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Vanadium Titanate Nanotube Arrays for Photocatalytic Application

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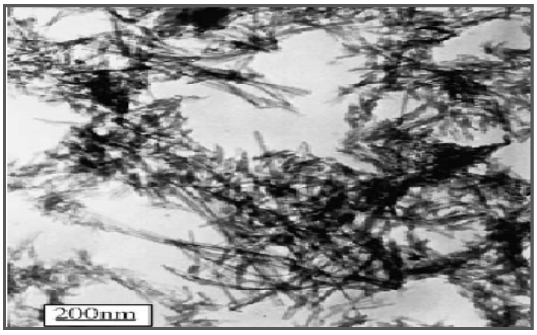
ABSTRACT

Titanate or vanadium nanocomposites consisting of titanate and vanadium oxide nanoparticles nanotubes were successfully prepared via a hydrothermal method. The samples were characterized by means of X-ray diffraction (XRD) and transmission electron microscopy (TEM). The activity of the nanocomposites was examined by photocatalytic depolarization of Remazole B under visible light irradiation. It is found that the nanocomposites exhibited a much improved photocatalytic activity in comparison with titanate nanotube, and anatase TiO_2 *nanoparticle.*

Graphical Abstract



TEM image of titnate nanotubes

Keywords: Hydrothermal cell, Vanadium/titanium oxide, Photocatalytic depolarization

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INTRODUCTION

In Recent years interest has been focused on the use of semiconductor materials as photocatalysts for decomposition of pollutants in wastewater effluent from industrial manufacturers and normal households, and for the removal of organic species from aqueous or gas phase. Moreover, photocatalysts can be utilized for the decomposition of inorganic compounds, and removal of trace metals as well as destruction of viruses and bacteria. It can be used also to decompose natural organic matter, which has much environmental and industrial impact. It has the advantage not leaving toxic by product or sludge to be disposed. This technology also might be useful for water pre-treatment of desalination process especially with reverse osmosis technique.

Harmful pollutants, especially dyes and aromatic hydrocarbons, are typical pollutants emitted from industrial and domestic activities [**1**]. Among the technologies developed for the treatment of harmful pollutants, the photocatalytic oxidation process using heterogeneous photocatalysis is regarded as a promising technology to decompose harmful pollutants to final non-toxic products. Titanium dioxide has been proved to be a very efficient photocatalyst for the degradation of harmful pollutants in water and air because of its high stability, nontoxicity and inexpensiveness [**2**].

Many researchers have proven that nano-structured TiO_2 has the higher photochemical reactivity than that of bulk TiO_2 particles [**3-5**]. Advances in the nanoscale technology facilitated the synthesis of highly ordered nano-structured materials. In recent years, considerable efforts have been focused on new techniques for synthesizing titania with a unique nanoarchitecture consisting of vertically oriented, immobilized, highly ordered and high-aspect ratio nanotubes such as hydrothermal treatment [**6-7**], template synthesis [**8**], and anodic oxidation [**9**]. However, the photocatalytic oxidation technology involving TiO_2 photocatalysts always suffers from the difficulties of separating suspended TiO_2 nanoparticles from aqueous solution as well as low quantum yield caused by the rapid combination of photogenerated electrons and holes [**10**]. In comparison, the immobilized TiO_2 film on a solid carrier by spin [**11**] or dip-coating [**12**] methods is more desirable in its photocatalytic application, whereas it still has defects such as poor adhesion of TiO_2 film to supporting carriers [**13**] and low surface area of supported TiO_2 photocatalyst exposed to solution. Accordingly, TiO_2 nanotube-array film growing on Ti substrate by anodization process appears a progress compared to immobilized TiO_2 film. As an integrative electrode, nanotubular TiO_2 film possesses good mechanical adhesion strength and electronic conductivity, and also provides greater surface area for photochemical action. Particularly, the tubular structure makes the regions both inside and outside the tubes (intertubular region) easily accessible to the redox couples in the electrolyte and also offers the ability to influence the absorption and propagation of light by precisely designing and controlling the geometrical parameters of the architecture [**14-15**] where, the thickness and morphology of such a nanotubular TiO_2 film could be easily controlled by tailoring the anodization conditions such as applied potential, anodization duration and electrolyte composition [**16-21**]. Ruey-an Doong showed that one-dimensional (1-D) nanotubes are promising nanostructured materials for a wide variety of environmental applications. In this study, the 1-D titanate nanotubes (TNTs) were fabricated using an alkaline hydrothermal method and then calcined at various temperatures ranging from 200 to 600°C in air for 4 h for coupled removal of bisphenol A (BPA) and Cu(II) ion. The as-synthesized TNTs showed tubular structures with diameter of 8–10 nm and length of few µm. After calcination at 400–600°C, the well-crystallized anatase TiO_2 nanoparticles were produced on the tube walls to form titania/TNT nanocomposites, resulting in the decrease in specific surface area and the increase in isoelectric point. The as-synthesized and calcined TNTs have good Cu(II) adsorption capacity, and the maximum Langmuir adsorption capabilities decreased from 160 mg g^{-1} for as-synthesized TNTs to 35 mg/g for TNT-600, presumably due to the decrease in specific surface area. In addition, the calcined TNT showed a good photocatalytic activity towards BPA degradation when compared with the as-synthesized TNTs. The coexistence of Cu(II) ion and BPA exhibited the synergistic effect on the enhancement of photocatalytic activity of calcined TNTs. Electron spin resonance results indicated that the copper ion was first adsorbed onto the negatively charged TNTs, and then served as the electron trap to prolong to retention time of photo-generated radicals, resulting in the enhancement of photodegradation efficiency and rate of BPA by calcined TNTs [**22**]. The current investigations for photochemical properties of M-doped TiO_2 are mainly carried out using its powdery form. It is expected that combining small-sized anatase crystallite of M-doping TiO_2 with unique nanotubular structure would exhibit an improved photoactivity. To the best of our knowledge, however, there are no details reports so far regarding metal-doped TiO_2 nanotube arrays electrode and its photocatalytic characteristics.

