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Template-based growth of TiO_2 nanorods by sol-gel process

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Abstract. In this paper, the preparation of TiO_2 nanorods by sol-gel-template process has been considered. The prepared sols were characterized by using FTIR spectroscopy, and the obtained nanorods were characterized by X-ray diffraction and SEM microscopy. SEM images show that TiO_2 nanorods with uniform diameter of about 100-200 nm and a length of several micrometers. The results of XRD indicated that the TiO_2 nanorods were crystallized in the anatase and rutile phases after annealing to 400-700 ºC up to 2 hours.

Keywords: TiO_2 nanorods, sol-gel process, template-based growth, modifier ligands.

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1. Introduction

In recent years, there has been increasing interest in one-dimensional (1D) nanostructures (nanorods, nanowires, nanotubes, nanofibers) because of numerous potential applications in various areas such as photocatalysis, solar energy, electronics, optics, sensor and so on [1-5]. Numerous methods have been developed for the synthesis of 1D nanostructures such as vapor-liquid-solid (VLS) [6], chemical vapor deposition (CVD) [7], solution-liquid-solid (SLS) [8], laser-assisted catalytic growth [9], electron beam lithography [10], sol-gel [11], surfactant-directed [12], solvothermal [13], and the filling of templates with colloidal oxide particles [14-15]. Among them, the template assisted synthesis method due to its uniform pore size, high density of controllable-dimensions – shape pores, easy way of preparation and relatively low cost of production has been found as an effective way for the formation of 1D nanostructures [16-17]. In this manner, the template is dipped directly into the precursor solution for a required period. Therefore, the preparation of nanorod materials by template method needs to provide nanoparticles in precursor solution. These nanoparticles can be prepared by sol-gel process. This method is based on hydrolysis and condensation reactions of molecular precursors such as metal alkoxides and inorganic salts [18]. Metal alkoxides which are used as precursor materials for sol-gel process are generally highly reactive species. Thus, the control of reactivity of metal alkoxides is necessary in order to obtain sols and gels with desirable properties. This control may be achieved through the addition of "modifiers" such as β-diketones (e.g. acetylacetone), carboxylic acids or other complex ligands [19]. However, there are some limitations and difficulties with this technique such as weak driving force and low solid content. Heating-sol-gel-template and sol-gel electrophoresis are two reported methods for the preparation of dense TiO_2 nanorods, which can overcome the limitations of the direct sol filling method [20-21]. In this paper, the formation of TiO_2 nanorods by the method of template-assisted sol-gel has been investigated. Also, the influence of a number of processing parameters on the growth, structure and morphology of TiO_2 nanorods has been reported. The studied samples were characterized by using FTIR, XRD and SEM microscopy.

2. Experimental

2.1. Preparation of the TiO_2-sol

The TiO_2-sol is formed by mixing of titanium tetraisopropoxide (TTIP, Merck ≥ 98 %), acetylacetone (ACAC, Merck ≥ 99.5 %), deionized water and ethyl alcohol (EtOH, Merck ≥ 99.8 %) at molar ratios of 1:1:3:20, 1:3:40:70 and 1:1:275:86. Briefly, TTIP is dissolved in ethanol and then, a second solution is prepared by mixing ethanol with water and ACAC. The EtOH/ACAC/H_2O solution was slowly added into the TTIP/EtOH solution to form the TiO_2 sol. The mixture was then stirred for approximately 2 h at the room temperature.

2.2. Synthesis of TiO_2 nanorods

The formation of TiO_2 nanorods was done using direct sol filling and heating-sol-gel-template method. The porous anodic alumina templates (Whatman Anodisc 25) with 60 µm thickness and 100-200 nm diameter pores were used as template. The anodic alumina membranes (AAMs) were firstly boiled in ethanol at about 75-77 ºC for 10 min to enhance the hydrophilicity of alumina pore with TiO_2-sol, and then these anodic alumina templates were immersed into TiO_2-sol solutions (at room temperature and about 80 ºC) for different dipping times (10-60 min). After drying in the air at room temperature for 24 h, the prepared specimens were put into a muffle furnace and then were heat-treated as the followed procedure. The samples were firstly held at 100 ºC for 8-10 h to completely remove the residual water. For preparation of anatase TiO_2, the samples were heated up to 400 and 500 ºC at the rate of 2.5 ºC/min and held at this temperature for 2 h. For preparation of rutile TiO_2, the specimen heated up to 700 ºC rapidly to avoid the formation of the low temperature phase of anatase and held at this temperature for 2 h, the furnace was shut down and the samples were cooled back to room temperature naturally.

