Preparation of fine, uniform nitrogen- and sulfur-modified TiO$_2$ nanoparticles from titania nanotubes

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Received 10 June 2010
Accepted for publication 17 September 2010
Published 17 November 2010
Online at stacks.iop.org/STAM/11/055001

Abstract

TiO$_2$ nanoparticles modified with nitrogen and sulfur were prepared from titania nanotubes by a facile wet chemistry method. The samples synthesized with different thiourea/TiO$_2$ ratios showed a uniform nanoparticle size distribution centred at approximately 10 nm with a developed specific surface area of 246 m$^2$ g$^{-1}$. These modified nanosized photocatalysts exhibited higher photocatalytic activity for the degradation of gaseous isopropanol than unmodified titania nanotubes under visible illumination. This could be attributed to the synergistic effects of a large specific surface area, strong absorption in the visible region, a redshift in the adsorption edge, and surface adsorption modification induced by nitrogen and sulfur compounds.

Keywords: titania nanotube modification, photocatalysis, TiO$_2$ doping

1. Introduction

Among the various oxide semiconductors, titanium dioxide is recognized as the most suitable for a wide range of applications such as photocatalysis, gas sensing, photovoltaic cells, superhydrophobic coatings and photoelectrolysis [1]. In particular, environmental remediation using TiO$_2$ is widely studied owing to the compound’s biological and chemical inertness, strong oxidizing power, non-toxicity, and long-term stability against chemical and photochemical corrosion. With potential applications in air purification, wastewater treatment, as well as an antibacterial, deodorant and self-cleaning material, TiO$_2$ powder has been widely studied for the advantages it offers.

However, titania absorbs only 5% of incoming sunlight in the visible region ($\geq$ 380 nm), which greatly limits its efficient application. In the late 1980s, researchers began to develop the next generation of titanium dioxide that could absorb both UV and visible light to enhance process efficiencies. Sato reported NO$_x$-doped TiO$_2$ with visible light absorption, produced by annealing titania with NH$_4$Cl or NH$_4$OH [2]. This opened the way to doping TiO$_2$ with non-metallic elements. Asahi et al [3] and Irie et al [4] reported in 2001 and 2003, respectively, that doping TiO$_2$ with nitrogen in an NH$_3$ atmosphere extends its light absorption to the visible region, but some authors indicated that this technique is very reductive and generates many defects in the crystals [5]. Titania photocatalysts were later doped with N [6], C [7], S [8] or F [9] anions or Pt [10], Fe [11], Co [12] or Cu [13] cations or co-doped with several ions [14]. They exhibited an absorption edge that is red-shifted to lower energies as well as enhanced photocatalytic performance in the visible range. Tokudome and Miyauchi reported the synthesis of N-doped TiO$_2$ nanotubes by surface protonation followed by immersion in an NH$_3$ solution and annealing in air [15].

Modification and doping of titania-based nanotubes is now attracting considerable interest. However, little work has been reported on preparing doped or modified TiO$_2$ nanoparticles from titania nanotubes. Titania nanotubes have a high specific surface area and unique properties.
that could lead to increased surface absorption and thus enhanced doping levels. Moreover, photocatalytic reactions are surface-related, so a large specific surface area usually increases the reaction rate because it can supply more adsorption sites and photocatalytic reaction centres. Note that doping under calcination often leads to a low specific surface area because the porous structure collapses. In addition, the average transfer time of photogenerated electrons and holes is reported to be shorter for small and uniform TiO$_2$ particles than for large particles [16]. The reduced recombination rate is advantageous for photocatalytic activity.

In this work, a facile method is presented for preparing fine TiO$_2$ nanoparticles, which are modified with nitrogen and sulfur and have a high specific surface area, by coupling hydrothermal reaction and wet impregnation methods. Thiourea was used as the source of nitrogen and sulfur. The photocatalytic activity was evaluated by photodegradation of gaseous isopropanol under visible light ($\lambda > 420$ nm).

### 2. Experimental details

#### 2.1. Synthesis

In a typical synthesis, titania nanotubes were produced by mixing a commercial TiO$_2$ powder (P25 Degussa-Evonik$^\text{TM}$) with 10 M sodium hydroxide for 24 h in a Teflon autoclave at 130 °C. After rinsing with a large amount of 1 M HCl and distilled water until the pH reached at least 6, the powder was dried at 110 °C for 24 h.

TiO$_2$ was modified with nitrogen and sulfur via thiourea decomposition. Titania nanotubes were soaked for 15 h in 50/50 deionized water to pure ethanol solutions having a thiourea/titania molar ratio of 0.5, 1, 2 or 5; then the solvent was evaporated at 90 °C until dryness. The obtained powder was then calcined at 450 °C for 2 h (heating rate 5 °C min$^{-1}$) to produce materials with a slight to strong yellow colour (TiO$_2$-NS-x, with 0.5 $< x < 5$).