MATERIALS AND METHODS

Synthesis of vanadium oxide/titanate composites nanotubes: Titanate nanotubes were prepared as reported in [23–24]. Anatase titanium dioxide (0.5 g) and 32 mL of a 10M KOH aqueous solution were mixed homogeneously in a Teflon-lined autoclave with a stainless steel shell, which, in turn, was placed in an baking oven at 200°C for 20 h. After cooling to room temperature naturally, the final white product was vacuum-filtered, neutralized with 1M HCl, washed with distilled water until the pH value of the filtrate was up to 7 and dried at 60°C for 5 h. Titanate nanotubes were obtained.

$V_2O_5{\cdot}nH_2O$ sols were synthesized according to an earlier publication [25]. This synthesis involved the dissolution of crystalline V2O5 (1 g) in a solution of hydrogen peroxide (50 mL, 30%). The system temperature was controlled at 0°C by ice-water bathing. The reaction led to a partial decomposition of the hydrogen peroxide and the formation of V(V) peroxo complexes [26], which also went with oxygen release and heat liberation. A bright orange solution formed after about 20 min (final pH $\approx$ 1.5), and then gradually turned into a red-brown gel after ca. 24 h. This sol had been proved to be $V_2O_5{\cdot}nH_2O$, while the amount of water depended on the experimental conditions. 0.1 g of titanate nanotubes were added to the $V_2O_5{\cdot}nH_2O$ sol (weight ratio titanate nanotubes:V_2O_5 = 1:10). The resulting brown mixtures were stirred for 24 h. Finally, the brown mixtures were removed into a Teflon-lined autoclave with a stainless-steel shell, maintained at 200 ◦C for about 48 h. The resulting black-green powders were washed with distilled water and ethanol until the filtrates were transparent, then dried at 60°C for 5 h. VO*x*/titanate-CNRs were obtained.

Characterization: XRD tests were performed on a powder diffractometer (Oxford, England) operating with Cu Kα radiation. SEM studies were performed on a scanning electron microscope (Schimadzu, Japan). TEM investigations were carried out on a Japanese microscope (Hitachi-600). EDAX was recorded on an energy-dispersive spectrometer (Link-200, Britain).