2.3. Characterization of TiO_2 nanorods

The size and morphology of TiO_2 nanorods were characterized by scanning electron microscopy (SEM, CamScan MV2300). The surface layer was removed by mechanical polishing of the anodic alumina membrane and then the anodic alumina membrane was dissolved away by immersion in the 6M NaOH solution at room temperature at 10 min. Finally, it was washed several times with distilled water to remove the dissolved AAM and the remaining NaOH solution. FTIR spectra were recorded at the room temperature with a Bruker (model Vector 22) spectrophotometer in the range of 400-4000 cm^{-1}. The phase structure characterization of TiO_2 nanorods was carried out by a Philips PW 1800 diffractometer using filtered monochromatized CuK_α radiation.

3. Results and discussion

For a better control of the hydrolysis-condensation process and preparation of stable TiO_2 sol, we have to use the acetylacetone as modifier. Fig. 1 shows FTIR spectra of TiO_2 sols at various molar ratios in the presence of acac-modifier. Infrared spectra (Fig. 1c) clearly exhibit bands at 1590 cm^{-1} (ν(C-O)+ν(C-C)), 1450 and 1380 cm^{-1} ($\delta(CH_3)$), 1180 and 1080 cm^{-1} ($\rho(CH_3)$) due to acetylacetonat-groups which have bound to titanium.

Acetylacetone provides a strongly bind with precursors and complex species that remain bound to titanium. The hydrolysis reaction in the presence of acetylacetone is incomplete and acetylacetonat-groups still remain bound to Ti even when hydrolysis is preformed with a large excess amount of water (H_2O/Ti ratio = 275).

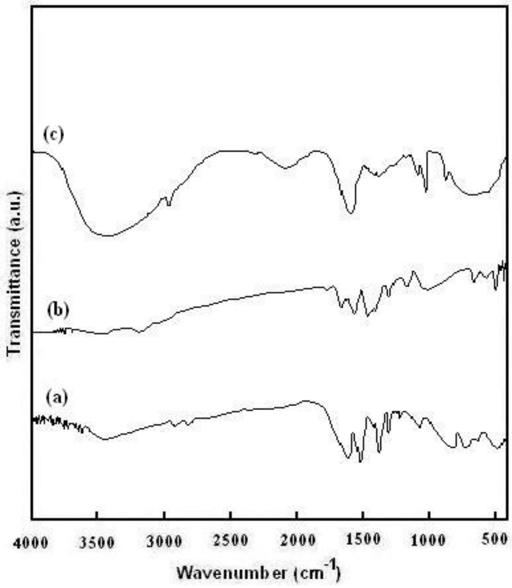

Fig. 1. FTIR spectra of the TiO_2 sols with various molar ratios of TTIP/ACAC/EtOH/H_2O 1:1:275:86 (a), 1:3:40:70 (b), 1:1:3:20 (c).

The size and shape of the final product is deeply dependent on the size and shape of template. So, a uniform template means regular and ordered guest. Fig. 2 shows a SEM image of AAM template used in this article. From the cross-sectional image, it can be confirmed that the uniform-size pores were arranged ideally over the sample.

Fig. 3 shows the XRD spectra of TiO_2 nanorods annealed at 400, 500 and 700 ºC for 2 h. The peak positions and their relative intensities in samples are consistent with the standard powder diffraction pattern of anatase TiO_2 for Fig. 3a, b and rutile TiO_2 for Fig. 3c, respectively. Comparison of the XRD patterns shows that there are identical peaks in both samples. The broadening of TiO_2 peaks is due to the small particle size.