#### 2.2. Characterization

The crystal structure of the as-prepared photocatalysts was determined using an x-ray diffractometer (XRD, JEOL JDX-3500, Cu-K$_\alpha$ radiation) operated at 35 kV and 100 mA. The UV-visible diffuse reflectance spectra were recorded at room temperature with a UV-2500 spectrophotometer (Shimadzu Corp.) and converted to absorption spectra. Transmission electron microscopy (TEM) micrographs were taken on a JEOL-2100F microscope operated at 200 kV. Selected-area electron diffraction (SAED) patterns were recorded using a 10 nm beam and combined with energy-dispersive X-ray spectroscopy (EDS). Surface area was measured by the conventional Brunauer–Emmett–Teller (BET) method with the observations of Dong et al wherein a tubular structure was retained for samples calcined at the same temperature of 450 °C [18]. The particle size distribution was rather homogeneous with an average diameter of 10 nm (inset, figure 1(c)).

Figure 1(d) shows the SAED pattern of the TiO$_2$-NS-1 sample. Homogeneous and relatively broad rings reveal a poorly crystallized structure, with rings assigned to the (101), (004), (200) and (005) reflections of the anatase phase. EDS results revealed the homogeneous distribution of all constituent elements. These results contrast with the observations of Dong et al wherein a tubular structure was retained for samples calcined at the same temperature of 450 °C [18]. The dissimilarities may arise from different preparation conditions: Dong et al carried out the

2.3. Photocatalytic activity

The photocatalytic activity was evaluated via decomposition of gaseous isopropyl alcohol (IPA) over the photocatalyst irradiated with visible light. Typically, 0.1 g of the photocatalyst was spread uniformly in a dish with an irradiation area of 7.8 cm$^2$, and the dish was placed on the base of a 500 mL reactor. After the reactor was sealed with a quartz cover and the inside atmosphere was replaced with synthetic air, gaseous IPA was introduced into the reactor. The reactor was stored in the dark until the concentration stopped changing and the system reached adsorption equilibrium. The reactor was then irradiated with visible light ($\lambda > 420$ nm) obtained by passing the output of a 300 W Xe lamp through a low-pass filter (L-42, Hoya Corp.) and a water filter. The distance between the sample and the lamp was approximately 15 cm and the light intensity was approximately 30 mW cm$^{-2}$. The concentrations of IPA, acetone and CO$_2$ were monitored using a gas chromatograph (GC-14B, Shimadzu) equipped with a flame ionization detector and a methanizer.

### 3. Results

#### 3.1. Sample characterization

Figure 1(a) shows a TEM image of the nanotube sample before calcination. It was taken in conjunction with a previous study, which used the same synthesis method yielding many multiwalled nanotubes with a diameter of 5–15 nm and a length of several hundred nanometres. The same sample after thermal treatment at 400 °C is shown in figure 1(b), which reveals partial degradation of the tubular shape and the formation of grains resulting from the dislocation of titania nanotubes after annealing. Figure 1(c) shows the morphology of the sample doped with 1% thiourea and calcined at 450 °C. TEM observations confirm the porous structure without long-range order, indicating that the mesoporosity mainly originates from interparticle porosity, with a developed specific surface area of 234 m$^2$ g$^{-1}$. High-resolution TEM of individual nanocrystals revealed well-resolved crystalline planes with a spacing of 0.34 nm, which is similar to that of the (101) planes in anatase [17]. The particle size distribution was rather homogeneous with an average diameter of 10 nm (inset, figure 1(c)).
Figure 1. TEM images of titania nanotube sample (a) before and (b) after calcination at 400 °C, and (c) of TiO$_2$-NS-1 sample calcined at 450 °C with its representative SAED pattern (d). Inset in (c) shows the particle size distribution.

hydrothermal reaction at a higher temperature (150 °C instead of 130 °C) and for a longer duration (48 h versus 24 h).

Figure 2 shows the UV-visible diffuse reflectance spectra of the TiO$_2$-NS-x samples and titania nanotubes (TiNT). The TiNT sample shows only a single sharp edge, whereas the doped powders exhibit two absorption edges. The edge at 380 nm is attributed to titania absorption, whereas the shoulder between 400 and 500 nm is assigned to N or S compounds interacting with TiO$_2$. The optical absorption spectra show that the band gaps of the samples prepared with the thiourea/TiO$_2$ ratios of 0.5, 1, 2 and 5 are 2.92, 2.87, 2.79 and 2.73 eV, respectively, and visual inspection confirmed that the colour of the samples changed from yellowish-white to intense yellow with increasing thiourea content. The visible light absorption by TiO$_2$-NS-x samples may be caused by the excitation of electrons from a localized doping level in the band gap. It was previously reported that nitrogen doping can lead to a mixing of N 2p orbitals with O 2p orbitals, creating midgap levels and shifting the absorption edge towards the visible light region [3].

