Photocatalytic degradation of Rhodamine B by microwave-assisted hydrothermal synthesized N-doped titanate nanotubes

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ABSTRACT

Microwave-induced nitrogen-doped titanate nanotubes (NTNTs) were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), Zeta potential analysis, specific surface area (S_{BET}), and UV–Visible spectroscopy. TEM results indicate that NTNTs retain a tubular structure with a crystalline multiwall and have a length of several hundred nanometers after nitrogen doping. XRD findings demonstrate that the crystalline structure of NTNTs was dominated by anatase, which is favored for photocatalytic application. The Ti–O–N linkage observed in the XPS N 1s spectrum is mainly responsible for narrowing the band gap and eventually enhancing the visible light photoactivity. FT-IR results demonstrated the existence of H_3O^+, which could be excited by photo-generated holes to form hydroxyl radicals and degrade environmental pollutants. After sintering at 350°C, the UV–Vis absorbance edges of NTNTs significantly shift to the visible-light region, which indicates N atom doping into the nanotubes. Photocatalytic degradation of Rhodamine B (RhB) via NTNTs show good efficiency, with pseudo first-order kinetic model rate constants of 3.7×10^{-3}, 2.4×10^{-3} and 8.0×10^{-4} sec^{-1} at pH 3, 7, and 11, respectively.

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Introduction

Photocatalytic semiconductor materials have attracted extensive attention due to their wide applications in waste treatment, water remediation, and air purification (Hoffmann et al., 1995; Fujishima and Honda, 1972; Yu et al., 2007). Among various photocatalysts, TiO$_2$ is the most studied material because it can generate powerful oxidants (holes) and reductants (electrons) by absorbing photo energies (Hoffmann et al., 1995; Stone and Davis, 1998; Adachi et al., 2000). The photo-generated holes can then react with an intermediate, such as water molecules, to form hydroxyl radicals (.OH) to oxidize pollutants. To employ TiO$_2$ more efficiently, a higher surface area is preferred in order to increase opportunities for contact. Therefore, the development of methods to increase surface area is an important issue for TiO$_2$ application. Since Kasuga et al. (1998, 1999) discovered titanate nanotubes (TNTs), TNTs have received widespread attention due to their one-dimensional nanostructure, large surface area and versatile applications, which include solar cells, photocatalysis, and electroluminescent hybrid devices (Sun and Li, 2003; Ou et al., 2007; Hodos et al., 2004; Tsai and Teng, 2006; Peng et al., 2012a,b). However, the high band gap in TNTs in the range of 3.3–3.87 eV

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obstructs application (Jang et al., 2006). In other words, only UV light, which occupies less than 5% of the solar spectrum, excites TNTs. Many efforts have been made to modify the band gap of TiO$_2$ by size control (Tristao et al., 2006; Kongkanand et al., 2008; Lin et al., 2006), manipulating the oxygen vacancy (Parida et al., 2010; Bai et al., 2008), and doping impurities (Chen and Mao, 2007). Asahi et al. (2001) were the first investigators to demonstrate that, among nonmetal dopants such as C, N, F, P and S, the substitution doping of N was the most effective because its p states contribute to the band gap narrowing by mixing with the O 2p state. Nevertheless, only a few studies have focused on TNTs' band gap reduction (Jiang et al., 2008; Qamar et al., 2009; Wu et al., 2009; Tian et al., 2012). Tokudome and Miyauchi (2004) first examined the visible light activity of N-doped TNTs. Geng et al. (2009) proposed that instead of substituting O$_2^-$ ions in the TNT lattice, the doping N is likely located at interstitial sites. N-doped TNTs have been proved to perform good photocatalytic ability under visible light irradiation (Jiang et al., 2008; Tian et al., 2012). Similar results were also observed in C-doped TNTs and Ni-TNTs, that can reduce the TNT band gap and shift absorbance to the visible-light region (Wu et al., 2009; Qamar et al., 2009).

Recently, many methods have been tested in attempts to synthesize TNTs, including the sol–gel process (Khan et al., 2006), electrochemical anodic oxidation (Tsai and Teng, 2006; Nian and Teng, 2006; Yoshida et al., 2005), and hydrothermal treatment (Serpone et al., 1995; Ou et al., 2006). Although the formation mechanism and chemical structure of TNTs are still controversial, applications of TNTs and even their derivates (nanoparticles and nanorods) on photocatalysis have recently emerged. Some researchers considered TNTs an effective photocatalyst for pollutant degradation (Nakahira et al., 2004; Tsai and Teng, 2004), whereas others came to the opposite conclusion (Stengl et al., 2006). The typical hydrothermal procedure, involving synthesis at 110–130°C in an autoclave for 20–120 hr, is relatively time- and energy-consuming. A previous study used a novel method, microwave hydrothermal treatment (M-H treatment), modified from the traditional hydrothermal method by the use of microwave radiation, to synthesize TNTs (Ou et al., 2007) and TiO$_2$/MWCNTs (Alosfur et al., 2013). M-H treatment has several advantages, such as a shorter reaction time, lower energy usage, and an enhanced TNT wall-structure intensity. A previous study successfully synthesized TNTs under 400 W irradiation at 130°C for only 1.5 hr with an S$_{BET}$ value of 256 m^2/g, finding that the TNTs were preferentially assigned to Na$_x$H$_{2-x}$Ti$_3$O$_7$, with a vague rutile phase and no clear anatase phase. Unfortunately, similar to the traditional hydrothermal method, the TNTs prepared by the M-H method showed weak photocatalytic activity.