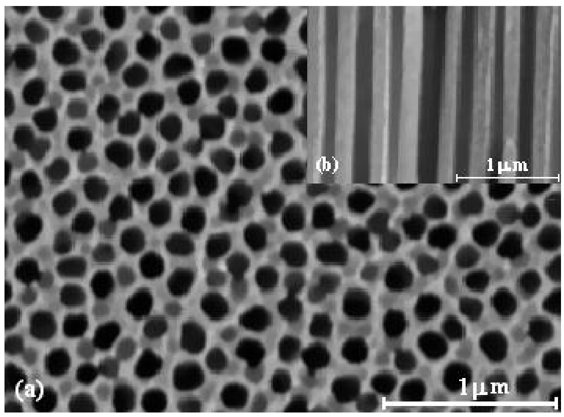

Fig. 2. SEM images of AAM template: (a) top and (b) side views.

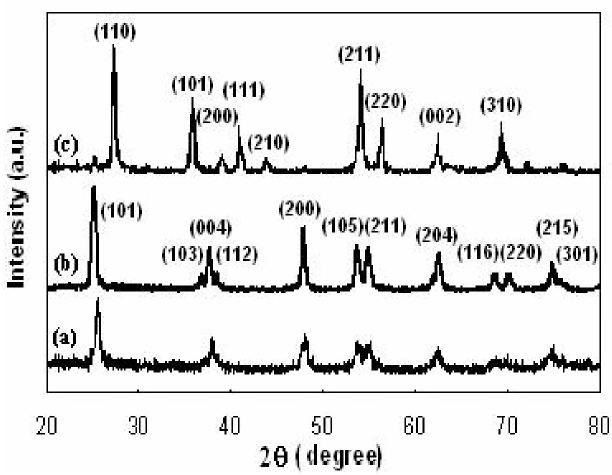

Fig. 3. XRD pattern of the TiO_2 nanorods annealed at 400 °C (a), 500 (b), 700 (c).

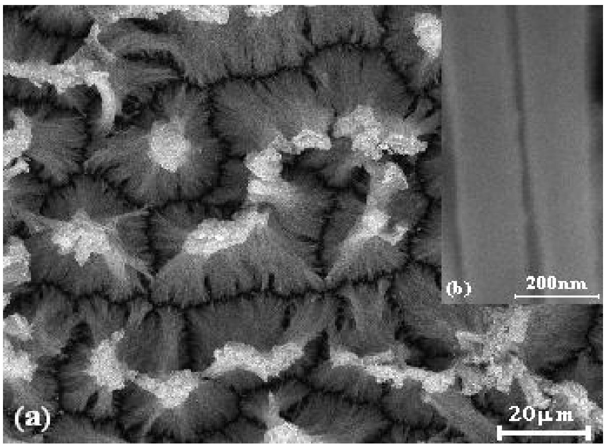

Fig. 4. SEM images of TiO_2 nanorods grown in AAM template: lower (a) and higher (b) magnification images of the nanorods.

Fig. 4 shows SEM image of the grown TiO_2 nanorods in the AAM template with diameter of 100-200 nm and length of several micrometers. The length and diameter of nanorods can be changed by changing of the dipping time.

Fig. 4b shows an individual TiO_2 nanorods picture that is continuous and uniform through the entire length of the rods. The diameter of these nanorods almost coincides with AAM template pores diameter. This indicates that the diameter of the prepared nanorods is controllable by the pore size of AAM template. Meanwhile the high density of the nanorods fabricated by heating-sol-gel process is compared with direct sol filling process without hitting.

4. Conclusions

In summary, TiO_2 nanorods with the anatase and rutile structures have successfully been prepared by sol-gel template process. Uniformly sized TiO_2 nanorods of approximately 100-200 nm in diameter, length of several micrometers and with large areas have been grown. The nanorods have the desired stochiometric chemical composition with anatase and rutile crystal structures after annealing at 400, 500 and 700 °C for 2 h, respectively.

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