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Electrochemical synthesis of doped TNT as a nano photocatalyst for color degradation applications

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ABSTRACT

The preparation of high aspect-ratio TiO_2 nanotubes and their photocatalytic activity were demonstrated in this study. The high aspect-ratio TiO_2 nanotube thin films were produced by electrochemical anodic oxidation of Ti in chloride-containing electrolytes. Nanotubes were doped with different concentrations of ZnO particles through anodization. The catalytic behavior was evaluated under batch reactor with photo-degradation test of Red Dye. The experimental results collectively demonstrate the successful ZnO doping of the resultant nanotube layers with significant abundant OH groups on their increased surfaces. The nanotubes doped with high content combined with an anatase as a two phase semiconductor led to the formation of very active photocatalyst with highly surface reaction sites. In contrast, to the undoped TNT, its anatase/rutile phase ratios are increased. These effects could be attributed to the enhanced critical active-site density on the surface, which provides better photocatalytical properties.

Keywords: Photocatalyst; Titania nanotube; Microstructure; Electrochemical

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1. Introduction

Titania nanotubes are materials of increasing interest due to their excellent applications to photocatalyst [1], liquid solar cell [2], and electroluminescent hybrid device [3], hence considerable effort has focused on developing efficient routes to fabricate titania nanotubes of controllable dimensions. Titania nanotubes of different geometrical shapes and microstructures have been fabricated by various methods, such as sol–gel, anodization, electrodeposition, sonochemical deposition, and other methods involving the chemical treatment of fine titania particles [4–14]. Among the methods, TiO_2 nanotubes with diameters of 70–100 nm were produced a sol–gel processing [5]. Zhao et al. [8] fabricated titanium oxide nanotube arrays by anodic oxidation, which the nanotubes had an inner diameter of 100 nm and the length of 200 nm. Kasuga et al. [6] reported the first evidence that titanium oxide nanotubes with the diameter of 8 nm and length of 100 nm could be obtained via chemical treatment. Zhang et al. [15] got much longer nanotubes, which is about 500 nm long and the diameters about 12–18 nm with the ultrafine rutile phase nanoparticles in size of 7.2 nm by chemical treatment.

Titanium dioxide (TiO_2) as a photocatalyst for degrading organic pollutions has attracted much attention because of its various advantages [16]. Unfortunately, the technological use of TiO_2 is limited by its wide band gap (3.2 eV for anatase), which requires UV light irradiation to obtain its photocatalytic activity. Because UV light only accounts for a small fraction (5%) of the Sun's energy compared to visible light (45%), any

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attempt making TiO_2 absorb effectively will have a profound positive effect on its photocatalytic performance. The morphology and additives are two main way to increase TNTs photocatalytic activities. ZnO has been conceived as a significant candidate that was reportedly known to be more efficient than TiO_2 in photooxidation of organic compound [17–19]. The band gap energies of ZnO and TiO_2 are similar to each other (approximately 3.2 eV). Therefore, some techniques have been adopted to fabricate nanostructured ZnO/TiO_2 composite.

In this work, we report a two-step route to fabricate ZnO/TiO_2 nanotube composite film by anodic oxidation and hydrothermal process. The crystallographic structure, microstructure, chemical composition and optical property of the samples are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV–Vis spectroscopy.

2. Methods

ZnO/TiO_2 nanotube composite film was synthesized through anodic oxidation and hydrothermal process. Firstly, the highly ordered TiO_2 nanotube was grown on the titanium foil by potentiostatic anodization using a platinum sheet as a counter electrode. The electrolyte was 1 M $(NH_4)_2SO_4$ with the addition of small amounts of 0.1 M NH_4F. The applied anodic potential was initially ramped from 0 to 20 V at a rate of 1 V/min and then held constant at 20 V for 4 h. The resulting sample was then calcinated at 773 K for 1 h with a heating/cooling rate of 2 °C min^{-1} and annealed to room temperature.

Then synthesis of ZnO/TiO_2 nanotube composite was completed on TiO_2 nanotube substrate through hydrothermal method. A typical synthesis process was given by Liu Jinping and coworkers, the TiO_2 nanotube film was suspended in 100 ml of aqueous solution containing 0.3 M $NH_3 \cdot H_2O$ and 0.02 M zinc acetate in a sealed Teflon lined stainless autoclave followed by heating at a constant temperature of 120 °C for 24 h. After the reaction, the products were thoroughly washed and dried in air. Other chemicals used in the experiments were analytical grade. X ray diffraction (XRD; SIEMENS D500; CuK_α), used to identify the crystalline size by means of the Scherrer's equation, the rutile and anatase phases was determined by using the (101) reflection of anatase and the (110) reflection of rutile. The specific surface area of the semiconductors was measured by the BET using N_2 as adsorbed gas. Microstructure was analyzed by the scanning electron microscopy (SEM, LEO 360, UK) operating at 20 kV.

