

Preparation of Visible Light-Activated Titania Photocatalyst by Mechanochemical Method

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(Received November 22, 2002; CL-020998)

Nitrogen-doped yellowish rutile titania prepared by high energy ball milling of P-25 titania - 5% HMT (Hexamethylenetetramine, $C_6H_{12}N_4$) mixed powders followed by calcination in air at 400 °C possessed two absorption edges around 400 and 540 nm and showed excellent photocatalytic ability for nitrogen monoxide oxidization under irradiation of the visible light of wavelength > 510 nm.

Titania nanocrystals have attracted increasing attention because of its wide applications in many fields especially in photochemical research.^{1,2} Under light irradiation, titania photocatalyst can decompose many pollute substances, such as poisonous nitrogen monoxide in atmosphere and/or organic pollutants in water. Although three of titania polymorphs, rutile, anatase, and brookite have been occurred in nature, few researches have been carried out on brookite. Usually, only anatase and rutile titania are utilized as photocatalyst. It is reported that anatase shows higher photocatalytic activity than that of rutile.^{3,4} The enhancement is ascribable to the differences of the Fermi level and the extents of surface hydroxylation of the solid.⁴ In addition, rutile usually showed harder agglomeration and larger particle size than those of anatase since rutile is normally prepared by calcination of anatase at high temperatures. A problem in application of anatase as photocatalyst is the large band gap energy, i.e. anatase only shows photocatalytic activities under UV light irradiation of wavelength < 387 nm, which corresponds to its band gap value of 3.2 eV. It is known that solar energy only contains about 5% of UV light and large parts of the rest are visible light. In order to utilize the solar energy efficiently, it is necessary to develop a visible light reactive photocatalyst. Asahi et al.⁵ reported that nitrogen doped titanium oxide with high visible light photocatalytic activity could be prepared by sputtering TiO_2 target in an N_2 (40%) Ar gas mixture followed by annealing in N_2 gas at 550 °C for 4 h. It was observed that nitrogen doped titania was yellow. Ihara et al.⁵ reported that visible light-activated titania could also be prepared by RF plasma treatment. Recently, mechanochemical technology has become a promising method for material synthesis, surface modification, waste processing and recycling etc. In many cases, the mechanical stressing induces the formation of fresh oxygen-rich surface, results in the electron transfer from O^{2-} ion on oxide surface to other organic substance, and as a result, leads to the destruction of weak bonding in organic substance and the formation of new bonding between oxide and nonmetallic element.^{7,8} In the present study, rutile titania powder with visible light activity was prepared by the mechanochemical reaction. It is a novel process for the synthesis of nitrogen doped titania photocatalyst.

Commercial titania powder P-25 (Degussa) was used as a raw material. Hexamethylenetetramine (HMT) and urea (Kanto Chem. Co. Inc., Japan) were used as nitrogen sources. P-25 titania powder was mixed with 5 wt% HMT or 10 wt% urea before introduced into

reaction pot. A planetary ball mill (Fritsch Pulverisette 7, Germany) was used for grinding of the samples. Seven zirconia balls of 15 mm diameter and 4 grams of mixtures were introduced to a zirconia pot of 45 cm^3 inner volume. The grinding was operated at 700 rpm of rotation speed for 1 h. The phase constitution of the products was determined by X-ray diffraction analysis (XRD, Shimadzu XD-D1). The absorption edges and band gap energies of the products were determined from the onset of diffuse reflectance spectra of the sample measure using an UV-vis spectrophotometer (Shmadzu UV-2000). The photocatalytic activity for nitrogen monoxide oxidization was determined by measuring the concentration of NO gas at the outlet of the reactor [373 cm^3] during the photo-irradiation of constant flowed 1 ppm NO-50 vol% air mixed (balance N_2) gas [200 cm^3/min]. The photocatalyst sample was placed in a hollow place of 20 × 15 × 0.5 mm on a glass holder plate and set in the center of the reactor. A 450-W high-pressure mercury lamp was used as the light source, where the light wavelength was controlled by selecting various filters, i.e., Pyrex glass for cutting off the light of wavelength < 290 nm, Kenko L41 Super Pro (W) filter < 400 nm and Fuji, triacetyl cellulose filter < 510 nm.

