

Nitrogen-Doped Titanium(IV) Oxide Particles as a Visible-Light-Responsive Photocatalyst Prepared from Exfoliated Titanate Nanosheets

Fumiaki Amano,* Ryu Abe and Bunsho Ohtani

Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

Fax: +81-11-706-9130, e-mail: amano@cat.hokudai.ac.jp

Nitrogen-doped titanium(IV) oxide (NT) particles were synthesized from titanate nanosheets prepared by exfoliation of lepidocrocite-like layered titanate using tetrabutylammonium hydroxide. The layered composites of nanosheets with ammonium ions intercalated in the interlayer spaces, which were prepared by treatment of the nanosheets with a solution containing ammonium ion at room temperature, were transformed to anatase crystallites of titanium(IV) oxide (TiO_2) by calcination in air at 723 K. The powders exhibited a yellow color corresponding to photoabsorption in the visible region (400-500 nm) presumably due to generation of a localized dopant level within the band gap. Incorporation of nitrogen anion species was confirmed by N 1s X-ray photoelectron spectroscopy. In the case of visible light irradiation (> 400 nm), the NT particles showed photocatalytic activity for oxidative decomposition of acetic acid in the presence of iodate anion (IO_3^-) as an electron acceptor, while a commercial TiO_2 showed no photocatalytic activity under similar photoirradiation conditions. The fact that the photocatalytic reaction occurred negligibly over NT particles in the absence of IO_3^- indicates that IO_3^- acts as an electron acceptor in the visible-light-induced photocatalytic reaction and retards recombination of photogenerated carriers in the NT particles.

Key words: visible light response, anion-doping, titania nanosheets, exfoliation, delamination

1. INTRODUCTION

Titanium(IV) oxide (TiO_2) particles are known as a potential photocatalyst to drive, e.g., photocatalytic oxidative decomposition of organic compounds. Pristine anatase TiO_2 can work only under ultraviolet (UV) irradiation due to its wide bandgap of 3.2 eV. TiO_2 powders absorbing visible light (vis), such as nitrogen-doped TiO_2 (NT) particles, have been extensively investigated in order to utilize indoor light and solar light effectively.¹⁻⁷ Nitrogen doping changes the white color of TiO_2 particles to yellow. X-ray photoelectron spectroscopy (XPS) indicates the presence of nitrogen anion species in the particles.^{2,4,7,8} The vis photoabsorption is attributable to electronic excitation from a localized dopant level, which is located above the top of the valence band, composed of N 2p orbitals of nitrogen anion species.⁹⁻¹¹ NT particles exhibited vis-induced activities for photocatalytic oxidative decomposition of organic compounds, such as acetaldehyde and 2-propanol, and for degradation of dyes such as methylene blue.¹⁻⁷ However, the activity levels were still low compared with those of conventional TiO_2 photocatalysts under UV irradiation. Improvement of the vis-induced photocatalytic activities is an important issue to be resolved.

Recently, titanate nanosheets have been prepared by delamination of layered titanate

compounds into their elementary layers.^{12,13} The exfoliated nanosheets are characterized by high two-dimensional anisotropy: each layer has a thickness of less than 1 nm and lateral size of several hundred nanometers. The negatively charged titanate nanosheets are utilized for constructing hybrid nanostructures of ultrathin films or hollow shells using an electrostatic interaction.¹³⁻¹⁵ Since the titanate nanosheets are converted into TiO_2 by calcination, preparation of TiO_2 materials with novel functions and high levels of photocatalytic activity from the nanosheets is expected.

In the present study, NT particles were prepared by intercalation of ammonium ion into exfoliated titanate nanosheets followed by calcination to produce anatase TiO_2 crystallites. Different from conventional techniques of nitration, this method allows doping of nitrogen anion species in relatively large amount in the lattice and, hence, enhances vis photoabsorption and photocatalytic activity. In this paper, preparation, characteristics and results of photocatalytic activity tests under UV and vis irradiation of the NT particles are reported.