Figure 3 shows the XRD patterns of the product after the hydrothermal reaction (TiNT) and the TiO$_2$-NS-x samples after calcination at 450 °C with different thiourea/TiO$_2$ ratios. The XRD profile of pure TiNT is essentially the same as that previously reported for titinate nanotubes, with relatively low crystallinity and characteristic 2θ peaks at 24.7 and 48.7° [19]. The XRD patterns for TiO$_2$-NS-x are close to the reported values of the anatase TiO$_2$ phase with peaks at 25.3, 37.7, 48.1, 54.2 and 62.4° (Joint Committee on Powder Diffraction Standards, card No. 21-1272). No notable changes were observed in the lattice parameters, but the diffraction intensity decreased when more thiourea was used.

We determined the size of the coherent diffraction domains $D$ using Scherrer’s equation: $D = 0.8\lambda / \beta \cos \theta$, where $\lambda$ is the x-ray wavelength (0.1542 nm for Cu-Kα...
radiation, $\beta$ is the full width at half maximum, and $\theta$ is the diffraction angle. The particle sizes vary from 7 to 12 nm, which agree well with the results of TEM observations. As the amount of thiourea increases, the catalyst particle size decreases, but the unit cell parameters do not change.

The Raman scattering spectrum of TiNT in figure 4(a) features bands at 185, 270, 388, 448, 669, 835 and 928 cm$^{-1}$, which are ascribed to titanate nanotubes [20, 21]. Figure 4(b) shows Raman spectra for TiO$_2$-NS-x with different thiourea/titania ratios. The peaks at 635, 510, 390 and 140 cm$^{-1}$ in doped samples originate from the anatase TiO$_2$ phase [22]; they weaken with increasing thiourea content—a trend also seen in the XRD patterns (figure 3). Okata et al reported the role of nitrogen in epitaxial films of anatase and had the same observations [23]. A small concentration of N can promote the growth of anatase; however, the effect is controversial at high dopant levels.

XPS spectra were examined to identify the surface properties of the samples with the addition of nitrogen and sulfur. Figure 5(a) shows the wide-range spectrum revealing the presence of Ti, O, N, S and C atoms. The doping level of this sample is approximately 0.6 at.% for N atoms, as estimated from the XPS spectra, and 1.6 at.% for S atoms. The C 1s peaks at 284.6 eV represent organic carbon pollutants and were used for calibration.

The Ti 2p XPS spectrum (not shown here) shows the spin-orbit split peaks of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ at 458.6 and 464.7 eV, respectively, which is characteristic of the Ti (IV) oxidation state. No reduction in the Ti(III) signal was observed. The O 1s XPS spectrum (not shown) exhibits a strong peak at 529.9 eV, which is characteristic of the oxides of transition metals. The peak at 530.7 eV is attributed to hydroxyl groups on the surface of the photocatalyst, and peaks at higher energies correspond to contamination with carbon compounds.

Figure 5(b) shows the N 1s XPS spectrum; a clear asymmetric broad peak centred at approximately 400 eV reveals that more than one chemical state of nitrogen exists in the sample. Fitting of the experimental line shape was achieved with three peaks centred at 402.1, 400.1 and 397.8 eV. The attribution of each peak to a specific compound or chemical bond has been debated recently and depends on the synthesis method. The peak at 397.8 eV is assigned here to anionic N-doping, O-Ti-N, where oxygen atoms are replaced by nitrogen atoms involving substitutional N doping [24]. The peaks at 400.1 and 402.1 eV are attributed to molecular nitrogen compounds adsorbed on the surface of TiO$_2$ (NO$_x$, NH$_3$ or NH$_4^+$). Therefore, it could be concluded that the lattice oxygen atoms of TiO$_2$ were replaced by N, altering the energy band structure.

Figure 5(c) shows the S 2p XPS spectrum, which exhibits a similar asymmetry. After fitting the experimental spectrum profile, two different peaks were identified as the S$^{2-}$ oxidation states of S 2p$_{3/2}$ and S 2p$_{1/2}$; the intensity ratio is about 1/2. The S$^{4+}$ peak is expected at around 166 eV and is not present in the sample. This sulfur signal may be assigned to the SO$_x$ ions adsorbed on the surface of TiO$_2$ nanoparticles. No signal has been detected that can be assigned to S atoms replacing O atoms in the TiO$_2$ lattice, which would produce a peak at about 160–161 eV.

