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Ceramic letter

Preparation of TiO_2 Nanorods by Heating-Sol-Gel Template Method

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TEM observation showed that densely assembled TiO_2 nanorods have been synthesized by heating-sol-gel template process in a diameter of 150∼200 nm and a length of several micrometers by adjusting the dip coating time, dry temperature, dry time, aging period of TiO_2 sol and the molar ratio of precursors. XRD proved that the obtained nanorods were anatase–TiO_2 nanorods. TEM image revealed that the nanorods were the aggregates of many nanoparticles with about 10 nm in diameter and indistinct polygonal shape. The results of SAED and EDS under TEM confirmed that the obtained nanorods were single-phase anatase–TiO_2 with good compositional uniformity in the entire length along the rod axis. [Received August 7, 2003; Accepted January 5, 2004]

Key-words : *Anatase–TiO_2 nanorods, Heating-sol-gel template process, TEM analysis, EDS profile.*

1. Introduction

Since Fujishima and Honda discovered the photocatalytic splitting of water on TiO_2 electrods,[1] photocatalytic effect has become one of the most important applications as a promising method for environmental purification. The optical and reactivity properties of a high-performance TiO_2 photocatalyst must be optimized, which means that specific surface area, crystallinity, crystal structure and band gap width of TiO_2 suitable to the application. The sensitivity and/or efficiency of photocatalyst are proportionate to the specific surface area, crystallinity, crystal structure and band gap width. Nano-sized TiO_2 materials provide a large surface area compared to that of films and/or bulk materials. They also offer a possibility to adjust the physical properties of one-dimensional structure for the quantum confinement effect; for example, the optical band gap of semiconductor nano-sized material could be expanded according to the quantum size effect.[2–5]

The sol-gel template method has been reported to synthesize TiO_2 nanotubes, nanorods and nanowires from the porous anodic alumina membranes (AAMs), organogel and supramolecular template. However, a limitation of this technique is a weak driving force and low solid content. In order to overcome this shortcoming, we developed an easy approach, that is to dip the AAMs into boiled ethanol and TiO_2 sol, to fabricate indirectionally arranged and uniformly sized nanorods with high solid content. This low cost and easy boiled-sol process does not require complex control which only depends on the natural convection effect of the boiled solution to provide an additional driving force besides the capillary action of AAM pore.

2. Experimental

Anatase–TiO_2 nanorods were prepared by dipping AAMs into TiO_2 sol which is similar to Zhang *et al's* report.[6] The AAMs purchased from Whatman International Ltd., UK commercially (Whatman Anodisc 25) have pores with diameters of about 130∼230 nm and a thickness of about 60 μm. Lots of experiments were carried out by varying the parameters such as: dip coating time, dry temperature, dry time, aging period of TiO_2 sol and molar ratio of precursors. The TiO_2 sol was prepared from a mixture of titanium tetraisopropoxide (TTIP), acetyl acetone (ACAC), deionizer water (H_2O) and ethyl alcohol (EtOH) at a molar ratio of 1 : 1 : 3 : 20 in the typical case and then stirred for 20 min. In the sol-gel dip coating process, AAM was firstly boiled in ethanol at about 78°C for 10 min to enhance the hydrophilicity of alumina pore with TiO_2 sol, and then this AAM was immersed in boiled TiO_2 sol solution at about 80°C for 10 min. After drying in the air at room temperature for 24 h, the specimen was put into a muffle furnace (FO300, Yamato) and then was heat-treated employing the following procedure: The sample was firstly held at 100°C for 4 h to completely remove the residual water, then heated up to 400°C at a rate of 2°C/min and held for 10 h. At last the furnace was shut down and the sample was cooled down to room temperature naturally.

TEM sample was prepared by dissolving AAM template into 10 wt% H_3PO_4 aqueous solution at 50°C after removing the surface–TiO_2–layer by mechanical abrading. Then the pipetted solution of the dispersed nanorods was dropped onto carbon-film-coated TEM micro-grid.

The crystal structure of the obtained TiO_2 nanorods was characterized by X-ray diffractometry (XRD, Cu Kα radiation) with a normal θ-2θ scan. The microstructure of them was observed by two transmission electron microscopy (TEM): one is Philips Technai 20 (200 KeV) with point to point resolution of 2.3 Å and fully digitalized imaging system and the other one is JEM–4000EX (400 KeV) with point to point resolution of 1.8 Å for high resolution image. The phase formation and chemical composition were also analyzed with selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDS) under TEM.

