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Photocatalytic Properties of Mixed-Crystalline Titanate Nanotubes Prepared by Hydrothermal Reaction

YANLI WANG, JIA WANG, QIUXIA WU, SHUN TAN, HUIJIAO GUO, MINGHONG WU and ZHENG JIAO*

Institute of Nanochemistry and Nanobiology, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, P.R. China

*Corresponding author: Tel/Fax: +86 21 66135275; E-mail: zjiao@shu.edu.cn

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In this paper, mixed-crystalline titanate nanotubes (TiO_2-NTs) are grown by hydrothermal reaction in a 10M NaOH aqueous solution for the application in photocatalysis. The morphology and structure of prepared samples are characterized by XRD, SEM, TEM and BET. TiO_2-NTs have uniform shapes. XRD analysis indicates that the mainly phase are anatase TiO_2 and rutile TiO_2. The photocatalytic properties of TiO_2-NTs were investigated. It is found that the TiO_2-NTs with mixed crystal structures exhibited improved photocatalytic activity in comparison with rutile TiO_2 nanoparticle and the commercial Degussa P-25. The photocatalytic mechanism of TiO_2-NTs was also discussed.

Key Words: Titanate, Nanotubes, Photocatalytic activity.

INTRODUCTION

In the past decade, many efforts have been taken on the semiconductor photocatalysts for their environmental applications in air purification, water disinfection and hazardous water remediation[1-3]. Titanium(IV) oxide has been extensively applied as a photocatalyst due to its high stability and semiconductor abilities capable of generating charge carriers by absorbing energy[4]. With the decrease of particle's size, the photocatalytic activity of titania increased dramatically, which is probably due to the significant particle-size effect and the large specific surface[5-7]. TiO_2 nanoparticles with large surface area shows highly photocatalytic activity when it is used as a photocatalyst[8-10]. Recently, much effort has been directed at obtaining TiO_2 nanotubes with a large surface area and high photocatalytic activity. TiO_2 nanotubes with diameters of 70-100 nm were produced using the sol-gel method reported by Kasuga *et al.*[11]. High-purity nanotubes are formed depending on the treatment temperature and holding time[12]. Most of the titanium dioxide nanoparticles used as photocatalysts is single crystalline, but many researchers reported that the photocatalytic activity of anatase TiO_2 can be improved by mixing other nanostructures, which is well-known by mixed crystal effect[13]. The frequently used high activity P-25 is a good example, which is composed of approximately 80 % anatase and 20 % rutile TiO_2[14]. In this paper, the titanate nanotubes (TiO_2-NTs) were grown by hydrothermal reaction. TiO_2-NTs have a good photocatalytic activity compared with rutile TiO_2 nanoparticle and P-25. The photocatalytic mechanism of the TiO_2-NTs was discussed based on experimental results.

EXPERIMENTAL

Preparation of titanate nanotubes: All chemical reagents were analysis pure, supplied by Sinopharm Chemical Reagent Co. Ltd. The rutile TiO_2 powder of 80-100 nm was provided by Professor Shi Liyi from Shanghai University (purity ≥ 95 %, coated with SiO_2, water dissolvable). TiO_2-NTs were prepared as follows[11]: 200 mg TiO_2 powder was added in 140 mL of 10M NaOH solution and ultrasonic dispersed for 0.5 h. The mixture was placed in a 200 mL Teflon-lined autoclave; the autoclave was heated to 150 ºC for 35 h. After that, the mixtures were centrifuged at 8000 rpm. Precipitate were separated and washed with 0.5M HCl solution and distilled water several times until the pH of the rinsing solution reached 6.5. The washed precipitate was dried at 60 ºC overnight to get TiO_2 nanotube samples.

Photocatalytic activity: The photocatalytic activity of TiO_2-NTs was performed by measure the photocatalytic discolourization of methyl orange aqueous solution at ambient temperature using SGY-IB multifunctional photochemical reaction instrument (Stonetech Eec LTD., Nanjing). A 300 W high pressure mercury lamp was used to provide the ultraviolet light and a 350 W xenon lamp to simulate the visible light irradiation condition at room temperature.