Photocatalytic activity: In order to investigate the photocatalytic activity of the samples, photo decolorization of Remazole B under visible light irradiation was carried out in the presence of nanocomposites at room temperature. A 300W halogen lamp as the visible light source was put in a cylindrical glass vessel with a recycling water glass jacket; meanwhile a cut-off filter was placed outside the water jacket to completely remove any radiation at wavelengths below 420 nm, thereby ensuring illumination by visible light only. Reaction suspension was prepared by adding 80 mg of sample into a 100 mL beaker containing 80 mL $\times 10^{-5}$ M RzB. Prior to illumination, the suspension was magnetically stirred for 30 min in dark to establish an absorption/desorption equilibrium of RzB. Subsequently, the dispersion containing RzB and photocatalyst was irradiated under visible light. At given intervals, 3 mL of the suspensions were extracted and subsequently centrifuged at a rate of 9000 rpm for 15 min. UV–Vis absorption spectra of the supernatant were then measured using a Perkin Elmer UV WinLab Lambda 35 spectrophotometer. For comparison, similar measurements were also carried out on as-prepared nanotube, and pure anatase and titanate nanoparticle.

RESULTS AND DISCUSSION

Figure 1a shows the XRD pattern of synthesized titanate nanotubes, which can be indexed to $H_2Ti_3O_7$ according to current structural investigations [27, 28]. We prefer to regard it as a kind of titanate nanotubes that might be described as $K_xH_{2-x}Ti_3O_7$ *(x* $\approx$ 00.27*)* according to our EDAX studies (Fig. 2a). The patterns of VO*x*/titanate-CNRs (Fig. 1b) indicate the presence of two phases, titanate and a vanadium oxide. According to JCPDS X-ray powder data files (28-1433), the powder XRD pattern of the vanadium phase indicates the vanadium oxides possess the structure of vanadium oxide hydrate ($V_3O_7{\cdot}H_2O$). The powder XRD pattern (Fig. 1b) can be readily indexed with orthorhombic symmetry. The lattice parameters are *a* = 9.34 Å, *b* = 17.0Å, *c* = 3.626 Å. The EDAX analysis is a micro analytical technique that utilized the characteristic spectrum of X-rays emitted by the specimen after excitation with high-energy electrons to obtain information about its elemental composition. In our paper, EDAX studies on VO*x*/titanate-CNRs (Fig. 2b) exhibit the existence of O, Ti and V. Moreover, the ratio (weight) of Ti/V is about 1:6.

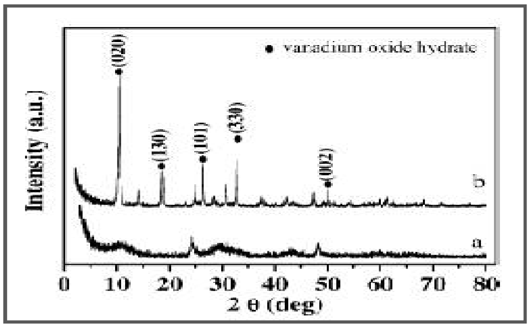

Figure 1. XRD patterns of titnate nanotubes (a) and VO_x/TiO_2-CRNs (b)

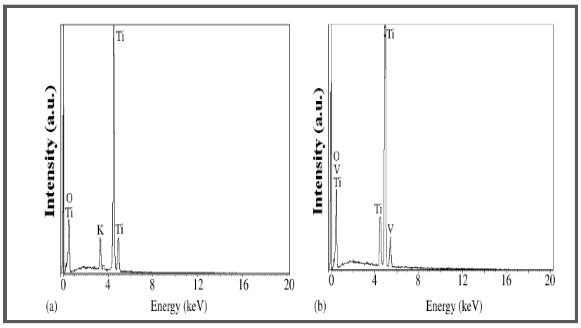

Figure 2. EDAX spectra of titnate nanotubes (a) and VO_x/TiO_2-CRNs (b)

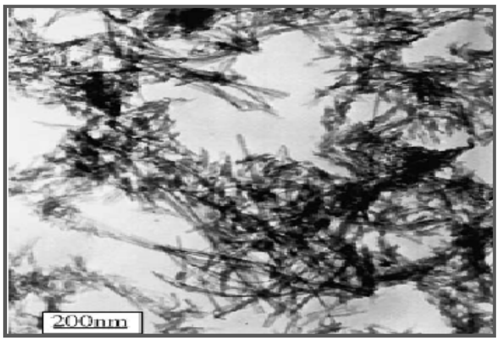

Figure 3. TEM image of titnate nanotubes.