3. Result and discussion

Figure 1 shows the XRD pattern of the prepared nanorods. The peak positions and their relative intensities are consistent with the standard powder diffraction patterns of anatase–TiO_2.[7] None of alumina or other foreign peaks is detected in this XRD pattern. The full widths at half maximum (FWHM) of all the peaks are very narrow, suggesting the fine crystallinity in the fabricated TiO_2 nanorods.

Figure 2(a) shows a representative TEM image of anatase–TiO_2 nanorods revealing the general morphology of the composite nanorods. Densely assembled and undirectionally arranged nanorods with a diameter 150∼200 nm and a length of several micrometers are observed. The diameter of these nanorods is almost fitting with AAM template pores diameter. This indicates that the diameter of the prepared nanorod is controlled by the pore size of AAM template. We

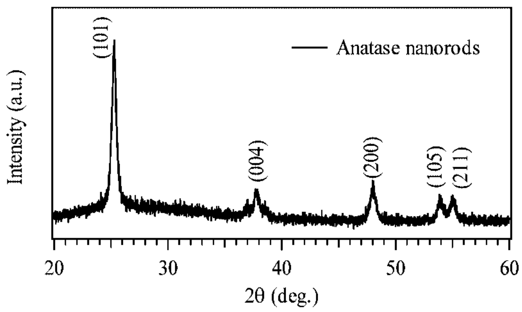

Fig. 1. XRD θ–2θ diffraction pattern of anatase–TiO_2 nanorods with AAM template.

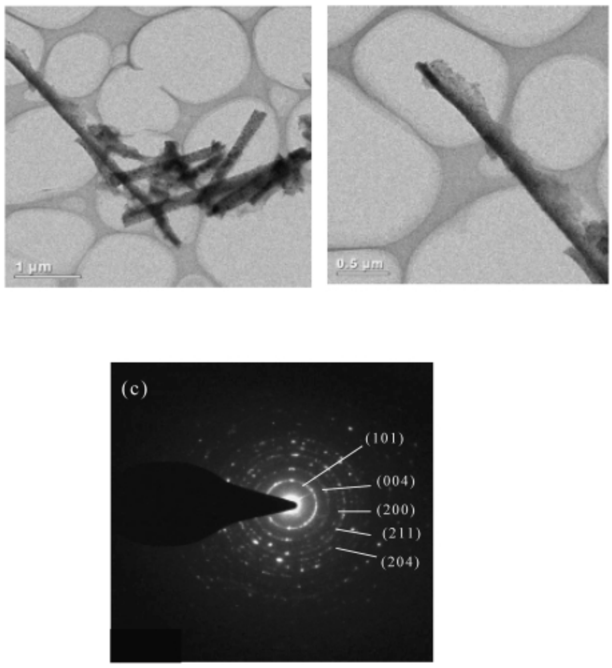

Fig. 2. (a) Low-magnification TEM image showing densely assembled and indirectionally arranged TiO_2 nanorods.
(b) An individual anatase–TiO_2 nanorod photograph.
(c) Typical SAED pattern of polycrystalline anatase nanorod taken from (b).

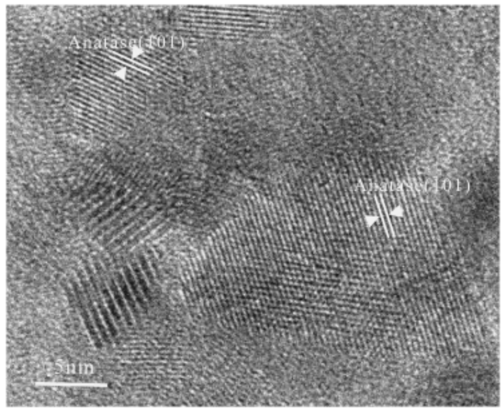

Fig. 3. An HRTEM image of some typical nanocrystallites composed of TiO_2 nanorod.