The photocatalytic activity of TiO_2 nanotubes were tested on the decolorization of Acid Red 27 solution. About 1 cm^2/1 mg TiO_2 nanotube arrays film was immersed into a 40 ml aqueous AR 27 solution with a concentration of 8 mg/l in a double-decker quartz reactor. The reaction temperature was controlled by constant temperature circular water. A 300 W UV lamp was used as the irradiation source, and the distance between the light source and the TiO_2 nanotube arrays film was 10 cm. The change of dye concentration as a function of the irradiation time was measured by a spectrophotometer (UV-2500, Shimadzu, Japan).

3. Results and discussion

The properties of synthesized samples are controlled by the hydrothermal and anodization conditions like temperature, duration of the synthesis and the type of salt used. The processing conditions, particle size, phase composition (derived from XRD) and specific surface area (derived from BET) of various nanosize powders are given in Table 1. These samples used to test photocatalytic properties with various phases ratios, crystalline size, and reaction time.

The samples which are named: "A", prepared by routine hydrothermal method. These samples were prepared by adding 100 ml of $TiCl_4$ solution to 800 ml of distilled water at pH 1.5 achieved by means of HCl and aged to reach a yellowish homogeneous transparent solution. 10 vol. % of triethylamine (TEA) were then added dropwise to 100 ml of the Ti-solution till pH values reached 9 and added 0–10 mol/l zinc acetate. The obtained white precipitate suspension was then placed in a Teflon recipient inside of stainless steel autoclave. Hydrothermal treatment was performed at two temperature and time conditions: 120 °C for 24 h (1) and 150 °C for 6 h (2). At these temperatures, the working pressures are 198.48 and 475.72 kPa, respectively. TiO_2 powders

Table 1
The name, preparation method, additives content and shape of samples

Sample name	Preparation routs	ZnO (mol/l)	Shape
A1	Hydrothermal	0	Nano powder
A2	Hydrothermal	0	Nano powder
AZ1	Hydrothermal	10	Nano powder
AZ2	Hydrothermal	10	Nano powder
P25	–	0	Nano powder
PZ1	Hydrothermal	10	Nano powder
T1	Anodization	0	Nano tube
TZ1	And./hyd.	5	Nano tube
TZ2	And./hyd.	10	Nano tube

Table 2
Phase composition and structural properties of samples synthesized by different methods

Sample	Anatase/rutile/ ZnO (mol%)	Crystalline size (nm)	Surface area (m^2/g)
A1	60/40/0	20	45
A2	60/40/0	50	25
AZ1	65/25/10	30	40
AZ2	65/25/10	50	20
P25	75/25/0	20	50
PZ1	70/20/10	25	40
T1	70/0/0	20	80
TZ1	80/0/5	20	85
TZ2	85/0/10	20	85

were obtained by centrifugation and repeatedly washing, filtered and dried at 120 °C for 6 h.

The samples which are named: "P", prepared by P25 Degussa Co. powder or added ZnO according to "A" samples.

The samples which are named: "T", prepared by anodization or anodization and hydrothermal methods.

Utilizing Scherrer formula ($d = k\lambda/B \cos \theta$, where d represents the average crystallite size of the particles, λ is the wavelength of Cu Kα, 1.54056 Å, B the full width at half maximum (FWHM) intensity of the peaks in radian, θ (1 0 1) , (1 1 0) are Bragg's diffraction angle and k is a constant usually equal to ~0.9), the average crystallite size of the particles was calculated and shown in Table 2. The results indicate that anodized samples have smaller crystalline size and samples with additives have been broaded the peak width at half maximum (FWHM) and the molar ratio of anataze have been increased. The hydrothermal process is time consuming and diffusion and reaction in high temperature and pressure increases the stable phase. The comparison between titania nanopowder and nanotube is not correct because their preparation routs and conditions were different.

Table 2 shows the specific surface area of samples which is related to powders size and agglomeration of powders. The effect of two parameters is observed, the additive [14] and process [15,16]. The sample with ZnO has lower surface area than pure ones in nanopowders but has higher surface area in nanotubes. TNT samples have higher surface area than powders because of their specific morphology.

Fig. 1 illustrates SEM images of samples synthesized at different condition with different additives. The images show that as-synthesized powders have different particle morphology. The powder synthesized without anodizing treatment consists of spherical particles with different particle size. The anodized samples have tube-like morphology and adding ZnO particles is clear in the TZ1 and TZ2 samples. The size and surface area of samples have good correlation with XRD and BET results.

