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Effects of donor doping and acceptor doping on rutile TiO_2 particles for photocatalytic O_2 evolution by water oxidation

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ABSTRACT

Crystalline defects of photocatalyst particles may be considered to be the recombination center of photoexcited electrons and holes. In this study, we investigated the photocatalytic activity of cation-doped rutile TiO_2 photocatalysts for O_2 evolution from an aqueous silver nitrate solution under ultraviolet light irradiation. The photocatalytic activity of rutile TiO_2 was enhanced by donor doping of Ta^{5+} and Nb^{5+} with a valence higher than that of Ti^{4+}, regardless of increased density of electrons and Ti^{3+} species (an electron trapped in Ti^{4+} sites). Conversely, acceptor doping of lower valence cations such as In^{3+} and Ga^{3+} decreased photocatalytic activity for O_2 evolution by water oxidation. The doping of equal valence cations such as Sn^{4+} and Ge^{4+} hardly changed the activity of non-doped TiO_2. This study demonstrates that Ti^{3+} species, which is a crystalline defect, enhanced the photocatalytic activity of semiconductor oxides, for example rutile TiO_2 with large crystalline size.

1. Introduction

Titanium dioxide (TiO_2), which is an inexpensive, chemically stable, and wide bandgap semiconductor, has been extensively studied for photocatalytic applications because nanocrystalline anatase TiO_2 particles exhibit relatively high photocatalytic activity [1–4]. Doping of impurities is used to control band structures of semiconductor photocatalysts. An impurity level and a sub-band can be formed in the bandgap by substituting an ion for one that constitutes a crystal, and it may be applied for developing visible-light-responsive photocatalysts [5,6]. However, the photocatalytic activity under visible-light irradiation has not yet been put into practical use because of its low quantum yield. Doping has frequently resulted in a decrease of photocatalytic activity, suggesting that the impurities and created defects work as a recombination center that decreases the lifetime of photoexcited electrons and holes.

The roles of impurities doped in TiO_2 photocatalysts are complicated and controversial because the role might depend on crystalline phase (anatase/rutile/brookite), particle size, crystallinity of TiO_2, property and amount of doping elements, and reaction conditions of the photocatalytic activity test [7–11]. Ying et al. investigated the role of particle size in cation-doped TiO_2 nanoparticles with anatase crystalline structure [7]. For TiO_2 nanocrystals with an average diameter of less than 11 nm, the doping of Fe^{3+} enhanced the photocatalytic activity for $CHCl_3$ degradation. The optimal concentration of Fe^{3+} dopants decreased with increasing TiO_2 particle size, suggesting that Fe^{3+} species' role inhibits surface recombination. The Fe^{3+} doping might work less effectively for large TiO_2 particles because the dominant recombination process is bulk recombination rather than surface recombination. In contrast, the photocatalytic activity of TiO_2 with large particle size was increased by Nb^{5+} doping combined with Pt loading, while the activity was decreased by sole Nb^{5+} doping [7]. Karakitsou and Verykios reported the effect of aliovalent cation doping to the TiO_2 matrix on the photocatalytic activity of Pt/TiO_2 for H_2 evolution [8]. Because the doped TiO_2 was prepared at 900 °C, the crystalline structure was at the rutile phase and the particle size was large (BET-specific surface area, ~1 m^2 g^{-1}). The results of these studies suggest that donor doping enhanced photocatalytic activity of Pt-loaded TiO_2 [7,8].

