Enhanced Visible Light Sensitivity of Nitrogen-doped Nanocrystalline Si-modified Titania Prepared by the Glycothermal Method

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Nanocrystalline silica-modified titania prepared by the thermal reaction of titanium tetraisopropoxide and tetraethyl orthosilicate in 1,4-butanediol was treated in an NH_3 flow at high temperatures. The thus-obtained nitrogen-doped silica-modified titania showed a strong absorption in the visible region (400–500 nm) and exhibited a high photocatalytic activity for decomposition of acetaldehyde under visible light irradiation.

The photocatalytic and photoelectrochemical applications of semiconductor materials have attracted great attention. Among various photocatalyst materials, titanium dioxide (TiO_2) has been most widely used and investigated,[1,2] because it has advantages in inexpensiveness, chemical stability, and nontoxicity in addition to its favorable optoelectronic property. However, the band gap of anatase TiO_2 is 3.2 eV; therefore, the photocatalytic reaction proceeds only by irradiation of ultraviolet (UV) light (wavelength (λ) < 388 nm), which means only about 3% of the incoming solar energy on the earth's surface can be utilized. In recent years, a number of attempts have been made to expand the photosensitivity of TiO_2-based photocatalysts into the visible-light region. One approach is doping of transition metal cations such as Cr, V, and Fe.[3–6] However, the introduction of these cations causes an increase in the population of recombination centers. Another approach is use of anionic species, such as C, N, F, and S.[7–13]

We previously reported that the thermal reactions of titanium tetraisopropoxide (TIP) and tetraethyl orthosilicate (TEOS) in 1,4-butanediol afforded nanocrystalline silica-modified titania with the anatase structure having large surface areas and superior thermal stabilities.[14] The thus-obtained silica-modified titania showed high activities for photocatalytic oxidation of acetic acid.[15] In this paper, the silica-modified titania was heated in an NH_3 flow at high temperatures and their photocatalytic activities under visible light irradiation were examined.

Titania and silica-modified titania were prepared by the glycothermal method and collected as a xerogel form.[15] The xerogels were calcined in a box furnace in air at 500 °C for 30 min to remove the surface organic moieties. The thus-obtained products are designated as XG(x), where x is the Si/Ti charged ratio. The product was heated to a desired temperature in an argon flow and then treated in an NH_3 flow (100 mL/min) for 1 h. After the NH_3 treatment, the sample was annealed in air in a box furnace at 400 °C for 30 min in order to eliminate the NH_3 adsorbed on the catalyst. JRC-TIO-4 (equivalent to Degussa P-25) was nitrified in the same way. The BET surface areas of XG(0), XG(0.1), and JRC-TIO-4 were 81, 152, and 51 m^2/g, and after the nitrification and the annealing they decreased slightly to 70, 149, and 46 m^2/g, respectively.

Photocatalytic activity was evaluated by photodecomposition of acetaldehyde. The catalyst (0.2 g) dispersed on a 90 mmϕ glass filter was placed in a closed glass vessel (1.0 L) and then 0.2 mmol of acetaldehyde was injected in the vessel. The vessel was placed in the dark for 1 h, and then irradiated with visible light was applied using a 300 W xenon lamp equipped with a UV cut-off filter ($<$420 nm) and an infrared cut-off filter ($>$1050 nm). After a certain period of irradiation time, the concentration of generated CO_2 was measured by gas chromatography.

White powders of the mother TiO_2, XG(0), turned into gray, dark blue and black by the NH_3 treatment at 600, 650, and 700 °C, respectively, and the colors of NH_3-treated XG(0.1) were vivid yellow, yellowish-green, and dark blue, respectively. Figure 1 shows the UV–vis absorption spectra of XG(0) and XG(0.1) nitrified (i.e., treated in NH_3 at 600 °C for 1 h followed by annealing at 400 °C in air). Whereas XG(0) exhibited an absorption only in the UV region ($<$400 nm), the nitrified samples have a shoulder absorption band at 400–500 nm and a broad band at higher wavelength ($>$500 nm). The former band is attributed to the nitrogen doped into the anatase structure, and the latter corresponds to the formation of Ti^{3+}.[16] Apparently, nitrified XG(0.1) had a stronger absorption at 400–500 nm and a weaker absorption at higher wavelength than nitrified XG(0). The latter result indicates that the formation of Ti^{3+} was significantly suppressed by the silica modification. By XRD measurement (data not shown), only diffraction peaks for anatase were observed for XG(0) and XG(0.1) after NH_3 treatment at 600 °C for 1 h. On the other hand, the NH_3 treatment at 700 °C resulted in the formation of TiN with the rock salt structure. The intensities of the peaks of the rock salt structure were quite low for NH_3-treated XG(0.1), which supports the argument that the formation of Ti^{3+} was suppressed by the silica modification.

As shown in Figure 2 (inset), the N1s XPS spectrum of

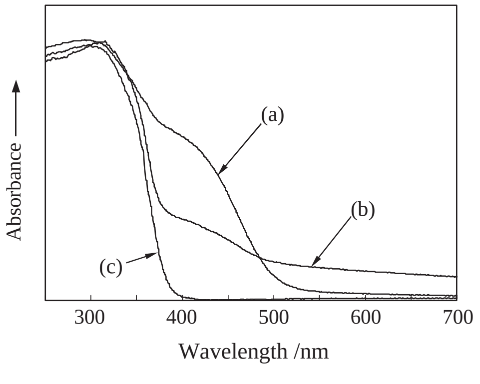

Figure 1. UV–vis spectra of: (a), XG(0.1); (b), XG(0); treated in an NH_3 flow at 600 °C for 1 h and annealed in air at 400 °C for 30 min, and (c), XG(0).

