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Effect of nitrogen doping on the microstructure and visible light photocatalysis of titanate nanotubes by a facile cohydrothermal synthesis via urea treatment

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ABSTRACT

A facile one-step cohydrothermal synthesis via urea treatment has been adopted to prepare a series of nitrogen-doped titanate nanotubes with highly efficient visible light photocatalysis of rhodamine B, in an effect to identify the effect of nitrogen doping on the photodegradation efficiency. The morphology and microstructure of the thus-prepared N-doped titanates were characterized by nitrogen adsorption/desorption isotherms, transmission electron microscopy, and scanning electron microscopy. With increasing urea loadings, the N-doped titanates change from a porous multi-layer and nanotube-shaped to a dense and aggregated particle-shaped structure, accompanied with reduced specific surface area and pore volume and enhanced pore diameter. Interstitial linkage to titanate via Ti—O—N and Ti—N—O is confirmed by X-ray photoelectron spectroscopy. Factors governing the photocatalytic degradation such as the specific surface area of the catalyst and the degradation pathway are analyzed, a mechanistic illustration on the photodegradation is provided, and a 3-stage degradation mechanism is identified. The synergistic contribution due to the enhanced deethylation and chromophore cleavage on rhodamine B molecules and the reduced band gap on the catalyst TiO_2 by interstitial nitrogen-doping has been accounted for the high photodegradation efficiency of the N-doped titanate nanotubes.

1. Introduction

TiO_2 has been proven to be one of the best semiconductor materials to degrade organic pollutants efficiently through oxidation under ambient condition, because it possesses (i) suitable redox potential of conduction band and valence band to ensure simultaneous reduction of O_2 and oxidation of H_2O or other organic compounds; (ii) high photodegradation efficiency with non-toxicity, and (iii) high resistance to photo-corrosion and great photo-stability. However, one obstacle toward its practical applications is that photocatalytic processes can only be activated by UV light (with wavelength < 380 nm) because of its wide band gap value of 3.2 eV. Since UV light accounts only for a small fraction (4–5%) of the natural sunlight as compared to visible light (45%), any shift in the optical response of TiO_2 from UV to visible spectral range would have a profound positive effect on its photocatalytic efficiency [1,2].

The overall photocatalytic activity efficiency of TiO_2 depends on two factors: (i) the separation efficiency of electrons and holes and (ii) the recombination rate of the photogenerated electron–hole pairs. There are also two basic strategies to overcome the limitations and to improve the photocatalysis efficiency of TiO_2. One is to enlarge the light absorption range of the photocatalysts to enhance the harvesting efficiency of sunlight by doping metal or non-metal ions into TiO_2; the other is to control the morphology, the particle size and its distribution, the phase composition, and the porosity of the photocatalyst. For the former case, various transition metal cations (such as V, Cr, Mn, Fe, and Ni) are doped into TiO_2. However, such cationic doping also leads to the localized *d*-state deep in the band gap of TiO_2, which usually acts as the recombination centers for photo-excited electrons and holes, resulting in lower photocatalytic activity [3,4]. In addition, when the expensive ion implantation facilities are also considered, doping by metal ions to the efficiency enhancement of sunlight seems impractical.

Modifications of TiO_2 by single doping with certain non-metal elements such as boron, carbon, sulfur, fluorine, and nitrogen [1,5–9] to efficiently extend the photo-response from UV to visible light region have been attempted. Asahi et al. showed an effective shift to visible light region by doping with nitrogen [1]. The reason for the improvement of photocatalytic activity has been often attributed to the decrease of the band gap, which is due to either

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mixing the N 2p with O 2p on the top of valence band or the creation of an ion-induced mid-gap level. The nitrogen dopant was shown to effectively retard the anatase to rutile transformation, to increase anatase crystallinity, and to improve the valence band maximum of O 2p (2.3 eV) [9]. Modifications of TiO_2 by multiple doping with metal or non-metal elements have also been studied [10–12]. For the nitrogen and sulfur co-doped anatase TiO_2 nanosheets [11], a titanium alkoxide was adopted as the titania precursor and a thiourea was used as the sources of nitrogen and sulfur atoms. The authors claimed an enhancing visible-light photocatalysis due to the more reactive {0 0 1} facets and more surface active sites available for adsorption of reactant molecules. For the nitrogen, fluorine, and tantalum tri-doped TiO_2 nanocatalysts [12], the titanium alkoxide sol was hydrothermally gelled and then mixed with TaF_5 aqueous solution. Incorporation of fluorine and nitrogen facilitated the formation of hybridized N 2p–Ta 5d states which could help to separate the photo-excited electron–hole pairs; thus the band gap of TiO_2 was narrowed.

Recently, nitrogen-doped titanate nanotubes with a simple cohydrothermal processing method in concentrated NaOH solution have been synthesized [13]. This method combines the non-transition metal doping (with nitrogen) with controlled morphology (by nanotube) in one process. The thus-prepared titanate nanotubes showed a higher interfacial charge transfer rate and larger specific surface area as compared to those of the spherical titanate particles, since the transfer of the charge carriers along the length of the titanate nanotubes efficiently reduced the recombination rate of the electron–hole pairs [14].