Figure 1 shows the XRD patterns of the starting P-25 powder and the samples prepared by the mechanochemical reaction. The P-25 titania consists of about 70 wt% anatase phase and 30 wt% rutile phase. After planetary ball milling with urea and HMT at

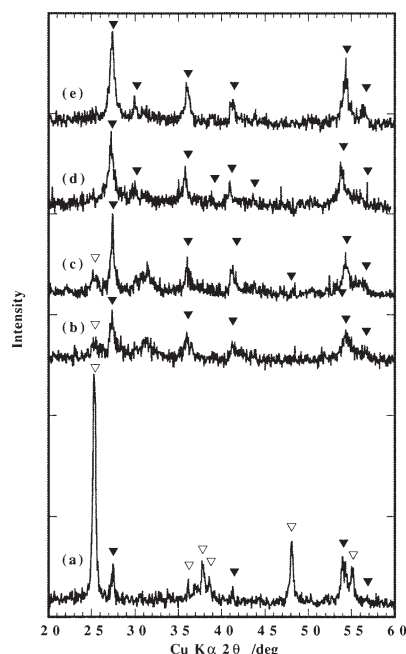


Figure 1. XRD patterns of the prepared samples. (a) P-25 titania; (b) planetary milled P-25 - 10 wt% urea mixture at 700 rpm for 1 h; (c) calcined (b) in air at 400 °C for 1 h; (d) planetary milled P-25 - 5 wt% HMT mixture at 700 rpm for 1 h; (e) calcined (d) in air at 400 °C for 1 h. (▽)anatase, (▼)rutile.

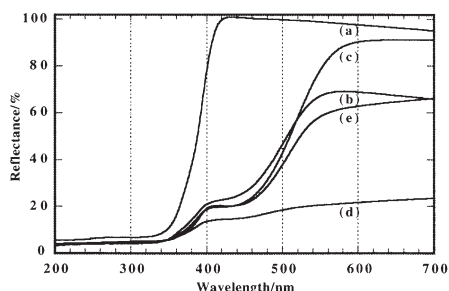


Figure 2. Diffuse reflectance spectra of the prepared samples. (a) P-25 titania; (b) planetary milled P-25 - 10 wt% urea mixture at 700 rpm for 1 h; (c) calcined (b) in air at 400 °C for 1 h; (d) planetary milled P-25 - 5 wt% HMT mixture at 700 rpm for 1 h; (e) calcined (d) in air at 400 °C for 1 h.

700 rpm for 1 h, the peak intensity of anatase greatly decreased and the samples mainly consisted of rutile. Usually, anatase transforms to rutile at high temperature such as 700 °C in air. These results indicated that high mechanical energy accelerated the phase transformation of anatase. TG-DTA analysis indicated that residual organic substances burned out at about 395 °C, therefore the prepared samples were calcined at 400 °C for 1 h. After calcination, the crystallinity of rutile increased.

Figure 2 shows the diffuse reflection spectra of P-25 titania powder and the samples prepared by mechanochemical reaction. The P-25 titania possessed an absorption edge at 405 nm corresponding to the band gap of 3.1 eV (Figure 2-(a)). No change was observed after calcination of P-25 in air at 400 °C. The powder prepared by planetary milling of P-25 TiO₂ - 10% urea mixture was yellow-green, indicating the formation of nitrogen doped titania during the planetary milling. It is obvious that nitrogen doped rutile titania prepared in the present study showed two absorption with the onsets of diffuse reflectance spectra of 402 nm [3.1 eV] and 543 nm [2.3 eV] (Figure 2-(b)). While the powder after calcination was bright-yellow with larger absorption and the second absorption edge shifted to around 562 nm [2.2 eV] (Figure 2-(c)). Instead of urea, when the powders was prepared by planetary milling of P-25 TiO₂ - 5% HMT mixture, the product was black-gray and also showed two absorption edges at 400 nm [3.1 eV] and 520 nm [2.4 eV] (Figure 2-(d)). The powders after calcination was dark yellow with larger absorption and the second absorption edge shifted to around 542 nm [2.3 eV] (Figure 2-(e)). The black-grayish color is thought to be caused by the decomposition of HMT during grinding. It might suggest that C-H bond and C-N bond in HMT were destroyed to form carbon during the planetary milling. After calcination at 400 °C, carbon content decreased, and the powder was dark yellow which related to the formation of nitrogen doped TiO₂.