RESULTS AND DISCUSSION

The structure of TiO_2-NTs was analyzed with a D/max-2550 X-ray diffraction (XRD). In Fig. 1 it can be found that main crystal structure is anatase, but still a certain amount rutile TiO_2 exists. It is reported that TiO_2 crystals become amorphous while treated in NaOH aqueous, because the Ti-O bond was broken and Ti-O-Na or Ti-OH bonds were arbitrarily formed. TiO_2-NTs were generated after the treatment of TiO_2 crystals in acidic solution. Both rutile-type and anatase-type TiO_2 crystals can be used as starting material to subjected to hydrothermal treatment in NaOH aqueous[11,15]. Several characteristic peaks correspond to the crystal structure of $H_2Ti_3O_7$ ($Na_2Ti_3O_7$) and $Na_xH_{2-x}Ti_3O_7$ were also observed. By controlling the conditions of acid treatment, the amount of residual Na^+ ions changes and it is possible to form either titania or titanate nanotubes[16]. Depending on the conditions of the formation process and type of residual Na, several types of crystal, such as TiO_2, $H_2Ti_3O_7$ and $Na_xH_{2-x}Ti_3O_7$ were reported to be deposited[17-19]. After treated with 400 ºC for 5 h, only TiO_2 nanotubes exists.

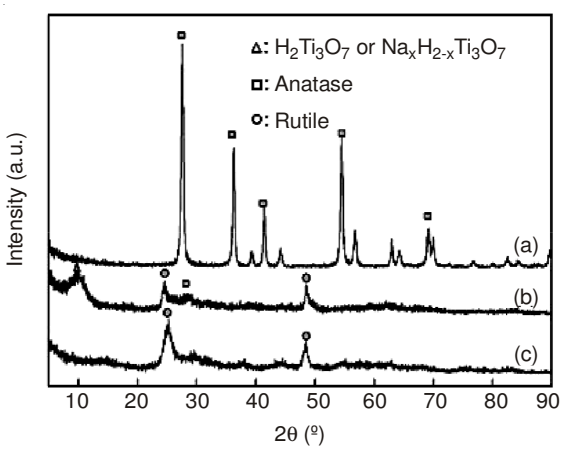


Fig. 1. X-Ray diffraction patterns for samples (a) the rutile-type TiO_2 nanoparticle. (b) titanate nanotubes obtained in the 10M NaOH aqueous for 35 h at 150 ºC. (c) prepared titanate nanotubes after calcined for 5 h at 400 ºC

The morphology of TiO_2-NTs were observed by JEM-2010 transmission electron microscopy, results were shown in Fig. 2. It was reported that TiO_2-NTs are formed by the curl of nanobelts[3]. In this paper, the morphology of nanotubes or nanobelts was substantially affected by changing the hydrothermal treatment temperature and holding time. At lower treating temperature 110 ºC and shorter holding time about 15 h, the unreacted TiO_2 particles still exists (Fig. 2a). At higher temperature (170 ºC) and prolonged duration (72 h), there are abundant nanobelts (Fig. 2b). Numerous nanotubes were found (Fig. 2c) when the powders were treated with 10M NaOH for 35 h at 150 ºC. After being calcined at 400 ºC for 5 h, TiO_2-NTs had no obvious change expect the length is comparatively shorter (Fig. 2d). The shape of the single TiO_2 nanotube was observed by Shimazu SPM-9600 atomic force microscopy and JSM-670 scanning electron microscopy (Jeol) (Fig. 3). TiO_2-NTs has uniform inner and outer diameters along their length (Fig. 3a), a large amount of nanotubes had a narrow

