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Photocatalytic activities of NH_3-treated titanias modified with other elements

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Abstract

Nanocrystalline titanias were obtained by thermal reaction of titanium tetraisopropoxide in 1,4-butanediol (glycothermal reaction). In this study, titanias modified with various elements (B, Mg, Al, P, Zn, and Ga) were prepared by the glycothermal method. The obtained samples were nitrified and their physical and photocatalytic properties were investigated. Among the six modifiers examined, addition of P was the most effective for photocatalytic decomposition of acetaldehyde under visible-light irradiation. After nitrification and annealing, the P-modified titania showed a strong absorption in the visible region (400–550 nm). It was found that the photocatalytic activity was related to the amount of nitrogen atoms doped in the anatase structure.

Keywords: Visible-light photocatalyst; Nitrogen-doping; Nanocrystals; Glycothermal method

1. Introduction

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.

The visible-light responsibility of nitrogen-doped TiO_2 material was reported by Sato for the first time in 1986 [3], and recently, several groups reported the visible-light responsibility of N-doped TiO_2 materials prepared by different methods [4–9]. Co-doping of nitrogen and other elements into TiO_2 have been also examined to improve photocatalytic activity under visible-light irradiation [10–13]. Sakatani et al. prepared metal ion-and-nitrogen co-doped titanias by a polymerized complex method and found that the photocatalyst prepared with Sr^{2+} exhibited high activity for decomposition of acetaldehyde under visible-light irradiation [11]. They reported that Sr^{2+} is distributed uniformly in the TiO_2 lattice and that the formations of Ti^{3+} and lattice defects were suppressed by the optimum dosage of Sr^{2+} [11]. Wei et al. investigated the preparation and photocatalysis of TiO_2 powder co-doped with La^{3+} and N [13] and found that the 0.5% La^{3+}-doped TiO_2 treated in an NH_3 flow exhibited superior catalytic activity for degradation of methyl orange under visible-light irradiation. They reported that the recombination of the carriers could be prevented by co-doping [13]. However, these co-doped titanias showed a weak absorption in the visible region (400–500 nm), indicating that only small amounts of nitrogen atoms were introduced into the TiO_2 lattice.

We previously reported that the thermal reactions of titanium tetraisopropoxide (TIP) and tetraethyl orthosilicate (TEOS) in 1,4-butanediol (glycothermal reaction) afforded nanocrystalline silica-modified titanias with the anatase structure having large surface areas and superior thermal stabilities [14]. The obtained silica-modified titanias were characterized by XPS and XANES, and it was found that the Si atoms are inserted in the distorted octahedral vacant sites of the anatase structure [15]. Recently, we examined the nitrification of the silica-modified titanias and found that the titanias co-doped with Si and N showed a strong absorption in the visible region (400–500 nm) and exhibited high photocatalytic activities for degradation of RhB and decomposition of acetaldehyde

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under visible-light irradiation [16]. In the present paper, the titanias modified with other elements (B, Mg, Al, P, Zn, and Ga) were prepared by the glycothermal method and the nitrification of the products was investigated. The photocatalytic decomposition of acetaldehyde by using the obtained co-doped titanias under visible-light irradiation was also examined.

2. Experimental

2.1. Preparation of the catalysts

Titania and modified titania samples were prepared by the glycothermal method and the products were collected as a xerogel form [17]: TIP (25 g) and one of the modifiers were added to 100 mL of 1,4-butanediol (1,4-BG). As the modifiers, trimethyl borate, magnesium acetate tetrahydrate, aluminum triisopropoxide, triethyl phosphate, zinc diacetylacetonate, and gallium triacetylacetonate were used for B, Mg, Al, P, Zn, and Ga, respectively. This mixture was placed in a 300 mL autoclave equipped with two valves, one of which was used as a gas inlet and the other was connected to a Liebig condenser of stainless steel tubing. After the atmosphere inside the autoclave was replaced with nitrogen, the assembly was heated to 300 °C at a rate of 2.3 °C/min and kept at that temperature for 2 h. After the glycothermal reaction, the valve of the autoclave was slightly opened in order to remove the organic vapor from the autoclave by flash evaporation while keeping the autoclave temperature at 300 °C. After cooling, bulky solid product was directly obtained. The product was 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 M–XG(x), where M represents the element used for the modification and x is the M/Ti charged ratio. The product without any modifiers is designated as XG(0).