BET experiments were conducted to determine the specific surface area and pore size distribution. Unmodified material, i.e. TiNT, had a large specific surface area of 390 m$^2$ g$^{-1}$. It decreased to around 246 m$^2$ g$^{-1}$ after calcinations.
Figure 5. XPS spectra of TiO$_2$-NS-1: (a) wide-scale spectrum, (b) N 1s and (c) S 2p regions. Underlying curves in (b) and (c) represent fittings.

Figure 6. Isotherm of low-temperature nitrogen adsorption and desorption, and pore size distribution for TiO$_2$-NS-1.

at 450 °C, which is still about five times higher than that of the commercial TiO$_2$ powder used in the hydrothermal synthesis. The nitrogen sorption (adsorption and desorption) isotherm and the corresponding Barrett–Joyner–Halenda (BJH) pore size distribution of TiO$_2$-NS-1 material are shown in figure 6. The N,S-modified TiO$_2$ isotherm corresponds to type IV in the IUPAC classification, which is associated with mesopores and shows a specific surface area of 234 m$^2$ g$^{-1}$; this value is very close to that of undoped material. The specific surface area was almost independent of the thiourea/TiNT ratio indicating that the doping procedure did not affect the sample’s porosity. Furthermore, the measurement reveals a monomodal pore size distribution centred between 4 and 6 nm. According to a t plot, no micropores were detected in any sample. The mesopores allow rapid diffusion of gas reactants and products during photocatalytic reactions and enhance the reaction rate.

3.2. Photocatalytic activity

The photocatalytic activity of mesoporous TiO$_2$ modified with nitrogen and sulfur was examined using the decomposition of IPA under visible light irradiation. In a dark test, the IPA concentration went to zero, and no CO$_2$ formation was detected. No catalytic process was observed, and a rapid decrease in the concentration occurred with IPA adsorption due to the high specific surface area of the powder. Under visible light irradiation, gaseous IPA is gradually oxidized through an acetone intermediate to CO$_2$. However, the concentration of acetone in the system was very low, only a few ppm in the first hour, probably owing to the high specific surface area of the powder and its high adsorption capability. Therefore, we focused on the process of complete conversion into CO$_2$. The changes in IPA and CO$_2$ concentration versus time are shown in figure 7. TiO$_2$ nanoparticles prepared without thiourea (TiO$_2$-NS-0) show no photocatalytic activity under the present conditions even if IPA was completely adsorbed on the photocatalyst during the experiments, as only a few ppm of CO$_2$ was detected. The photocatalytic activity under visible irradiation increased when the thiourea/titania
mass ratio was 1. Thus, we can conclude that the TiO₂-N₃-x samples exhibit enhanced activity relative to the pristine TiNT material. The best results are obtained for the powder with a thiourea/titania ratio of 1, which showed a complete conversion of IPA to CO₂ within the first 12 h under visible light.

The photocatalytic activity of a nanopowder is typically associated with different parameters such as surface area, surface-reactive species density, phase structure and crystallinity [25]. The enhanced photocatalytic activity at a thiourea/titania mass ratio of 1 can be ascribed to (i) a clear improvement in the crystallinity of anatase, as shown by XRD and Raman spectroscopy, (ii) the high specific surface area of the powder, which provides not only more surface area for visible light absorption but also more catalytic sites for reactions, (iii) reduction of the bandgap by N doping via the introduction of midgap levels and (iv) surface modification (mainly with NH₃ and SO₃ species) and interaction with reactants and products. Although doping of TiO₂ with N and/or S atoms is discussed in numerous publications, point (iv) has been insufficiently discussed in the past. The presence of sulfate species on the surface of titania has been found to enhance its catalytic activity towards oxidation processes owing to an increase in surface acidity and synergy with the support [26]. It is also well known that surface groups play an important role in the photocatalytic degradation of organic contaminants, particularly hydroxyl and acidic groups.

4. Conclusions

TiO₂ nanoparticles modified with nitrogen and sulfur were synthesized by an impregnation method for titania nanotubes and thiourea as a nitrogen and sulfur source. Their photocatalytic activities were evaluated via degradation of gaseous IPA under visible light irradiation. The modified nanoparticles exhibited a high specific surface area and their bandgap decreased with increasing thiourea content. TiO₂-NS with 1 wt% thiourea showed the highest photocatalytic activity. Such modification could enhance the photocatalytic activity of titania nanotubes, which are a promising starting material for doped TiO₂ nanoparticles. This strategy could also be applied to other anions or metal oxides.

Acknowledgments

This work was supported by the International Center for Young Scientists (ICYS), National Institute for Materials Science (NIMS), Tsukuba, Japan. The authors are grateful to Dr H Iwai for the XPS analysis.

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