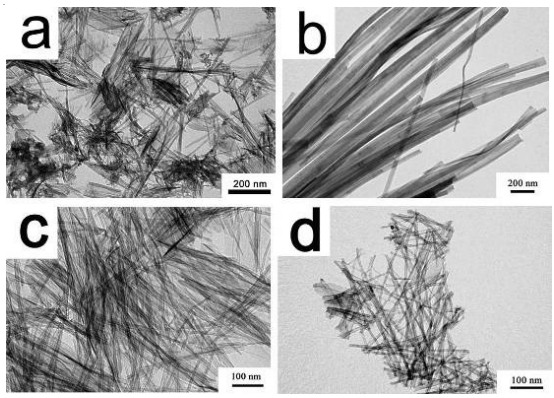
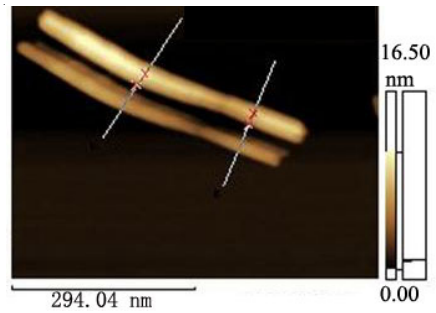
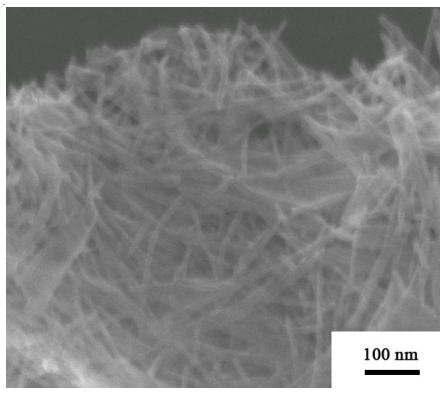


Fig. 2. TEM images of the TiO_2-NTs. (a) 15 h at 110 ºC; (b) 72 h at 170 ºC; (c) 35 h at 150 ºC; (d) calcined for 2 h



(a)



(b)

Fig. 3. SEM and AFM image of TiO_2-NTs. (a) AFM image; (b) SEM image

size distribution with an average diameter of 4-5 nm and several hundreds nanometers in length (Fig. 3b). Specific surface areas of TiO_2-NTs were measured in ASAP 2020M + C nitrogen adsorption apparatus (Micromeritics Instruments Company, USA). The nitrogen desorption/adsorption isotherms (Fig. 4) showed the TiO_2-NTs have the type IV isotherm with type H_3 hysteresis loop according to BDDT classification with high BET surface area of 323 m^2/g. The higher specific surface area of the nanotube is expected to enhance the photocatalytic activity of titanate nanotubes.

The photocatalytic activity of theTiO_2-NTs was evaluated by photocatalytic oxidation of methyl orange aqueous solution. TiO_2-NTs showed high photocatalytic activity in Fig. 5. Absorption peak gradually decreased with increasing irradiation time which indicates the relationships between photocatalytic activity of TiO_2-NTs and irradiation time in different irradiation conditions.