The nitrification was carried out as follows: a portion of XG(0) or M–XG(x)'s was placed in a quartz tube and the atmosphere inside was purged with an Ar flow (100 mL/min). The sample was heated to 600 °C at a rate of about 10 °C/min in the same flow of argon, and then the gas flow was replaced by an NH_3 flow (100 mL/min). The sample was kept at 600 °C for 1 h and then cooled. After the NH_3 treatment, the sample was annealed at 500 °C in air for 30 min using a box furnace. The thus-obtained nitrified and annealed products are designated as N–XG(0) or N–M–XG(x). As a reference TiO_2, JRC–TIO-4 (equivalent to Degussa P-25; rutile/anatase = 3/7; BET surface area = 49 m^2/g) was used. The JRC–TIO-4 nitrified in the same way is designated as N–JRC–TIO-4.

2.2. Characterization

The UV–vis absorption spectra of the samples were recorded on a Shimadzu MPS-2000 spectrophotometer. Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-D1 diffractometer using Cu Kα radiation and a carbon-monochromator. The specific surface areas of the samples were calculated by the BET single-point method on the basis of the nitrogen uptake measured at 77 K using a Micromeritics Flowsorb II 2300. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ULVAC-PHI Model 5500 spectrometer with 15 kV to 400 W Mg Kα emission as the X-ray source.

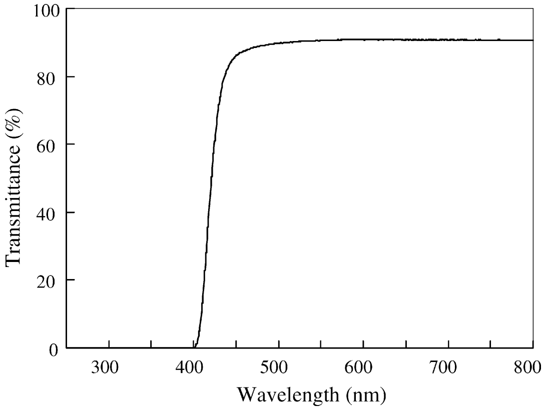

Fig. 1. Transmission spectrum of the UV cut-off filter (L-42).

2.3. Photocatalytic reaction

Decomposition of acetaldehyde was carried out to evaluate the photocatalytic activities of the samples. The catalyst (0.2 g) dispersed on a 90 mm ϕ glass filter was placed in a closed glass vessel (1.0 L) and 0.2 mmol acetaldehyde was injected in the vessel. The vessel was placed in the dark for 1 h, and then visible light was irradiated using a 300 W xenon lamp (Optical Modulex SX-UI300XQ, Ushio Inc.) through a UV cut-off filter (L-42, Asahi Technoglass Co. Ltd.) and an infrared cut-off filter (Super Cold Filter, Ushio Inc.). As shown in Fig. 1, ultraviolet light under 400 nm was cut-off by the UV-filter. After a certain period of irradiation time, the concentration of generated CO_2 was measured by a gas chromatograph, Shimadzu GC-8A.

3. Results and discussion

3.1. Physical properties and photocatalytic activities of N–M–XG(0.1)

In Fig. 2, XRD patterns of M–XG(0.1) as well as TiO_2 without modification, XG(0), are depicted, which show that the products with the anatase structure formed. After nitrification, the XRD patterns of the samples did not change significantly, and no other crystalline phases were observed for N-Mg-XG(0.1) and N-Zn-XG(0.1), and N-Zn-XG(0.1). However, small peaks due to $MgTiO_3$ and $Zn_2Ti_3O_8$ were detected for N–Mg–XG(0.1) and N–Zn–XG(0.1). The physical properties of the nitrified samples are summarized in Table 1. All the nitrified samples had large surface areas; especially, N–Al–XG(0.1) and N–P–XG(0.1) had quite large surface areas, 106 and 102 m^2/g, and small crystallite sizes, 10 and 14 nm, respectively. The surface areas of N–Zn–XG(0.1) and N–Ga–XG(0.1) were smaller than those expected from the crystallite sizes, which may be due to the presence of an amorphous phase on the surface of the nanocrystals of anatase.