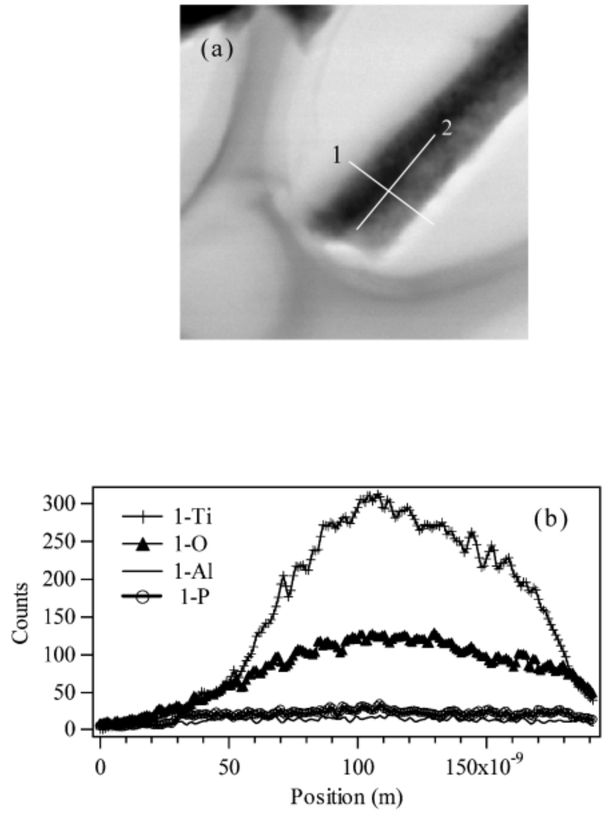

Fig. 4. (a) Bright field scanning-TEM image of one free isolated nanorod giving the position of EDS profile; (b) A typical line EDS spectrum taken from the position indexed in (a) of line 1.

have confirmed this conclusion by adjusting the AAM template pore diameter although here we only show some typical ones. Figure 2(b) shows an individual nanorod picture revealing that the morphology of heating-sol-gel process fabricated nanorod is the aggregates of many nanoparticles. The obtained nanorods are identified as polycrystalline anatase structure from SAED ring pattern. Anatase (101), (004), (200), (211) and (204) are detected in Fig. 2(c).

The high-resolution TEM image (HRTEM) recorded on the individual nanorod provids further insight into the microstructures of this material as shown in **Fig. 3**. The nanorods are composed of many nanocrystallites with indistinct polygonal shape in 10 mm diameter. Anatase (101) is observed in this HRTEM image.

The chemical composition of the obtained nanorod was analyzed by EDS. Two kinds of EDS profiles are obtained: spot and line profile. Line profiles are performed at two directions: parallel and perpendicular to the axis of nanorods in various positions for large quantity of nanorods. Here we omit the result of spot EDS profile. **Figure 4**(a) shows the bright field scanning–TEM image which giving the position of the line EDS profile. The representative EDS line profile perpendicular to the axis of nanorod is shown in Fig. 4(b). C, Ti, O, Al, P and Cu were detected either in spot or line profiles although we omitted C and Cu in line profiles. C and Cu obviously come from micro-grid while Al comes from AAM template, P comes from the solution of template dissolved. The peak intensity of Ti is much higher than that of other elements in the line profile. Combing this result with XRD and SAED results, we can confirm that the obtained nanorods are single-phase anatase–TiO_2 nanorods with good chemical uniformity throughout the entire rod.

4. Conclusion

In summary, densely assembled TiO_2 nanorods have been synthesized by heating-sol-gel template process in a diameter of 150∼200 nm and a length of several micrometers with precisely adjusting the dip coating time, dry temperature, dry time, aging period of TiO_2 sol and the molar ratio of precursors. Dipping the AAM template into boiled EtOH and sol was identified to be a desirable way for synthesis of high solid content nanorods due to the enhancement of driving force for sol solution into AAM pore. Hence, we emphasize that the heating-sol-gel template process is a desirable way to overcome the limitation of sol-gel template method for synthesis nanorods and/or nanowires. HRTEM image revealed that the obtained nanorods were the aggregates of many nanoparticles with about 10 nm in diameter and indistinct polygonal shape. XRD, SAED and EDS results confirmed that the obtained nanorods were anatase-TiO_2 nanorods with good compositional uniformity and fine crystal quality in the entire length.

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