2. EXPERIMENTAL

2.1 Preparation of titanate nanosheets

Layered cesium titanate with a lepidocrocite-like crystal structure,

$\text{Cs}_x\text{Ti}_{2-x/4}\text{Z}_{x/4}\text{O}_4$ ($x \sim 0.7$; Z, vacancy), was prepared by conventional solid-state reaction of a mixture of cesium carbonate and TiO_2 at 1073 K for 2 d in air with grinding in an agate mortar after 1-d calcination. The powders were stirred in a 1-mol L^{-1} hydrochloric acid solution at room temperature for 24 h three times to convert them into layered titanic acid, $\text{H}_x\text{Ti}_{2-x/4}\text{Z}_{x/4}\text{O}_4$. Exfoliation of the layered titanic acid into titanate nanosheets ($\text{Ti}_{1-\delta}\text{O}_2^{4\delta-}$, $\delta \sim 0.09$) was performed by stirring in an aqueous solution of tetrabutylammonium (TBA) hydroxide at room temperature for at least 3 d. Subsequent centrifugation at 3000 rpm yielded a colloidal suspension containing exfoliated titanate nanosheets with surface-adsorbed TBA.

2.2 Preparation of NT particles

Three samples of NT particles (NT-A, NT-B, and NT-ST01) were prepared. The powders of layered titanic acid were stirred in a 1-mol L^{-1} ammonium hydroxide solution at room temperature for 10 h. The powders were collected by centrifugation, dried at 353 K, and calcined in air at 723 K for 2 h. The yellow-colored powder is denoted by NT-A. Sample NT-B was prepared using exfoliated titanate nanosheets as a precursor. A 1-mol L^{-1} ammonium chloride solution was added to colloidal solution of titanate nanosheets, and resultant white flocculation was washed with water and dried at 353 K. The obtained white grains were grounded in an agate mortar and calcined in air at 723 K for 2 h. Yellow-colored powders were obtained and are denoted by NT-B. Sample NT-ST01 was prepared by nitridation of commercial anatase TiO_2 powders (ST-01, Ishihara Sangyo Co.) in a gaseous ammonia stream at 823 K for 3 h according to the previously reported method.^{4,9,10}

2.3 Characterization

Brunauer-Emmett-Teller (BET) specific surface area was determined from nitrogen adsorption at 77 K on a Yuasa Ionics NOVA 1200e analyzer. Before the analyses, samples were heated at 393 K under vacuum for 2 h. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT ULTIMA diffractometer with $\text{Cu K}\alpha$ radiation. Diffuse reflection photoabsorption spectra were recorded using barium sulfate as a standard material on a JASCO V-670 spectrometer equipped with a PIN-757 horizontal-type integrating sphere. Absorption is given by $1-R$, where R represents diffuse reflection relative to barium sulfate. XPS measurements were carried out using JEOL JPS-9010MC with $\text{Mg K}\alpha$ radiation. The binding energies were calibrated to C 1s peak at 284.7 eV of surface adventitious carbon. Prior to XPS measurement, the sample pellet surface was cleaned by argon ion etching.

2.4 Photocatalytic reaction

A photocatalyst powder (50 mg) was suspended in an aqueous solution (5.0 mL) of 5vol% acetic acid under ambient air in a glass tube. The suspension was magnetically stirred at

1000 rpm during photoirradiation (> 300 nm) with a 400-W high-pressure mercury lamp (Eiko-sha). In the case of vis irradiation (> 400 nm), a cut-off filter (Kenko L42) was used in order to eliminate UV. Sodium iodide (NaIO_3) was added to the solution in some experiments. The amount of liberated carbon dioxide (CO_2) in the gas phase of a reaction mixture was measured using a TCD-gas chromatograph (Shimadzu GC-8A) equipped with a Porapak-Q column.

3. RESULTS AND DISCUSSION

3.1 Preparation and characterization of NT particles

Figure 1 shows XRD patterns of starting materials for preparation of NT-A and NT-B. The patterns of layered cesium titanate and layered titanic acid coincided with the reported data.^{16,17} Energy dispersive X-ray analysis of the layered titanic acid indicated that 90% of cesium ion was exchanged by hydrochloric acid treatment. XRD patterns of the dried product of a colloidal solution containing titanate nanosheets exhibited a set of sharp diffraction lines in a low angle region indexed as $0k0$ ($k=1, 2, 3, 4$),¹² which indicates a lamellar structure with a gallery height of 1.98 nm (Fig. 1c). The patterns are attributed to restacks of titanate nanosheets intercalated with TBA cation. Absence of hkl reflections proved exfoliation of the titanic acid into unilamellar nanosheets.

