywords: ZnO nanorods; TiO₂ nanotubes; Nanocomposites; Hydrothermal process; Anodic oxidation.

ABSTRACT:

ZnO nanorod arrays were deposited by hydrothermal process, an aqueous solution with ammonia and Zinc nitrate as inorganic precursors, using TiO₂ asotube templates formed in HF solution by anodization method. The effect of NH₃, H₂O and TiO₂ concentration on ZnO nanorods morphology and crystallinity were investigated. XRD demonstrates that ZnO nanorods are wurzite 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], photocatalysts [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]. These approaches can produce high quality and vertically aligned nanorods over a length of several microns. But, these fabrication procedures require higher temperature, the costly processes and high cost vacuum equipments are often involved in these technologies as well. Compared with those techniques, chemical solution method is attractive to synthesize 1D nanostructures because of the low cost equipments, lower growth temperatures, promising for scaling 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 bath with distilled water for 10 min, followed by erosion 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 w% HF solution and distilled water with voltage of 200 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-7600F, and E0438v apparatus). The crystal phase composition of the samples were analyzed by X-ray diffraction (XRD, Bruker-Siemens D8 Advance, Cu.Kα radiation λ=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 2 peaks of titanium and titania, the diffraction peaks with 2θ value of: 32.1°, 34.7° and 48.0° agree well with the wurtzite hexagonal structure with the lattice constants of: a=0.32 nm and c=0.52 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 TiO2 Nts (a) before and (b) after annealing.

Figure 2. The XRD patterns of ZnO/ TiO2 at different hydrothermal temperature: at 80 °C (a), at 100 °C (b) and at 160 °C (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/ TiO$_2$ with (a) 0.3 M of ammonia and (b) 0.4 M of ammonia.

Figure 3a shows the XRD pattern for 0.3 M of ammonia, while Figure 3b shows the pattern for 0.4 M of ammonia. The peaks corresponding to different phases are indicated in the figure.
Figure 4. SEM images of (a) TiO2 nanotube and (b) ZnO/TiO2 nanocomposite.

The SEM image of the TiO2 nanotubes formed on the Si substrate by anodization method shown in Figure 4a, 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 TiO2 NTs as shown in Figure 4b, the ZnO grows oriented through the TiO2 NTs inner channels. The epitaxial growths of ZnO nanorods inside the TiO2 nanotube channels are spilled over the TiO2, which is in good agreement with one reported in Z. Zhang et al [20] and K. Yu et al [23].

4. CONCLUSION

ZnO/titanium nanocomposites were fabricated via two step route. The TiO2 nanotubes were fabricated by anodization method. The hydrothermal process was employed to form ZnO nanorods inside TiO2 nanotubes. The obtained TiO2 nanotubes and ZnO/TiO2 nanocomposite are characterized by different techniques: XRD, and SEM. TiO2 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.

ACKNOWLEDGMENT

This work was supported by Ceramic Laboratory of Physic department, University of Constantine, Algeria. The authors are grateful to J. Carru of Calais University, France, and O. Abdelkader of Cadi Ayyad University, Morocco for their help in using the Scanning electron microscope.
References


