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Synthesis of Nano Titanium Dioxide and Its Application in Photocatalysis

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This paper presents a simple way to synthesize titaniumdioxide nanotubes by using a microwave-assisted reaction of TiO_2 particles and NaOH solution. The main advantage of the introduction of microwave into the reaction system is the extremely rapid kinetics for synthesis. This method is simple and easy to reproduce. Structural and microstructural characterizations of titania nanotubes were accomplished using X-ray diffraction (XRD), scanning-electron microscopy (SEM) and transmission-electron microscopy (TEM) techniques. The specific surface area was calculated using the Brunauer-Emmett-Teller model and was found to be 52 m^2/g. A high photocatalysis of our TiO_2 nanotubes was obtained.

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I. INTRODUCTION

The synthesis and the characterization of one-dimensional (1-D) nanostructures (nanotubes, nanorods and nanowires) have received considerable attention. Much effort has concentrated on important metal oxides such as TiO_2, SnO_2, VO_2 and ZnO. Among them, TiO_2 materials are important for utilizing solar energy and for environmental purification. TiO_2 has been widely used for various applications, such as semiconductors in dye-sensitized solar cells, water treatment materials [1], catalysts, gas sensors and so on. A Nanometer scale with controlled particle size, structure and morphology is quite interesting because the performance of materials is influenced by many factors, such as the structure, the particle size, the surface area and the method of preparation. There are many methods for fabrication of TiO_2 nanotubes and nanowires: treating TiO_2 power with highly concentrated NaOH [2, 3], hydrothermal treatment [4], metallorganic chemical vapor deposition (MOCVD) [5], the sol-gel method [6] and so on.

Among the different chemical methods available for titania nanotube fabrication, a method introduced by Wenzhong Wang and coworkers [2] has received much attention because the method is suitable for producing thin-walled nanotubes. They utilized a simple treatment of anatase TiO_2 particles with NaOH solution at 180 °C for 30 h in a Pyrex breaker with the volume of the aqueous solution being maintained as a constant during the heat-treatment process by continual addition NaOH solution.

In this research, we used a similar method to fabricate titania nanotubes, but the thermal hydrolysis process was carried out in a modified microwave oven at a frequency of 2.45 GHz and operating at atmospheric pressure under a boiling reflux condition for 1 hour. The synthesis process for nanotubes titania reported herein is simple and is easy to reproduce.

II. EXPERIMENTS

Figure 1 shows the experimental setup for the synthesis of titania nanotubes. The starting materials included anatase TiO_2 powder (>99 %, Merk), NaOH (>99 %) and HCl (38 %, Merk). In a typical synthesis, 2 g of anatase TiO_2 particles were added to a 100 mL 10M NaOH aqueous solution. The specimen was transferred into a Pyrex beaker and statically heated in a modified microwave oven, 600 W, working at a frequency of 2.45 GHz for 1 hour, with the volume of the aque-

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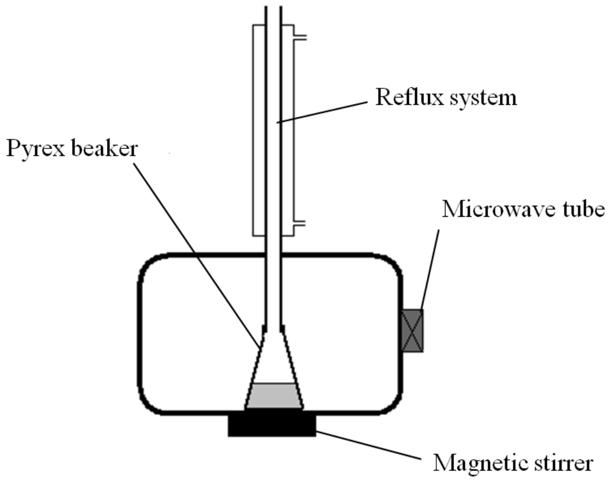

Fig. 1. Experimental setup for synthesis of titania nanotubes.

ous solution being maintained constant during the heat-treatment process under a boiling reflux condition.

The treated specimen was washed thoroughly with distilled water and 0.1M HCl and then distilled water. After filtrating and drying at room temperature, the product was investigated by using scanning electron microscopy (SEM). For the transmission-electron microscopy (TEM) observation, after calcining at 450 °C, the product was ultrasonically dispersed in ethanol and a drop of this solution was then placed onto a holey carbon film supported on a copper grid.