In general, recombination of photogenerated carriers in semiconductor materials is promoted by the presence of crystalline defects such as oxygen vacancy (V_O) and trapped electrons. Therefore, high crystallinity is required for semiconductor photocatalytic materials. However, we previously reported that the photocatalytic activity of rutile TiO_2 was drastically improved by H_2 reduction treatment despite the generation of V_O and Ti^{3+} species [12–16]. H_2 reduction generating an oxygen vacancy with double positive charge ($V_O^{\bullet\bullet}$) and two electrons (e') may be expressed by Eq. (1) using Kröger–Vink notation [17]. The electron is trapped in a Ti^{4+} lattice site ($Ti_{Ti}^{\times}$) to form a Ti^{3+} species (Ti_{Ti}'), as expressed by Eq. (2). Therefore, H_2-reduced TiO_2 photo-

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catalysts exhibit two crystalline defects, i.e., V_O and Ti^{3+} species, but as to which defect is an important factor that decides enhanced photocatalytic activity of H_2-reduced TiO_2 remains unclear.

$$H_2 + O_O^{\times} \rightarrow H_2O + V_O^{\bullet\bullet} + 2e' \tag{1}$$

$$Ti_{Ti}^{\times} + e' \rightarrow Ti_{Ti}' \tag{2}$$

In the present study, we attempted to dope altervalent cations into TiO_2 crystalline lattice to investigate the effects of V_O and Ti^{3+} species on photocatalytic activity. The addition of cations with valence higher than that of the Ti^{4+} lattice (Nb^{5+}, Ta^{5+}, and W^{6+}) would increase the concentration of electrons, as expressed in Eq. (3) using Kröger–Vink notation [18]. The electron is trapped in the Ti^{4+} lattice site to form Ti^{3+} species as shown in Eq. (2). This is called a donor doping, which improves the electrical conductivity of TiO_2 [19]. However, when the Ti^{4+} site of TiO_2 is isomorphously substituted by cations with lower valence (Ga^{3+}, In^{3+}, and Al^{3+}), an $V_O^{\bullet\bullet}$ is generated without forming Ti^{3+} species (Eq. (4)) [18]. This is referred to as acceptor doping, which can decrease the electron concentration of n-type oxides (Eq. (5)) [18].

$$Nb_2O_5 \xrightarrow{TiO_2} 2Nb_{Ti}^{\bullet} + 2e' + 4O_O^{\times} + 1/2\ O_2 \tag{3}$$

$$Ga_2O_3 \xrightarrow{TiO_2} 2Ga_{Ti}' + 3O_O^{\times} + V_O^{\bullet\bullet} \tag{4}$$

$$V_O^{\bullet\bullet} + 2e' + 1/2\ O_2 \rightarrow O_O^{\times} \tag{5}$$

The aim of this work is to investigate the effect of crystalline defects on photocatalytic activity of rutile TiO_2 using doping of metal cations with equal and different valences. We prepared a series of cation-doped TiO_2 particles using a solid state reaction method at high temperatures. Thus, the crystalline structure of TiO_2 samples was at the thermodynamically stable rutile phase. The photocatalytic activity of rutile TiO_2 is frequently low compared with that of anatase TiO_2. However, investigating the photocatalytic properties of rutile TiO_2 particles is important because Maeda et al. recently revealed that a rutile TiO_2 can induce overall water splitting to evolve H_2 and O_2 under UV irradiation [20–22], and we succeeded in preparing H_2-reduced rutile TiO_2 with high photocatalytic efficiency [14,16].

2. Materials and methods

2.1. Preparation of cation-doped TiO_2

High purity TiO_2, F-1R (0.02 wt% Cl, rutile 96 wt%, BET specific surface area 15 $m^2\ g^{-1}$), was sourced from Showa Titanium (Toyama, Japan). The TiO_2 powder was mixed with metal oxides, which are precursors of doping cation, using an alumina mortar in a wet condition using deionized water. The metal oxides were WO_3, Ta_2O_5, Nb_2O_5, ZrO_2, SnO_2, GeO_2, In_2O_3, Ga_2O_3, and Al_2O_3, which were purchased from Kojundo Chemical Laboratory (Sakado, Japan, > 99.9%) and Kanto Chemical (Tokyo, Japan, > 99.9%). The doping metals were selected from cations with oxidation numbers 3–6 under the condition where the electron shell is closed, such as in d^0 and d^{10} electronic configurations [23], and the ion radius is close to that of Ti^{4+} (Table 1). The content of doping cation was adjusted to be 2.0 atom% on a metals basis, for example $Ti_{0.98}Ta_{0.02}O_2$ is the composition of a sample. Doping at 0.1–10 atom% have been usually tested to study the effect of doping cation on the photocatalytic activity in literatures [6–10,24–27]. The mixture was dried at 100 °C, mixed again, and finally calcined in air at 1100 °C for 10 h.

