Electronic state of nitrogen in doped titanium dioxide

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Abstract. A yellow N-doped TiO₂ powder was prepared by the sol-gel method using titanium tetra-isopropoxide and hydrazine monohydrate. An EPR signal was induced by the irradiation of light with \( h \nu \geq 2.2 \text{ eV} \) to the yellow TiO₂ powder and the signal intensity gradually decreased in the dark. The EPR signal was due to thermally trapped carriers interacting with the doped N. The thermal activation energy of the trapped carriers was estimated to be 0.22 eV. XPS measurement was performed on the yellow powder as well as colorless and blue N-doped powders obtained by oxidation and reduction, respectively. The N1s bands at 399.5 eV can be assigned to nitrogen adsorbed on the surface. The atomic valence of nitrogen in the colorless, yellow and blue powders was positive, neutral and negative, respectively. The atomic valence of nitrogen in doped TiO₂ depends on the oxidation-reduction procedure.

1. Introduction

Titanium dioxide is a UV-driven photocatalytic material in practical use, whose valence and conduction bands are mainly formed by oxygen 2p and titanium 3d orbitals, respectively. The irradiation of UV light excites the valence electrons to the conduction band, resulting in the generation of holes in the valence band. The photogenerated holes and electrons contribute to the oxidation and reduction reactions at the surface, respectively. A first-principles calculation indicated that N-doped anatase titanium dioxide has an optical absorption band slightly below the band gap and is yellow [1]. Therefore, it is expected that such N-doped titanium dioxide can be used as a visible-light-sensitive photocatalyst. We have investigated the properties of anatase titanium dioxide, particularly its defects and impurities [2, 3]. As-grown anatase single crystals grown by chemical vapor transport with NH₄Cl as a transport agent generally exhibited a pale blue color. Yellow or colorless single crystals were obtained by heat treatment of the pale blue crystals in oxygen. Reduction of the colorless crystals in a hydrogen gas flow resulted in a change in their color to pale blue. This reversible change in the crystalline color depending on the oxidation-reduction procedure appears to be due to the effect of impurities and/or a variety of defects. Optical absorption measurement shows that an absorption band at 2.9 eV is a characteristic of the yellow crystal but cannot be observed in colorless and pale blue crystals [2]. Electron paramagnetic resonance (EPR) measurement of the yellow crystals revealed the presence of a pair of EPR triplets and the inclusion of nitrogen as an impurity [3]. The nitrogen impurity does not detach from the crystal during the heat treatments for oxidation and reduction. Thus, the colorless and pale blue crystals must also include nitrogen. Therefore, the dependence of the change in the electronic state of nitrogen on the heat treatment is of interest. To investigate the electronic state of doped nitrogen in crystals with different colors, we prepared a titanium dioxide powder rich in nitrogen by the sol-gel method and measured its EPR and X-ray photoelectron spectroscopy (XPS) spectra.
2. Experimental
N-doped anatase titanium dioxide powders were obtained by the sol-gel method. Titanium tetraisopropoxide and hydrazine monohydrate were dissolved in ethanol. The solution was stirred and refluxed at 80 °C for 3 h to obtain a precipitate. The precipitate was dried at room temperature and heated in an ammonia gas flow. Finally, a yellow powder was obtained by calcination at 500 °C. A colorless powder was also obtained by heat treatment of the yellow powder at 650 °C for 1 h in air. Reduction of the colorless powder at 650 °C for 1 h in a hydrogen gas flow resulted in a change in its color to blue.

X-ray diffraction (XRD) spectra of the powders were obtained using a SmartLab diffractometer (Rigaku). The diffusion reflectance was measured by a UV365 spectrometer (Shimadzu). EPR measurement with visible-light irradiation was performed on the yellow powder using a JES-FA200 spectrometer (JEOL). Resonance field and microwave frequency were calibrated using a R5372 microwave counter (Advantest) and an ES-FC5 NMR field meter (JEOL). The temperature of sample was provided by an ES-DVT4 thermal controller (JEOL). A tungsten lamp was used as the light source. XPS measurement was performed on the yellow, colorless and blue powders using a Quantera SXm-II spectrometer (ULVAC-PHI).

3. Results and Discussion

3.1. Heat treatment of sol-gel-derived powders
XRD measurement revealed that the sol-gel-derived yellow powder is composed of anatase TiO$_2$ single phase. After the heat treatment, a partial phase transition to rutile was observed. The fraction of the anatase phase was estimated to be 0.821 and 0.599 in the colorless and blue powders, respectively. In the diffusion reflectance spectra, a decrease in reflectance corresponding to the absorption band at 2.9 eV was observed in the yellow powder. The band disappeared after the heat treatment for oxidation or reduction. The diffusion reflectance spectra indicated that the colorless and blue powders were partly composed of rutile phase TiO$_2$ because of the shift of the absorption edge to 3.0 eV.