Figure 3 shows the relationship between wavelength of light source and photocatalytic ability for the oxidation of nitrogen monoxide. It is accepted that titania particles absorb light of energy greater than the band gap energy to generate electron/hole pairs. In the presence of oxygen, the electrons in the conduction band are trapped rapidly by the molecular oxygen to form $\cdot\text{O}_2^-$, which can then generate high active $\cdot\text{OOH}$ radicals.^{9,10} The NO reacts with these reactive oxygen radicals, molecular oxygen, and water to produce HNO₂ or HNO₃. It is obvious that the yellowish nitrogen doped titania possessed visible light photocatalytic activity. Under the irradiation of visible light of wavelength > 510 nm, nearly 27% of nitrogen monoxide could be continuously removed by the nitrogen doped titania that prepared by

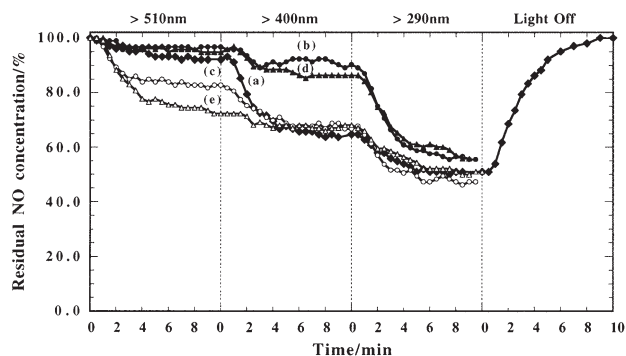


Figure 3. The relationship between light wavelength and the photocatalytic ability for the oxidation of nitrogen monoxide of the prepared samples. (a) \blacklozenge : P-25 titania; (b) \bullet : planetary milled P-25 - 10 wt% urea mixture at 700 rpm for 1 h; (c) \circ : calcined (b) in air at 400 °C for 1 h; (d) \blacktriangle : planetary milled P-25 - 5 wt% HMT mixture at 700 rpm for 1 h; (e) \triangle : calcined (d) in air at 400 °C for 1 h.

planetary milling of P-25 titania - 5% HMT mixture followed by calcination in air at 400 °C. The powders prepared by planetary milling of P-25 titania - 10% urea mixture showed lower activity than that with 5% HMT. On the other hand, the photocatalytic activity under visible light irradiation of the powders as-prepared without calcination was negligibly small. It may be due to the depression of NO adsorption by the remaining reaction products such as CO₂, NH₃, carbon, organic molecules, etc. In addition, as expected, no photocatalytic activity was observed for P-25 because of its large band gap energy of 3.1 eV. In the case of irradiation of the light of wavelength > 400 nm, similar results were observed, i.e., photocatalytic activity of the powders after calcination ((c) and (e): 30-33%) were larger than those before calcination ((b) and (d): 10-12%). Under near-UV light irradiation of wavelength > 290 nm, about 43%-53% of nitrogen monoxide could be removed. The activities of the powders after calcination ((c) and (e)) showed almost the same level as that of P-25 TiO₂ but slightly higher than those before calcination((b) and (d)). When the light was turned off, it was obvious that nitrogen concentration at the outlet of the reactor returned to initial concentration of 1 ppm within 10 min, indicating that light energy is necessary for the oxidation of nitrogen monoxide.

Based on the above results, it might be suggested that nitrogen doped rutile phase titania prepared by mechanochemical reaction possessed excellent visible light photocatalytic activity. The mechanochemical technology might be an effective method for nonmetallic element doping to oxides.

This work was partly supported by a grant in aid for Science Research (No. 14750660) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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