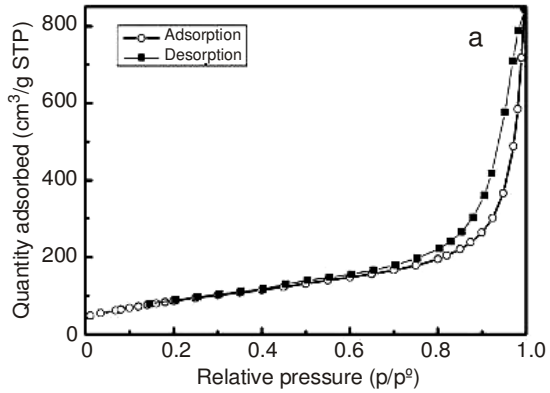


Fig. 4. Nitrogen adsorption-desorption isotherms of TiO_2-NTs

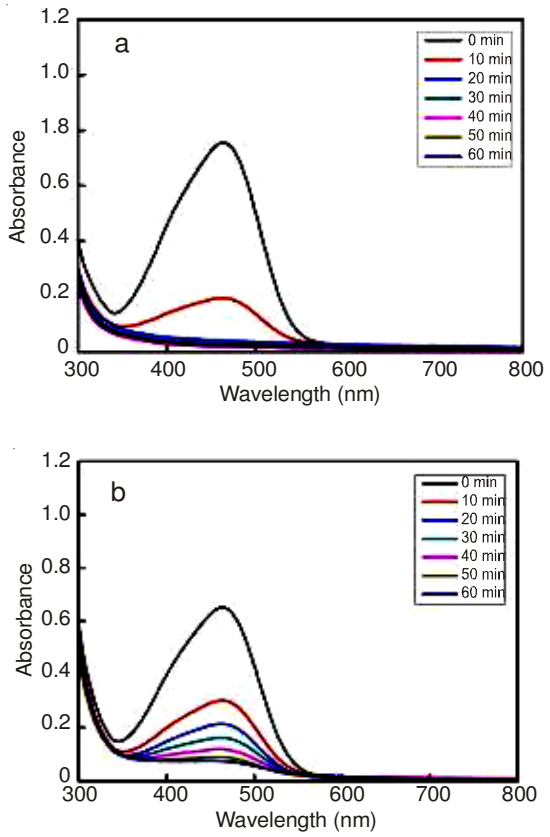


Fig. 5. Absorption spectra of the methyl orange aqueous solution (a) in UV irradiation conditions; (b) in visible light irradiation conditions

TiO_2-NTs exhibited decent photocatalytic activity for the photocatalytic oxidation of methyl orange. Under the UV irradiation, TiO_2-NTs showed high photocatalytic activity. Concentration of the methyl orange decreased rapidly with increasing UV irradiation time. It is reported that the higher radiation energy was discharged, the more efficiency was degraded[20]. After UV irradiation without filter for 20 min, the absorption peak of the aqueous solution of methyl orange was very weak. Moreover, experimental observation indicated that the colour of the aqueous solution of methyl orange changed from orange to nearly transparent after UV irradiation for 20 min, indicating a nearly complete degradation of methyl orange[21]. By comparing the Fig. 5 (a) and (b), it is observed that the photocatalytic ability of TiO_2-NTs in the UV irradiation conditions is better than visible light irradiation.

For comparison, the photocatalytic activity of commercial photocatalyst P25 was also tested under identical conditions. Fig. 6 also shows that the relationships between C_t/C_0 and photocatalytic reaction time under the different irradiation condition. From Fig. 6, it can be seen that photocatalytic degradation rates of the methyl orange decreased with the prolongation of the photocatalytic reaction time. The prepared samples have better photocatalytic effect than the commercially available Degussa P-25 in ultraviolet light exposure. TiO_2-NTs has large BET surface area of about 323 m^2/g and therefore shows an extremely high absorption capacity, which is beneficial to the collection of the organic pollute molecules like those of methyl orange. Under UV light irradiation, the methyl orange molecules absorbed on the surfaces of nanotubes and the produced electrons were transferred to TiO_2-NTs. Moreover, maxed-crystalline types play a crucial role in improving the photocatalytic activity of TiO_2-NTs.

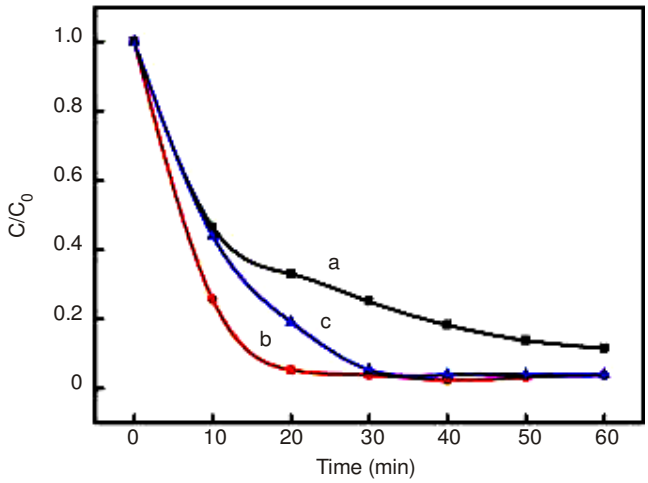


Fig. 6. (C_t/C_0) *versus* time curve for the methyl orange aqueous solution. (a) TiO_2-NTs as the photocatalyst: under visible light irradiation conditions; (b) under UV irradiation conditions; (c) the commercial photocatalyst P25 under UV irradiation conditions

Conclusion

In summary, maxed-crystalline titanate nanotube were prepared through hydrothermal treatment by controlling the conditions of treatment. Compared with Degussa P25, a widely used commercial TiO_2, TiO_2-NTs exhibited a much improved photocatalytic activity for the photocatalytic oxidation of methyl orange. This could be attributed to the fact that the former had larger specific surface area, higher pore volume and in the maxed-crystalline.

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