Figure 2 shows photoabsorption of TiO_2 ST-01 and the prepared samples. NT samples showed shoulder photoabsorption at around 400-500 nm. The absorption at a wavelength longer than the original band edge suggests the formation of a localized nitrogen state (N 2p level) located above the top of the valence band.^{9,11} The photoabsorption intensity of NT-B was higher than that of NT-ST01 nitridized at 723 K. The upward shift of photoabsorption at a wavelength longer than 550 nm for NT-B and NT-ST01 is attributable to oxygen vacancies, i.e., Ti^{3+} state located below the bottom of the conduction band.¹¹

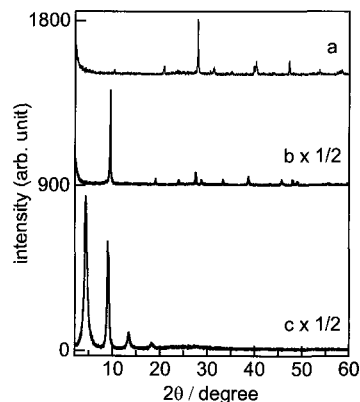


Fig.1 XRD patterns of (a) layered cesium titanate, (b) layered titanic acid, and (c) dried product of exfoliated titanate nanosheets with TBA hydroxide.

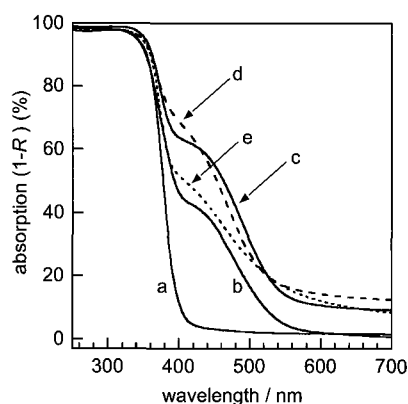


Fig.2 Diffuse reflection photoabsorption spectra of (a) ST-01, (b) NT-A, (c) NT-B, (d) NT-ST01, and (e) NT-ST01 nitrized at 723 K.

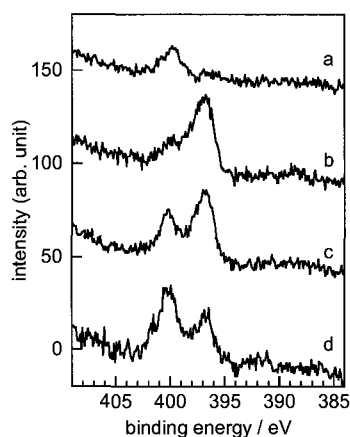


Fig.3 XPS peaks of N 1s region of (a) ST-01, (b) NT-A, (c) NT-B, and (d) NT-ST01.

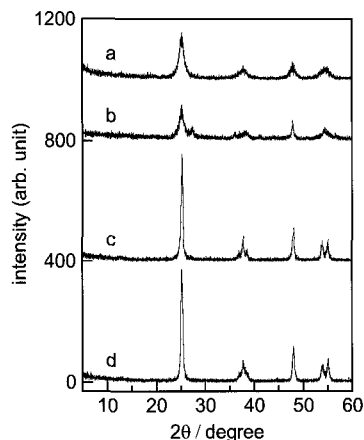


Fig.4 XRD patterns of (a) ST-01, (b) NT-A, (c) NT-B, and (d) NT-ST01.

In the XPS spectra (Fig. 3) of the argon-ion etched NT-samples, there are two peaks located at around 400 and 397 eV in N 1s region peaks. Since oxidized nitrogen species, nitrates and nitrites, may give high-binding-energy peaks (> 400 eV), the oxidation state of the nitrogen species seems to be relatively low. The peak at 400 eV, which was attributed to less negatively charged nitrogen species,⁸ was also observed for ST-01. The peak at 397 eV was attributed to

nitrogen anion species substituting oxygen in the anatase TiO_2 lattice.^{2,4,8} The peak area of 397 eV to the total N 1s area was decreased in the order NT-A $>$ NT-B $>$ NT-ST01. Therefore, it is thought that the present method using intercalation of ammonium cations in titanate layers is effective for doping of a large amount of nitrogen as an anionic species.

Figure 4 shows XRD patterns of samples. All the peaks were assigned to anatase TiO_2 , though the peaks of ST-01 and NT-A were broadened. An exception is the pattern of NT-A, which contained impurity peaks in addition to the anatase peaks. The high height and the small width of peaks for NT-B and NT-ST01 indicate the larger size of crystallites.

