Microporous and Mesoporous Materials 186 (2014) 168–175

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

High photocatalytic and adsorptive performance of anatase-covered titanate nanotubes prepared by wet chemical reaction

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ARTICLE INFO

Article history:
Received 15 May 2013
Received in revised form 27 November 2013
Accepted 9 December 2013
Available online 13 December 2013

Keywords:
Titanate nanotubes
Photocatalysis
Adsorption
Wet chemical reaction
Compound pollution

ABSTRACT

Anatase-covered titanate nanotubes (TiNTs) with high photocatalytic and adsorptive performance characteristics were prepared through wet chemical reaction. TEM and XRD analysis revealed that the morphology and composition of the modified TiNTs were directly related to the ambient pH and temperature conditions of the reaction. Lower pH and higher temperature tended to enhance the transition from titanate to anatase; moreover, the transition process involved an *in situ* rearrangement of the primary structural unit [TiO_6]. The photocatalytic performance of modified TiNTs depended on the amount of TiO_2 transformed from titanate, whereas the adsorptive property was primarily determined by the tubular titanate structure. TiNTs modified under optimal conditions of pH 2 and 120 °C (TiNTs-120-2) not only exhibited high photocatalytic degradation rate for methyl orange ($0.568 \times 10^{-2}\ \mathrm{min}^{-1}$), but also possessed a considerable capacity for adsorption of methylene blue (195.31 mg/g). Based on their excellent photocatalysis and adsorption properties, TiNTs-120-2 could simultaneously remove methyl orange, methylene blue, Pb^{2+}, and phenol initially present in a compound pollution system, and the materials could be efficiently reused after a simple further treatment. In addition, TiNT-120-2 is well suited to sedimentation, and so has strong potential for application as an easily separable and recoverable material.

1. Introduction

Titanium dioxide (TiO_2) is widely used as a photocatalyst because of its quantum size effect and strong adsorption of light in the ultraviolet or visible region of the electromagnetic spectrum [1–3]. Under UV irradiation, TiO_2 creates a conduction band (electron) and a valence band (hole) which is then captured by H_2O molecules and OH^- in solution. This produces hydroxyl radicals (OH) with considerable oxidizing power that can efficiently degrade organic matter present in water [1,4]. However, separation of TiO_2 particles from water is a challenging problem due to the particle structure and small aggregate size of TiO_2, which inhibits its application and reuse [5,6]. So it is critical to find a material with excellent photocatalytic and separation properties, as well as being cost-effective to manufacture.

In recent years, titanate nanotubes (TiNTs) synthetized by TiO_2 via hydrothermal method have attracted considerable interest given their potential applications in the electrochemical and environmental fields [7–10]. TiNTs have large surface areas, high length-diameter ratios, special layer titanate structures and good ion-exchange properties, and so act as efficient adsorbents for the removal of heavy metal ions and ionic organic pollutants [11–13]. As TiNTs are derived from TiO_2, it is reasonable to expect that they should have applications as photocatalysts. However, the photocatalytic ability of TiNTs has been demonstrated to be very weak because the electron-hole pairs soon recombine after being generated [14,15]. To overcome this fatal drawback, many researchers have focused on the modification of TiNTs in order to improve their photocatalytic performance. Such modification methods include semiconductor (e.g. CdS) compositing [16,17], precious metal (e.g. Ag, Pt, Pd) surface modification [18,19], transition metal ion (e.g. Fe^{3+}, Cu^{2+}) doping [20,21], and calcination and pickling [14,22,23]. Of these, calcination and pickling achieve the requisite modification through a process of crystal phase transition from titanate to anatase or rutile. However, the calcination temperature and acid concentration required is usually high [14,22,23], so a more practicable modification method is needed.

Heavy metal ions and organic pollutants often coexist in industrial wastewaters, an example being the simultaneous presence of lead, phenol and dyes [24,25]. So a material that can remove heavy metals and organic pollutants in a single operation would be ideal

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1387-1811/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2013.12.010

for application to industrial wastewater treatment. Although researchers have discussed the adsorption of heavy metals onto TiNTs and photocatalytic of organic pollutants by modified TiNTs [9,11,12], hardly any studies examine the integration of adsorption and photocatalysis using modified TiNTs, which may have great potential for application to systems containing both heavy metals and organic pollutants together.

This paper considers the synthesis of a composite high-performance material from titanate and TiO_2 that is capable of simultaneous photocatalysis and adsorption. To achieve this, a facile wet chemical reaction, involving a combination of calcination and pickling, has been conducted to modify as-prepared TiNTs to improve their photocatalytic performance while retaining their adsorptive property. Two typical dyes, methyl orange (MO) and methylene blue (MB), were chosen as objective pollutants by which to investigate the photocatalytic and adsorptive performance of the modified TiNTs. Investigations were then undertaken into the removal of pollutants by the modified TiNTs and reuse of materials in a compound pollution system. A detailed discussion is provided on the relationships between the overall photocatalytic-adsorptive performance and the morphology and crystal phase of the modified TiNTs. The outcome is a reusable material with excellent photocatalytic and adsorptive properties, which can simultaneously remove heavy metals and organic pollutants from industrial wastewater.

2. Material and methods

2.1. Preparation and modification of TiNTs

TiNTs were synthesized by a hydrothermal method devised by Xiong et al. [9,13]. 1.2 g of TiO_2 nanoparticles (P25, about 80% anatase and 20% rutile, Degussa, Germany) were heated in a 10 M NaOH solution at 130 °C for 72 h. After washing to neutral with deionized water, the as-prepared materials were kept for further characterization and modification. All the chemicals used in this work were at analytical grade or better.