Coupled with the existing literature, the objective of this research was to characterize the physical and chemical properties of nitrogen-doped titanate nanotubes (NTNTs) via M-H treatment and to illustrate their application in environmental fields.

1. Experiment

1.1. Preparation of N-doped titanate nanotubes

A microwave digestion system (ETHOS1, Milestone) was used during the experimental procedures, with a double-walled vessel consisting of an inner Teflon liner and an outer shell of high strength Ultem polyetherimide. In a typical procedure used in the literature (Ou et al., 2007; Peng et al., 2010), 0.6 g of TiO$_2$ (Degussa P25) was added to 70 mL of 10 mol/L NaOH in a Teflon container. The M-H reaction was promulgated at 120 W, 130°C for 3 hr, and cooled to room temperature. The

applied temperature, irradiation power, and time of treatment were programmable by computer. After the M-H process, the white powders were washed by mixing three times with 0.5 mol/L HCl, followed by washing five times with de-ionized water. Afterward, the white powders were dried at 80°C for 12 hr to obtain TNTs. Nitrogen-doped titanate nanotubes were prepared following the experimental method reported by Peng et al. (2010). Briefly, the as-prepared TNTs were dispersed in a 70 mL solution with a 1:1 volume ratio of ethanol and water containing 20 wt.% NH$_4$Cl. After stirring for 30 min, the mixing solution was heated by the M-H process at 120 W, 130°C for 2 hr. The white powders were then filtered, alternately washed with de-ionized water and ethanol, and dried under the same conditions as in previous TNT studies. To convert the nanotube layers into anatase, the samples were sintered under an atmosphere of 20% O$_2$/80% N$_2$ at a temperature of 350°C for 3 hr.

1.2. Characterization

XRD measurements were performed on a Rigaku D/max-2500 diffractometer (X'Pert Pro MRD, PANalytical, Holland) using graphite-filtered Cu Kα radiation (k = 0.154056 nm) at 40 kV and 100 mA. Diffraction data were recorded at an interval of 0.02° and a scanning speed of 1°/min in the range of 1–10°. TEM images of Ti-MCM-41 samples were obtained on a JEOL (Japan) JEM-100CX-II transmission electron microscope at 200 kV. Nitrogen adsorption–desorption isotherms were obtained at 77 K using a Tristar 3000 surface area analyzer (BET, Micromeritics, model ASAP 2020, USA). Before measurements, the samples were outgassed at 573 K for 3 hr in a degas port of the analyzer. Surface areas were calculated by Brunauer–Emmet–Teller method. FT-IR spectra of the samples were recorded in the range of 400–4000 cm^{-1} on a Nicolet 6700 spectrometer (Thermo Scientific, USA) with a KBr pellet. The acidity of catalysts was analyzed by FT-IR measurements of adsorbed pyridine using the same IR spectrometer with a 4 cm^{-1} resolution. The samples were pressed into a self-supporting wafer, followed by evacuation at 623 K for 0.5 hr. After cooling to 333 K, pyridine was adsorbed on the samples until saturation was reached. Subsequently, the samples were out-gassed for 0.5 hr at 333 K and the spectra were recorded. The light response of NTNTs was determined by diffuse reflectance UV–Visible (DRUV–Vis) spectroscopy. The measurement was performed at room temperature using a UV-3600 spectrometer (Shimadzu) in the wavelength range of 190–700 nm. XPS analysis was performed using a Perkin–Elmer PHI 1600 ESCA system with Mg Kα 1253.6 eV radiation as the excitation source. The sample was mounted on the specimen holder by means of double-sided adhesive tape. Spectra were collected in steps of 0.15 eV. The N 1s and Ti 2p binding energies were referenced to the C 1s peak at 284.6 eV. Zeta-potential, as a function of the solution pH, was used to determine the iso-electric point of the NTNTs. The solution pH was adjusted with 0.01 mol/L NaOH or 0.01 mol/L HCl, as required. The fresh-prepared iron nanoparticle slurry (0.1 g/L) was shaken for 20 min at 150 r/min until a stable ζ potential was reached. Samples were then collected with glass syringes and analyzed with a Nano-ZS90 (Malvern, United Kingdom).