3.2 Photocatalytic activity of NT particles

Photocatalytic activities of NT samples were investigated using photocatalytic oxidative decomposition of acetic acid in an aerated aqueous solution. Figure 5 shows CO_2 liberation from the NT-B suspension under vis irradiation (> 400 nm). In the absence of NaIO_3 , the photocatalytic reaction occurred negligibly under vis irradiation: the amount of liberated CO_2 was comparable to that in the dark due to possible thermal decomposition of acetic acid. On the other hand, a monotonic increase in the amount of CO_2 with vis irradiation was observed in the presence of iodate ion, i.e., electron transfer to iodate ion inhibits recombination of electron and hole pairs.

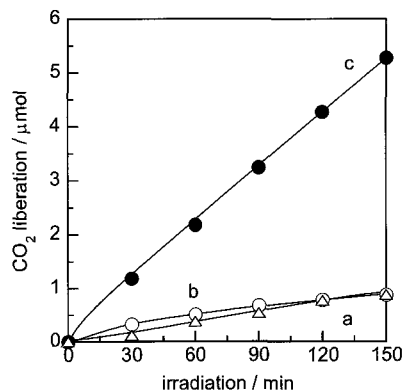


Fig.5 CO_2 liberation from aqueous NT-B suspensions containing acetic acid (a) in the dark and under vis irradiation (> 400 nm) without (b) and with (c) NaIO_3 .

Table I summarizes the results of photocatalytic oxidative decomposition of acetic acid under UV-vis and vis irradiation. NT samples photocatalyze the decomposition of acetic acid under UV-vis irradiation. It has been reported that the photocatalytic activity under UV irradiation was decreased by nitrogen doping to TiO_2 due to the generation of oxygen vacancies.⁴ Such vacancies work as a recombination center of photoinduced electron and hole pairs. Actually, the photocatalytic activity level of NT-ST01 was lower than that of ST-01, presumably due to not only the generation of oxygen vacancies but also

decrease in specific surface area. The activity level of NT-A was much lower than that of NT-B, because the crystallinity of NT-A particles is low. Despite the smaller surface area, NT-B exhibited a higher level of activity than that of NT-ST01.

Table I. BET specific surface area (S_{BET}), total nitrogen content determined by XPS measurement, and rate of CO_2 liberation in photocatalytic oxidative decomposition of acetic acid.

sample	S_{BET} / m^2 g^{-1}	N content (%)	$r(\text{CO}_2)^a$ / μmol h^{-1}	$\text{vis-}r(\text{CO}_2)^b$ / $\mu\text{mol h}^{-1}$	
				without IO_3^-	with IO_3^-
ST-01	319	0.8	25.8	0.25	0.45
NT-A	29.6	2.0	9.3	0.25	0.83
NT-B	36.8	2.2	23.4	0.27	2.00
NT-ST01	87.4	2.5	18.3	0.29	4.37

^aPhotocatalytic activity under UV-vis irradiation (> 300 nm). ^bPhotocatalytic activity under vis irradiation (> 400 nm) without and with iodate ions.

Under vis irradiation without iodate ions, negligible photocatalytic activity was observed for all samples. The vis-responsive photocatalytic activity with iodate ions was increased in the order NT-A < NT-B < NT-ST01. The low activity level of NT-A is probably due to the low crystallinity also in this case. Since undoped ST-01 could not induce appreciable CO_2 liberation, it was concluded that the vis-responsive activity was derived from the vis photoabsorption of NT particles.

It has been revealed that positive holes produced by vis absorption of NT particles and trapped in the localized nitrogen states have poor reactivity toward organic compounds due to their low mobility.^{9,10} Negligible vis-induced photocatalytic activity without iodate ions suggests that the rate of recombination of photogenerated carriers is much faster than the reaction rates of the trapped holes with acetic acid and of photoexcited electrons with molecular oxygen. Rapid consumption of photoexcited electrons by iodate ions resulted in extension of the lifetime of trapped holes escaping from recombination. Although the UV-responsive photocatalytic activity level of NT-B was high, its vis-responsive activity level was lower than that of NT-ST01, suggesting lower mobility of holes trapped in the localized nitrogen state in NT-B. A stronger localized nature of the nitrogen state in NT-B particles is suggested by the clear structure of a photoabsorption shoulder around the vis region.

4. CONCLUSION

NT particles were prepared by calcination of layered composites obtained by electrostatic interaction of exfoliated titanate nanosheets with ammonium ions. The particles contained nitrogen anion species in the lattice, and the amount was larger than that of NT particles prepared by the conventional nitrization method at the same temperature. These NT particles exhibited

vis-induced photocatalytic activity for acetic acid decomposition in the presence of iodate ions. Iodate ions act as an electron acceptor to retard recombination of photoexcited electrons and holes trapped in the localized nitrogen state.

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