Fig. 2 shows the effect of semiconductors on photodegradation of AR 27. It can be seen from the graph that the order of photocatalytic activity of powders for AR27 is TZ2 > TZ1 > T1 and AZ > A, it is not correct to compare powders and tubes. According to previously papers on AOP, the photocatalytic efficiency of TiO_2 depends on its phases, and crystalline size [20]. This variability has been attributed to difference in the rate of recombination, adsorptive affinity, or band gap between the phases of TiO_2. The rutile phase (R) implies a lower mobility of charge-carriers than anatase and electron hole pairs recombined without contributing in reaction. The anatase has a larger band gap (3.2 eV) than rutile (3.0 eV) and it is more active than rutile in UV irradiation. The Fermi level of anataze is higher than rutile, in mixed rutile and anatase sample (P) generally enhances the photocatalytic activity as seen in Fig. 2.

The surface of powder is the most effective structural parameter of catalyst, because photocatalysis is an interfacial reaction. Thus, a higher specific surface area induces a higher number of accessible active sites. It has other effects on the e^-/h^+ recombination time band gap energy, penetration of light, consequently, photocatalyst reactivity. The tubes have smaller crystalline size, more surface area and better activity than the powders with similar condition. The TiO_2 nanotube adsorbs over a larger fraction of UV spectrum than TiO_2 powder and degrades better than single phase titanium dioxides.

4. Summary

In this study, different type of semiconductor nanopowder and nanotubes were prepared by hydrothermal and anodization methods. It was shown that, nanotubes have more surface to volume ratio and more anatase phase. By doping ZnO to powders, the anatase formation increased but the surface area decreased. The optimization microstructure and phases ratio by doping and preparation route the photo activity of semiconductor increased.

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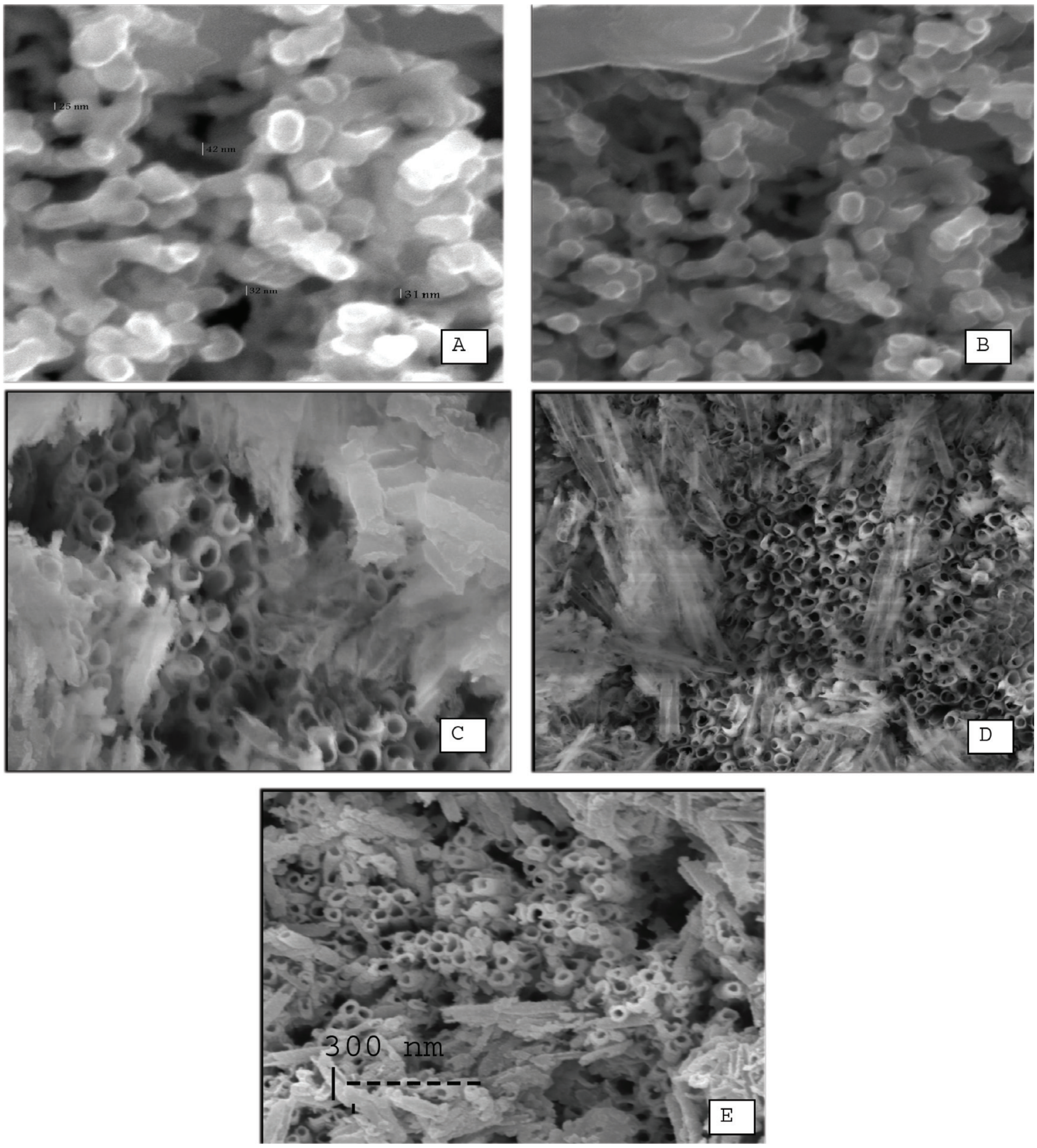