Another rationale for the development of the nitrogen-doped TiO_2 nanotubes is their easy separation from aqueous media after photodegradation, making them easy to be recycled and reused. On the other hand, the TiO_2 particles aggregate easily, showing poor dispersion ability during preparation and applications. Considerable efforts have been made to facilitate recycling. One study emphasized in particular the one-dimensional TiO_2 nanoparticles such as nanorods and nanostripses, which were synthesized via a hydrothermal process with relatively high specific surface area and high photocatalytic activities under both UV and visible-light, even though no doping was made [15]. Composite materials such as the nitrogen-doped nano-TiO_2/muscovite have also been proposed for efficient recycling [16]. The composite materials were synthesized via a hydrolysis-precipitation process, adopting the multi-layered muscovite as the carrier, $TiCl_4$ as the precursor for TiO_2, and urea as the neutralizer and dopant. Identification of O 1s peak from XPS suggested the formation of Si—O—Ti and O—Ti—N; this ensured the chemical bindings between TiO_2 and muscovite.

Numerous research efforts have been made on photodegradation of the environmentally harmful dye pollutants to become more biodegradable compounds or to allow mineralization into CO_2 and other inorganic compounds. Studies on TiO_2-mediated photodegradation of dyes under visible irradiation have shown that some of *N*-alkylamine-containing dyes, such as RhB [12,17,18] and sulforhodamine-B [19], appeared to be photodegraded via two competitive pathways: an *N*-dealkylation process and a cleavage of the whole conjugated chromophore structure. Considering that the photodegradation of dyes under visible irradiation is initiated by the interfacial electron injection from the excited dye molecules to the TiO_2-mediated catalyst or other catalysts such as Bi_2WO_6 [20], $NaBiO_3$ [21], TiO_2/SiO_2 [22], it is believed that the reaction kinetics depends, to a certain extent, on the efficiency of the electron transfer. Therefore the enhanced adsorption of dye is expected to contribute to the high photocatalytic activity of the TiO_2-mediated catalyst. In this study, N-doped titanate nanotubes were synthesized via a facile cohydrothermal process to evaluate the photocatalytic degradation of RhB dye solution under visible light irradiation, with particular emphasis on the effect of urea loading on the microstructure, morphology, and photocatalytic efficiency of the titanate nanotubes.

Table 1
Nitrogen adsorption properties of U-series samples.

Sample	Urea (g)	S_{BET} (m^2/g)[a]	$D_{BJH\text{-}ads}$ (nm)[b]	V_{pore} (cm^3/g)[c]
U-0	0.0	298	11.4	0.85
U-1	1.5	277	10.0	0.69
U-2	3.0	233	9.8	0.57
U-4	6.0	234	11.8	0.69
U-6	9.0	162	13.6	0.55
U-10	15.0	89	21.5	0.48

[a] BET surface area calculated from the linear part of BET plot.
[b] Estimated using the adsorption branch of the isotherm by BJH method.
[c] Single point total pore volume of pores at $P/P_0 = 0.97$.

2. Experimental

2.1. Preparation of N-doped titanate nanotubes

The N-doped titanate was prepared using a cohydrothermal process similar to that described by Kasuga et al. [23,24]. The TiO_2 used for the synthesis of titanate nanotubes was of commercial grade powder (P25, Acros) consisting of ca. 30% rutile and ca. 70% anatase with a primary particle size of ca. 21 nm In a typical synthesis, 1.5 g of the TiO_2 powder was mixed with 50 mL of 10 M NaOH solution and stirred for 30 min Then a certain amount of urea was added and stirred for another 30 min, followed by hydrothermal treatment of the mixture at 130 °C for 24 h in a PTFE-lined stainless steel vessel. After hydrothermal reaction, the precipitate was separated by filtration and washed with a 0.1 M HCl solution and distilled water until the pH value of the rinsing solution reached ca. 1.6 [25]. The acid-washed samples were dried in an oven at 80 °C for 8 h and stored in the glass bottles until used. Samples with different urea loadings are designated as U-0 to U-10 (Table 1), where the Arabic number represents the weight ratio of urea to P25 in the starting solution.

2.2. Characterizations

Porous structure of the N-doped titanate nanotubes, including the BET surface area, the pore volume, and the pore volume distribution, was measured at −196 °C with a Micromeritics ASAP 2010 apparatus. Prior to the measurements, the powdered samples were degassed at 200 °C in vacuum for 24 h. X-ray diffraction patterns were analyzed by a Siemens D5000 powder diffraction system equipped with a position-sensitive detector, using Cu Kα ($\lambda = 0.154$ nm) radiation under 40 kV working voltage and 30 mA working current. The patterns were collected in the range of $2\theta = 5–80^\circ$ with a speed of 1.5°/min in the continuous scan mode. Inspection of the morphology and characterization of the titanate nanotubes were done by transmission electron microscopy (TEM, JEOL™ AEM 3010, Tokyo, Japan) operating at 200 kV and field emission scanning electron microscopy (FESEM, JEOL™ SEM 6330, Tokyo, Japan). Samples for TEM observation were ultrasonically dispersed in ethanol and a drop of this solution was then placed onto a carbon film supported copper grid. The chemical nature of N in $TiO_{2-x}N_x$ was studied using X-ray photoelectron spectroscopy (XPS) by a Krato Axis Ultra DLD (delay line detector) with Al Kα radiation as the exciting source. All the binding energy was referenced to the C 1s peak at 285 eV of the surface carbon for calibration.

2.3. Photocatalytic activity

The photocatalytic activity of N-doped titanate was evaluated by the photodegradation of RhB dye under a 500 W xenon lamp