A TEM image for the structure of titanate nanotubes is shown in Figure 3, the nanotubes are better revealed. The morphology of VO*x*/titanate-CNRs is shown in Figure 4a and 4b, while the final VO*x*/titanate-CNRs consist mainly of nanorods (shown in Figure 4c). We can see that VO*x*/titanate-CNRs are orderly grown together in the form of bundles and a good rigidity is expressed. The typical VO*x*/titanate-CNRs length is about 10 µm, but its length can range from 10 to 20 µm. The diameter ranges from 100 to 300 nm. Length and diameter of the VO*x*/titanate-CNRs depend on the preparation, such as the dimension of template material and reaction time. The VO*x*/titanate-CNRs have a black-green color, indicating some vanadium in a IV oxidation state because mixed-valent V (IV, V) oxides are generally black-green.

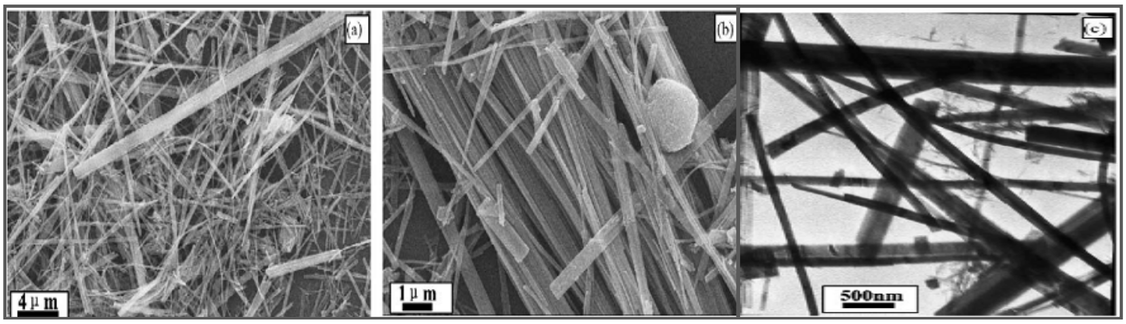

Figure 4. SEM (a, b) and TEM (c) of VO_x/TiO_2-CRNs.

Fig. 5 shows the normalized absorbance changes of all the solutions with irradiation time under visible light. Without any photocatalysts, RzB cannot be degraded by visible light, while the presence of the titanate, anantase and vanadium titanate nanocomposite, the normalized absorption of the solutions decreased with the prolonged irradiation time. From Fig. 5, it is clearly seen that RzB/composite system showed the minimum normalized absorbance after irradiation for 3 h, which means that the vanadium titanate nanocomposites showed the best photocatalytic activity in comparison with those of nanotubes, pure anatase nanoparticles, and titanate. This observation is likely due to the synergistic effect of vanadium and titanium nanoparticles as reported in BPA/TiO2/zeolite system by Fukahori *et al*. [29].

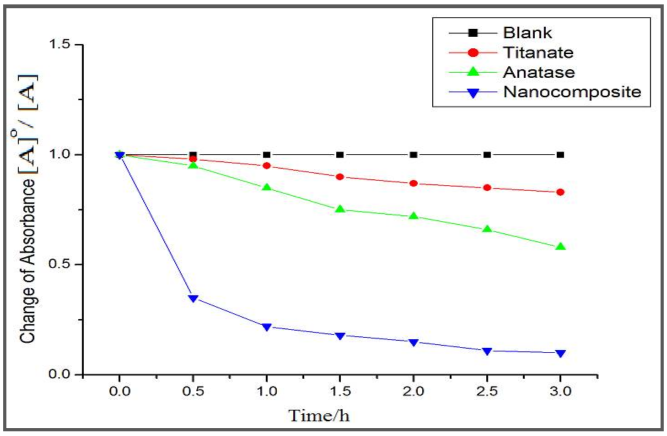

Figure. 5 The normalized absorbance changes of all the samples with irradiation time under visible light irradiation

APPLICATION

Vanadium/titanate nanocomposite photocatalysis is widely used in a variety of applications and products in the environmental and energy fields, including self-cleaning surfaces, air and water purification systems, sterilization, hydrogen evolution, and photoelectrochemical conversion.

CONCLUSION

It is found that the Vanadium/titanate nanocomposite photocatalysis exhibited a much improved photocatalytic activity in comparison with titanate nanotube and anatase TiO_2 nanoparticle.