To evaluate the photocatalytic activity, we conducted a photo-oxidation experiment of methylene blue in the presence of our TiO_2 nanocrystals and Degussa P-25, which is the most popularly used TiO_2 aided photocatalysis. For an accurate comparison of photocatalysis, 20 mg of each type of TiO_2 nanocrystal was added to 100 ml of aqueous methylene blue and stirred for 15 minutes. Two-batch reactor systems including 200 ml beakers were irradiated with ultraviolet radiation by using one UV 15 W fluorescent tube (λ = 254 nm) positioned 5 cm above the beakers. After a 30-min irradiation, 20 ml of both samples were pipetted out and kept in the dark. The irradiation was finished in 60 minutes. All samples were centrifuged and investigated by taking them UV-Vis absorption spectra.

III. RESULTS

Figure 2(a) shows the X-ray diffraction (XRD) pattern of the starting anatase TiO_2 powder (Merk). Figure 2(b) shows that a small amount of the rutile phase is observed in the XRD pattern of TiO_2 nanotubes prepared by using microwave assisted washing, filtrating, drying and calcining at 450 °C for 2 hours. Wenzhong Wang *et al.* [2] concluded from their synthesis conditions for titania

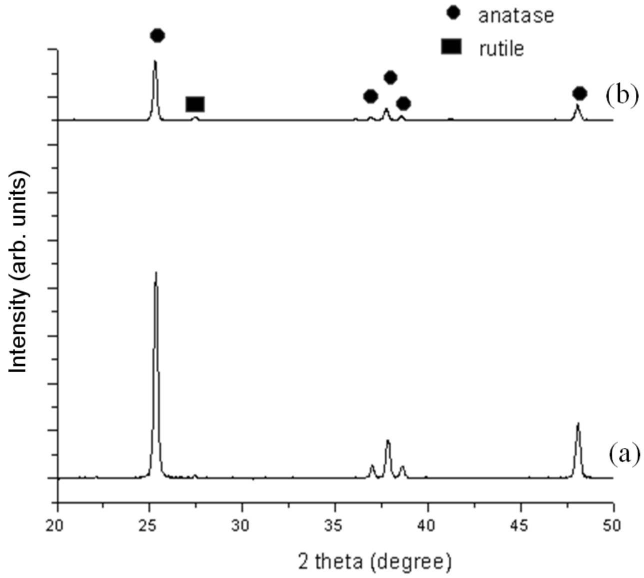

Fig. 2. XRD patterns of (a) the starting TiO_2 powder and (b) the TiO_2 nanotubes after calcining at 450 °C for 2 hours.

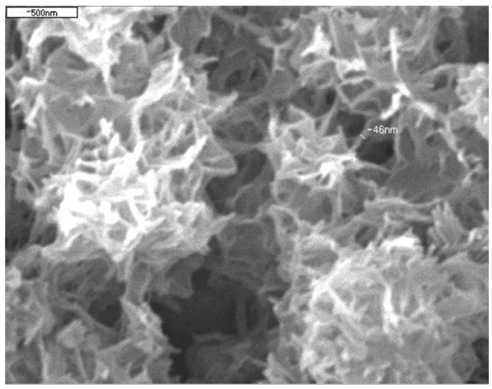

Fig. 3. SEM image of a sample after washing, filtrating and drying at room temperature.

nanotubes that there were no phase transfomations from the starting material even thought the sample had been calcined at 500 °C for 5 hours, but in this study, the titania nanotubes prepared by using a microwave assisted method are anatase TiO_2 and a small amount of rutile TiO_2.

Figure 3 shows that lamella structures were observed. From the figure, we can see that the lamella structures roll up to form cylindrical structures. This result agrees with the explanation of the nanotube formation mechanism in Refs. 2 and 3.

For the TEM observation of the sample after cacining at 450 °C for 2 hours, the calcined sample was ultrasonically dispersed in ethanol and a drop of this solution was then placed onto a holey carbon film supported on a copper grid. Figure 4 is a TEM image showing nanotubes with diameters from about 20 nm to 40 nm and

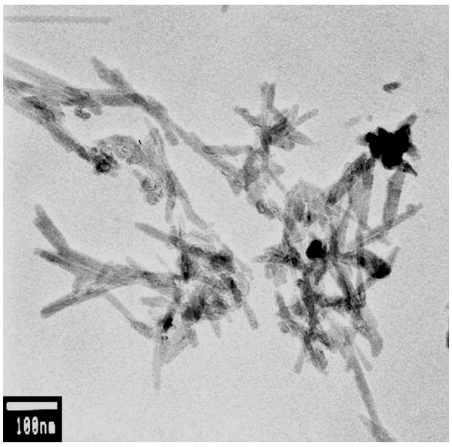

Fig. 4. TEM image of the sample after calcining at 450 °C for 2 hours.