Fig. 1. SEM images of samples synthesized at different conditions: (a) AZ2, (b) AZ2, (c) TZ2, (d) TZ1, and (e) T1. In Fig. 1(e) the scale bar is not completed.

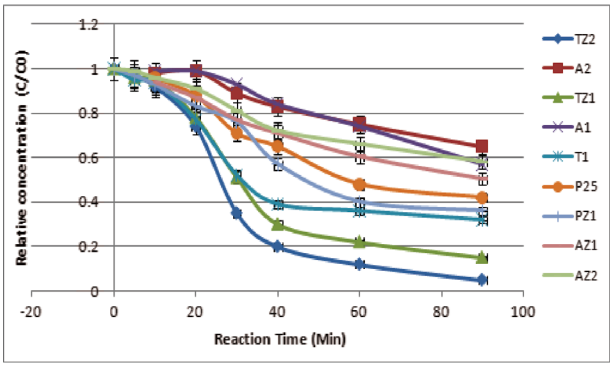

Fig. 2. Degradation of AR 27 in various semiconductors (A1, A2, AZ1, AZ2, P25, PZ1, T1, TZ1, TZ2).

References

[1] M.R. Hoffmann, S.T. Martin, W. Chot and D.W. Bahnemann, Chem. Rev., 95 (1995) 69–96.
[2] A. Hagfeldt and M. Gratzel, Chem. Rev., 95 (1995) 49–68.
[3] M. Thelakkat, C. Schmitz and H.W. Schmidt, Adv. Mater., 14 (2002) 577–589.
[4] D.W. Gong, C.A. Grimes, O.K. Varghese, Z. Chen, W.C. Hu and E.C. Dickey, J. Mater. Res., 16 (2001) 3331–3334.
[5] P. Hoyer, Langmuir, 12 (1996) 1411–1413.
[6] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino and K. Niihara, Langmuir, 14 (1998) 3160–3163.
[7] Q.H. Zhang, L. Gao, J. Sun and S. Zheng, Chem. Lett., 31 (2002) 226–230.
[8] J.L. Zhao, X.H. Wang, R.Z. Chen and L.T. Li, Solid State Commun., 134 (2005) 705–710.
[9] M. Adachi, Y. Murata, M. Harada and S. Yoshikawa, Chem. Lett., 29 (2000) 942–943.
[10] Y. Zhu, H. Li, Y. Koltypin, Y.R. Hacohen and A. Gedanken, Chem. Commun., 24 (2001) 2616–2617.

[11] H. Imai, Y. Takei, K. Shimizu, M. Matsuda and H. Hirashima, J. Mater. Chem., 9 (1999) 2971–2979.

[12] S.L. Zhang, J.F. Zhou, Z.J. Zhang, Z.L. Du and A.V. Vorontsov, Chinese. Sci. Bull., 45 (2000) 1104–1106.

[13] G.H. Du, Q. Chen, R.C. Che, Z.Y. Yuan and L.M. Peng, Appl. Phys. Lett., 79 (2001) 3702–3704.

[14] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino and K. Niihara, Adv. Mater., 11 (1999) 1307–1311.

[15] Q.H. Zhang, L. Gao, S. Zhang and J. Sun, Acta. Chim. Sinica, 60 (2002) 1440–1442.

[16] A.L. Linsebigler, G.Q. Lu and J.T. Yates Jr., Chem. Rev. 95 (1995) 735–758.

[17] F. Xu, Z.Y. Yuan, G.H, Du, M. Halasa and B.L. Su, Appl. Phys. A-Mater., 86 (2007) 181–185.

[18] S. Polarz, F. Neues, M.W.E. Van den Berg, W. Grunert and L. Khodeir, J. Am. Chem. Soc., 127 (2005) 12028–12045.

[19] C.L. Hsu, S.S. Yang, Y.K. Tseng, I.C. Chen, Y.R. Lin, S.J. Chang, et al., J. Phys. Chem. B, 108 (2004) 18799–18803.

[20] M. Anpo and M. Takeuchi, Int. J. Photoenergy, 3 (2001) 89–94.