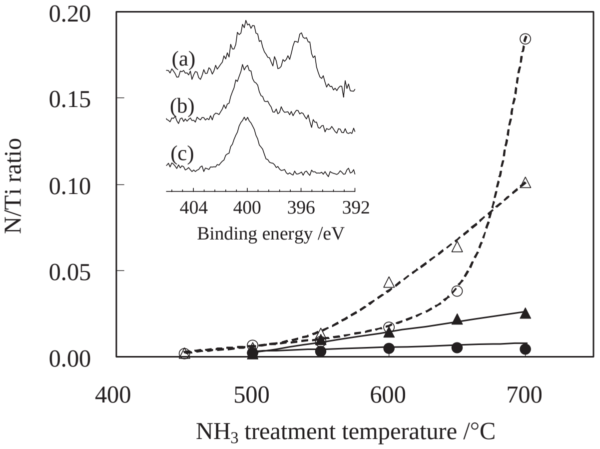

Figure 2. N/Ti ratios of the NH_3-treated samples determined by XPS: (△), XG(0.1); (○), XG(0); treated in an NH_3 flow at various temperatures for 1 h: (●), XG(0.1); (▲), XG(0); annealed in air at 400 °C for 30 min after NH_3 treatment. The inset shows N1s XPS spectra of: (a), XG(0.1); (b), XG(0); treated in an NH_3 flow at 600 °C for 1 h and annealed in air at 400 °C for 30 min, and (c), XG(0).

XG(0) (or XG(0.1); data not shown) without the NH_3 treatment exhibited a peak at 400-eV binding energy (BE), which is due to nitrogen adsorbed on the surface.[17] On the other hand, after the NH_3 treatment, another peak appeared at 396 eV BE, which is assigned to nitrogen doped in TiO_2. The intensity of the peak at 396 eV in nitrified XG(0.1) was larger than that of nitrified XG(0). The N/Ti ratios calculated from the intensities of the Ti and $N_{396\,eV}$ peaks are plotted as a function of the NH_3 treatment temperature (Figure 2). The N/Ti ratio increased with an increase in the treatment temperature, and NH_3-treated XG(0.1) showed higher N/Ti ratios at temperature up to 650 °C than NH_3-treated XG(0). However, at 700 °C the N/Ti ratio of NH_3-treated XG(0) significantly increased and became higher than that of NH_3-treated XG(0.1). This enhancement is due to the formation of TiN, as was observed by XRD. After annealing at 400 °C, the N/Ti ratio decreased in both the samples. This result indicates that annealing at 400 °C resulted in not only the desorption of the adsorbed NH_3 but also the denitrification of the samples. Here, it should be emphasized that the N/Ti ratios of nitrified XG(0.1) were several times higher than those of nitrified XG(0), suggesting that nitrogen atoms were more stably doped in silica-modified titania than in titania, XG(0).

Figure 3 shows the results of photocatalytic decomposition of acetaldehyde on the samples. Under visible light irradiation, evolution of CO_2 was not detected for XG(0). On the other hand, nitrified XG(x)'s exhibited photocatalytic activities. Nitrified XG(0.1) obviously showed higher photocatalytic activity than nitrified XG(0) and JRC-TIO-4. Although XG(*x*) had larger surface areas, the difference in surface area is not the dominant factor for the photocatalytic activity because the photocatalytic reaction in this study was carried out in a condition of a high concentration of the reactant under weak visible light irradiation. Therefore, we concluded that the enhanced photocatalytic activity of nitrified silica-modified titania is brought about by the increase in absorption at 400–500 nm, which in turn is due to the increase in the amount of doped nitrogen without the formation of Ti^{3+}.

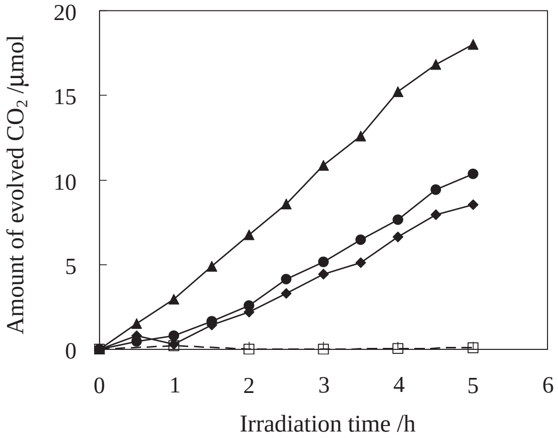

Figure 3. Photocatalytic decomposition of acetaldehyde under visible light irradiation: (▲), XG(0.1); (●), XG(0); (◆), JRC-TIO-4; treated in an NH_3 flow at 600 °C for 1 h and annealed in air at 400 °C for 30 min, and (□), XG(0).

In summary, NH_3 treatment at high temperatures nitrified both of TiO_2 and silica-modified titania. After NH_3 treatment and annealing, the amount of nitrogen introduced to the silica-modified titania was higher than that of pure titania. The thus-obtained nitrified silica-modified titania showed a strong absorption in the visible region (400–500 nm) and exhibited high photocatalytic activities for decomposition of acetaldehyde under visible light irradiation.

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