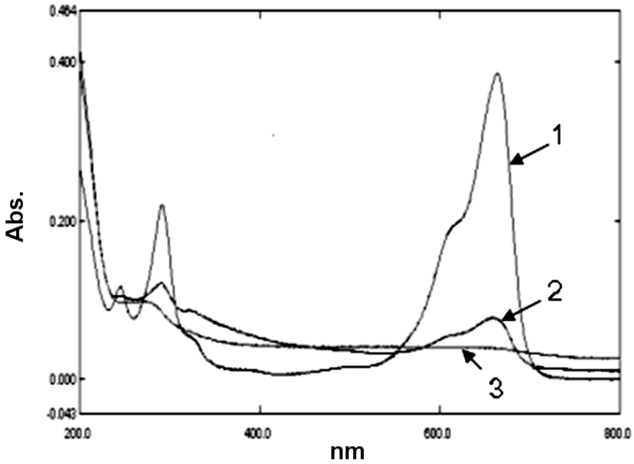

Fig. 5. UV-Vis absorption spectra of methylene blue irradiated for 30 minutes: 1- starting methylene blue without TiO_2, 2- methylene blue in the presence of Degussa P-25 and 3- methylene blue in the presence of our titania nanotubes.

with lengths ranging from approximately 0.1 μm to 0.5 μm. The specific surface area was calculated using the BET model and was found to be 52 m^2/g.

Methylene blue is commonly used as dye pigment in textile industries. Therefore, it is the most common contaminants in industrial wastewater. It is not easy to remove this compound because of its high stability and solubility in water. In this study, the photodecomposition of methylene blue was investigated by using our titania nanotubes and Degussa P-25. The analysis of the decomposition of methylene blue was evaluated by UV-Vis spectra from a Shimazu 2450 spectrophotometer. Figure 5 shows the methylene blue degradation of our titania nanotubes (3) and Degussa P-25(2) after irradiation for 30 minutes. As seen from Figure 5(3) the titania nanotube sample showed complete dye degradation (specific peak at 664 nm) in 30 min. The rate of degradation was found to be higher in the Degussa P-25 sample. Figure 6(3) shows that the decomposition of methylene blue is complete in the present of titania nanotubes after irradiation for 90 minutes, but there is still a little peak at 260 nm in the present of Degussa P-25 after irradiating under the same condition.

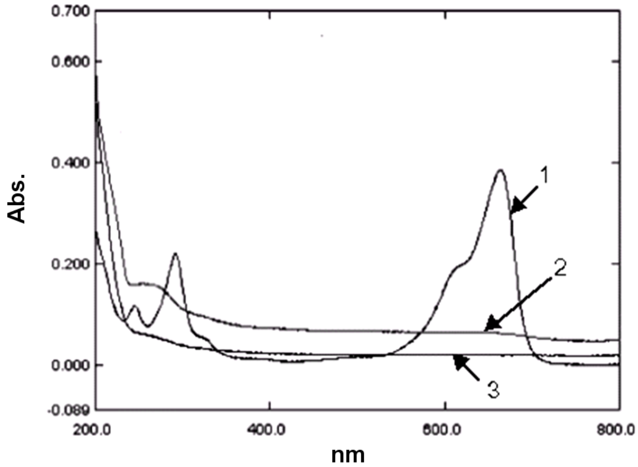

Fig. 6. UV-Vis absorption spectra of methylene blue irradiated in 60 minutes: 1- starting methylene blue without TiO_2, 2- methylene blue in the presence of Degussa P-25 and 3- methylene blue in the presence of our titania nanotubes.

IV. CONCLUSION

We synthesized titania nanotubes by using a microwave-assisted reaction of TiO_2 particles and a NaOH solution. The prepared titania nanotubes showed higher photoactivity than commercial TiO_2-P25 for decomposition of methylene blue. The synthesis process of titania nanotubes is simple and easy to reproduce.

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