Wet chemical reactions under different conditions were then carried out to modify the TiNTs. Firstly, the TiNTs were mixed with a series of HNO_3 solutions, and the mixtures heated in an airtight container. To be more exact, in each case 0.2 g of TiNTs in powdered form was added to a total of 16.5 mL of HNO_3 solution at a given pH. After stirring for 12 h, the mixture was transferred into an airtight Teflon container (25 mL of effective volume) with a stainless steel encloser, and then heat treated for 24 h at a prescribed temperature. Secondly, the mixture was separated, washed to neutral with deionized water, and dried at 80 °C for 4 h, to provide the desired precipitates. In the first series of tests, the pH values of the different HNO_3 solutions were set as 3, 2, 1.5 and 1 and heated at a fixed temperature of 120 °C (the corresponding products are marked as TiNTs-120-3, TiNTs-120-2, TiNTs-120-1.5 and TiNTs-120-1). In the second series of tests, the temperature was set at 100 °C, 120 °C and 150 °C while the HNO_3 solution had a fixed pH of 2 (the corresponding products are marked as TiNTs-100-2, TiNTs-120-2 and TiNTs-150-2).

Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to observe the morphology and crystal phase, and hence characterize the original and modified TiNTs. The TEM images were obtained using an electron microscope (Tecnai T20, FEI, USA) operating at 200 kV after the samples were dispersed on a copper microgrid by passing through a carbon membrane. XRD analysis was conducted using a Dmax/2400 X-ray diffractometer with a scanning speed (2θ) of 4°/min under 40 mA at 100 kV and Cu *Ka* radiation of wavelength $\lambda = 1.542$ Å. Scanning electron microscopy (SEM) analysis was carried out using an FEI microscope (XL30F, Philips, USA) at 20 kV.

2.2. Photocatalytic and adsorptive performance measurement

Removal of MO and MB by the modified TiNTs was undertaken through an adsorption-photocatalysis process in a quartzose reactor of volume 300 mL (dimensions 5 cm × 5 cm × 12 cm). MO and MB of guaranteed analytical standard were purchased from the Beijing Chemical Reagents Company (Beijing, China) and used without further purification. All the solutions used in the experiments were prepared with deionized water. For the adsorption-photocatalysis experiments, a 150 W mercury lamp (wavelength $\lambda = 365$ nm, Beijing Electric Light Sources Research Institute, China) was placed 10 cm away from the sidewall of the reactor. The UV light intensity of the photocatalytic reaction at the center of the reactor was measured to be 2.50 ± 0.5 mW/cm^2 by a UV-A radiometer (Photoelectric Instrument Factory of Beijing Normal University, China). Cooling air was introduced by a fan on the top of the reactor to maintain the reaction temperature of 25 ± 2 °C. 100 mL of MO (25 mg/L) or MB (100 mg/L) solution was mixed with 50 mg of a sample of TiNTs and the mixture stirred in the dark. After 4 h, when the adsorption–desorption equilibrium with TiNTs had been established, the UV light was turned on for 180 min during which the photocatalytic reaction took place. After the materials were separated by centrifuging at 10000 rpm for 5 min, the concentration of MO or MB was determined by an UV–visible spectrophotometer (UV 1800, Shimadzu, Japan).

Besides, batch isotherm experiments on adsorption of MO and MB onto modified TiNTs were then performed. The initial concentration of the dye varied from 0 to 200 mg/L for MB while 0 to 20 mg/L for MO, and the TiNTs dosage was fixed at 0.5 g/L. After the mixture of each dye and TiNTs were shaken for 3 h (200 ppm, 25 °C), samples were taken and filtered through a 0.22 μm membrance. Concentration of MB was also determined by the UV–visible spectrophotometer.

2.3. Application and reuse of modified TiNTs in compound pollution system

A compound system of heavy metal – organic pollutants comprising coexisting MO, MB, Pb^{2+}, and phenol in water was synthesized in order to investigate the simultaneous removal efficiency of TiNTs modified under optimal conditions. The four pollutants, with the same initial concentration of 10 mg/L in otherwise pure water, were mixed with 0.8 g/L of modified TiNTs, and the adsorption-photocatalysis experiment was carried out following the procedure described in Section 2.2. After the suspensions were sampled and centrifuged at prescribed time intervals, the concentrations of MO and MB were determined using the UV–vis spectrophotometer, while Pb^{2+} was measured by inductively-coupled plasma-atomic emission spectrometry (ICP-AES, Prodigy, Leeman, USA). The concentration of phenol was determined using high performance liquid chromatography (HPLC, HP1100, Agilent, USA) system fitted with a ZORBAX SB-C18 column (of dimensions 150 mm × 4.6 mm × 5 μm). The column temperature was held constant at 30 °C, and the mobile phase comprised a 50:50 mixture of methanol and water flowing at a rate of 1 mL min^{-1} in isocratic mode. The eluate was analyzed with a UV diode array detector at 230 nm. Total organic carbon (TOC) of the samples was determined using a TOC-analyser (TOC-VCPN, Shimadzu, Japan). Afterwards, the TiNTs samples were immersed in 0.2 M HNO_3 for 3 h to desorb the metal ions, and then immersed in 0.2 M NaOH for 3 h to regenerate. The desorbed and regenerated TiNTs were all reused in the compound system after washing with deionized water until the effluent was neutral.

A study on the sedimentation kinetics of raw and modified TiNTs was undertaken in order to evaluate their performance at separating from solution. 0.25 g L^{-1} TiNTs were dispersed in