REFERENCES

[1]. S. C. Wilson, V. Burnett, K.S. Waterhouse, K. C. Jones, *Environ. Sci. Technol.*, **1994**, 28, 259.
[2]. D. F. Ollis, E. Pelizzetti, N. Serpone, *Environ. Sci. Technol*., **1991**, 25, 1522.
[3]. J. M. Macak, M. Zlamal, J. Krysa, P. Schmuki, *Small*, **2007**, 3, 300.
[4]. M. A. Khan, H. T. Jung, O. B. Yang, *J. Phys. Chem. B,* **2006**, 110, 6626.
[5]. Y. S. Chen, J. C. Crittenden, S. Hackney, L. Sutter, D. W. Hand, *Environ. Sci. Technol., 2005*, 39, 1201.
[6]. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Adv. Mater.*, 1999, 11, 1307.
[7]. G. H. Du, Q. Chen, R. C. Che, Z. Y. Yuan and L. M. Peng, *Appl. Phys. Lett.*, 2001, 79, 702.
[8]. B. B. Lakshmi, C. J. Patrissi, C. R. Martin, *Chem. Mater.*, **1997**, 9, 2544.
[9]. V. Zwilling, E. Darque-Ceretti, A. B. Forveille, D. David, M. Y. Perrin, M. Aucouturier, *Surf. Interface Anal.*, **1999**, 27, 629.
[10]. A. Choi, W. Termin, M. R. Hoffmann, *J. Phys. Chem.*, **1994**, 98, 13669.
[11]. K. X. Wang, B. D. Yao, M. A. Morris, J. D. Holmes, *Chem. Commun.*, 2005, 17, 4825.

[12]. Y. Hu, C.W. Yuan, *J. Cryst. Growth*, 2005, 274, 563.
[13]. R. J. Candal, W. A. Zeltner, M. A. Anderson, *Environ. Sci. Technol.,* **2000**, 34, 3443.
[14]. K. G. Ong, O. K. Varghese, G. K. Mor, C. A. Grimes, *J. Nanosci. Nanotechnol.,* **2005**, 5, 1801.
[15]. F. Cao, G. Oskam, G.J. Meyer and P.C. Searson, *J. Phys. Chem.,* **1996**, 100, 17021.
[16]. J. M. Macak, K. Sirotna, P. Schmuki, *Electrochim. Acta.*, **2005**, 50, 3679.
[17]. Q. Y. Cai, M. Paulose, O. K. Varghese, K. Shankar and C. A. Grimes, *J. Mater. Res.,* **2005**, 20, 230.
[18]. J. M. Macak, H. Tsuchiya, L. Taveira, S. Aldabergerova,P. Schmuki, *Angew. Chem. Int. Ed.,* **2005**, 44, 7463.
[19]. M. Paulose, K. Shankar, S. Yoriya, H. E. Prakasam, O. K. Varghese, G. K. Mor, T. A. Latempa, A. Fitzgerald, C.A. Grimes, *J. Phys. Chem. B,* **2006**, 110, 16179.
[20]. Woo-Jin Lee, M. Alhoshan, W. H. Smyrl, *Electrochem. Soc.*, **2006**, 153(11), B499.
[21]. Woo-Jin Lee, M. Alhosan, Sara L. Yohe, Nathan L. Macy, and William H. Smyrl, J. Electrochem. Soc., **2008**, 155, B915.
[22]. Ruey-an Doong, *J. Separation and purification Technology*, **2011**, 7.
[23]. J. Y. Jung, S. B. Park, *Appl. Catal. B: Environ.,* **2000**, 25, 249.
[24]. Q. H. Zhang, L. Gao, J. Sun, S. Zhang, *Chem. Lett.,* **2002**, 226.
[25]. G. T. Chandrappa, N. Steunou, S. Cassaignon, C. Bauvais, *J. Livage, Catal. Today*, **2003**, 78, 85.
[26]. B. Alonso, J. Livage, *J. Solid State Chem*., 1999, 148, 16.
[27]. Q. Chen, G. H. Du, S. Zhang, L. M. Peng, *Acta Crystallogr*., 2002, 58, 587.
[28]. X. M. Sun, Y. D. Li, *Chem. Eur. J.*, 2003, 9, 2229.
[29]. S. Fukahori, H. Ichiura, T. Kitaoka, H. T. Anaka, *Environ. Sci. Technol.* 2003, 3, 1048-1051.