3.2. EPR measurement
Figure 1 shows the temperature dependence of the EPR signals of the N-doped yellow anatase powder measured under the irradiation with a W-lamp of whole wavelengths. The lineshape of the observed EPR signal is different from that of the single crystal because, in the powder, the principal axes of the crystallites have random orientations relative to the direction of the external magnetic field. The observed EPR signal appears to be derived from the paramagnetic species of $S = 1/2$ interacting with a nuclear spin of $I = 1$. The spectrum simulated using the parameter sets $(g_{xx}, g_{yy}, g_{zz}) = (2.0070, 2.0060, 2.0047)$ and $(A_{xx}, A_{yy}, A_{zz}) = (2.26, 3.60, 31.8)$ in the unit of Gauss by EasySpin software [4] shows...
good agreement with the observed spectrum of the N-doped powder. The parameter set used for spectral simulation of the powder is similar to that of yellow single crystal [3]. This indicates that the spin structure in the yellow powder is the same as that in the single crystal. Figure 1 shows that the intensity of the EPR signal decreases with increasing temperature, and the signal cannot be observed above 443 K. In addition, the signal was not observed after cooling to room temperature in the dark.

The EPR signal of the yellow powder was induced by the irradiation of visible-light whose energy was selected using short-wavelength cutoff filters. It was initially confirmed that the yellow powder kept in the dark for 2 weeks had weak EPR signals derived from surface defects [5]. Figure 2 shows the change in the EPR spectra of the yellow anatase powder irradiated by cutoff light with different energy for 5 min. The powder pattern of EPR signals was induced by the irradiation of light with $h\nu \geq 2.2$ eV, in agreement with a previous report [6]. The EPR signal gradually decayed in the dark. Figure 3 shows temporal changes in the intensity of EPR signals shortly after stopping light irradiation for different temperatures, where each signal intensity is normalized to the intensity under light irradiation. To estimate the thermal stability of the trapped carriers, the decay curves were analyzed using the stretched exponential function

$$I(t) = \exp \left[ -\left( \frac{t}{\tau} \right)^\beta \right],$$

where $\tau$ and $\beta$ represent the average decay time and decay exponent, respectively [7]. The average decay time decreases with increasing temperature. The values of $\beta$ were estimated to be 0.3 which was independent from temperature. The decay of the intensity of the EPR signal is due to a relaxation process caused by thermal activation of the trapped carriers. We assume that the lifetime has an activated behavior and can be described as

$$\tau(T) = \tau_0 \exp \left(-\frac{\Delta E}{kT} \right),$$

where $\Delta E$ and $k$ are the thermal activation energy and Boltzmann constant, respectively. In Figure 4, the activation energy was estimated to be 0.22 eV from the good line fitting based on $\tau(T)$.

3.3. XPS measurement

The XPS measurement revealed that the binding energies of the O1s and Ti2p bands were independent of the color of the powder. This indicates the atomic valences of O and Ti in the powders were independent of the crystalline phase because of the structural similarity between rutile and anatase. Figure 5 shows XPS N1s spectra measured for the yellow, colorless and blue powders. The N1s band at 399.5 eV was observed for all powders. To remove adsorbed N$_2$ from the surface of the powder particles, we performed sputtering using argon ions. Because of the reduced intensity of the N1s band at 399.5 eV due to the sputtering, the band was assigned to nitrogen adsorbed on the surface of the powders. The lack of change in the band intensity after the sputtering suggests that the bands at 402.9 and 396.5 eV can be assigned to doped nitrogen in the bulk of the colorless and blue powders, respectively. The binding energy of the bulk nitrogen in the yellow powder appears to be about 399.5 eV. These suggested
that the change in the color of the powders mainly depends on the atomic valence of nitrogen. Therefore, the difference among these binding energies of N1s reveals that the atomic valence of doped nitrogen depends on the oxidation-reduction procedure. Many experimental results [8] have indicated a correlation between the binding energy and atomic valence; nitrogen with positive or negative atomic valence has a binding energy larger or smaller than 400 eV, respectively. The atomic valence of the doped nitrogen in the yellow powder resembles to be almost neutral, based on the adsorbed N\textsubscript{2} has a neutral atomic valence.

4. Conclusion
The irradiation of light with $\nu \geq 2.2$ eV to a sol-gel-derived yellow TiO\textsubscript{2} powder resulted in the appearance of a powder pattern of EPR signals, which gradually decayed in the dark. The decay of the intensity of the EPR signals is due to a relaxation process caused by thermal activation of the trapped carriers. The thermal activation energy of the trapped carriers was estimated to be 0.22 eV. In the XPS spectra of the colorless, yellow and blue powders, N1s bands were observed at 402.9, 399.5, and 396.5 eV, respectively. The atomic valence of the nitrogen in the yellow powder is almost neutral. The colorless and blue N-doped titanium dioxide powders also contained nitrogen with a positive and negative atomic valence, respectively. The atomic valence of doped nitrogen depends on whether the heat treatment was performed oxidation or reduction.

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References
[1] Asahi R, Morikawa T, Ohwaki T, Aoki K and Taga Y 2001 Science 293 269.
[2] Sekiya T, Yagisawa T, Kamiya N, Mulmi D, Kurita S, Murakami Y and Kodaira T 2004 J. Phys. Soc. Jpn. 73 703.
[3] Sekiya T, Kamiya N, Ohya S, Kurita S and Kodaira T 2009 J. Phys. Soc. Jpn. 78 114701.
[4] Stoll S and Schweiger A 2006 J. Magnetic Resonance 178 42.
[5] Anpo M, Shima T and Kubokawa Y 1985 Chem. Lett. 14 1799.
[6] Kokorin A, Konstantinova E and Kisch H 2013 Kinetics and Catalysis 54 373.
[7] Redfield D and Bube R H Photoinduced Defects in Semiconductors (Cambridge University Press, Cambridge, 1996).
[8] NIST X-ray Photoelectron Spectroscopy Database https://srdata.nist.gov/xps/Default.aspx.