2.2. Evaluation of photocatalytic activity

Photocatalytic activity was evaluated by O_2 evolution from water in the presence of 50-mmol L^{-1} $AgNO_3$ as a sacrificial electron acceptor ($4Ag^+ + 2H_2O \rightarrow 4Ag^0 + O_2 + 4H^+$) under UV irradiation. The suspension of 50 mg of TiO_2 powders in a 9-mL aqueous solution was purged with argon, sealed with a rubber plug, and magnetically stirred at room temperature. Photoirradiation was performed for the suspension in a glass test tube with an outside diameter of 18 mm using light emitting diodes (401-nm peak wavelength, and approximately 13-nm peak width, Supporting Information Fig. S1). The onset wavelength of the interband transition of rutile TiO_2 (band gap 2.9–3.0 eV) was located at approximately 413–428 nm. The irradiance was measured to be approximately 19 mW cm^{-2} at the surface of the glass tube using an optical power meter. The amount of evolved O_2 in the gas phase was quantified every 20 min by a gas chromatograph (Shimadzu GC-8A) with a Molecular Sieve 5A column and a thermal conductivity detector using an argon carrier.

2.3. Characterization

BET specific surface areas were determined from N_2 absorption isotherms measured at −196 °C using a Bel Japan BELSORP-mini instrument. Before measurement, samples were heated in vacuum at 200 °C for 2 h. The doped cation amount was determined by energy dispersive X-ray fluorescence (XRF) technique using a Rigaku NEX CG. X-ray diffraction (XRD) pattern was recorded using a Rigaku RINT-2000/PC with Cu Kα radiation. TiO_2 powder was mixed in an agate mortar with 30 wt% NiO powder as an internal standard. Scanning electron microscope (SEM) images were taken using a Hitachi S-5200. Electron spin resonance (ESR) spectra were recorded at −150 °C in dark on a JEOL JES-X320 equipped with a variable temperature unit. Samples were pre-evacuated at room temperature before ESR measurements. Diffuse reflection UV–Vis spectra were obtained by using an ALS SEC. 2000 spectrometer with a fiber light source.

3. Results

3.1. Characterization of cation-doped TiO_2

X-ray diffraction (XRD) analysis confirmed that the prepared TiO_2 exhibited a single-phase rutile structure except for the TiO_2 doped with Ta_2O_5 and In_2O_3 (Fig. 1). The XRD pattern of TiO_2 doped with Ta_2O_5 contained peaks with 2θ values of 22.9°, 28.3°, 28.8°, and 36.6° assigned to orthorhombic Ta_2O_5, indicating the difficulty of the thermal dispersion of Ta_2O_5 in TiO_2. This indicates that 2 atom% Ta^{5+} ions were not completely doped in the TiO_2 lattice. Ta^{5+} can reportedly be enriched on the surface in Ta_2O_5-doped TiO_2 under oxidizing conditions due to slower transport kinetics compared with that under reduced conditions [28]. For In_2O_3-doped TiO_2, additional diffraction peaks with 2θ values of 30.5° and 31.2° appeared, which could be indexed to the (203) and (112) crystal planes of orthorhombic In_2TiO_5. The radius of In^{3+} might be too large to incorporate into a TiO_2 lattice considering the cation-anion radius ratio. The segregation-induced enrichment of the surface layer results in the formation of low-dimensional In_2TiO_5 structures [29].

In the case of substitutional solid solution, the diffraction peak position should be shifted owing to the change of lattice constant relating to the ion radius of the dopant cation. In practice, we found that TiO_2 doped with Nb_2O_5, SnO_2, and GeO_2 showed corresponding shifts (Fig. 2). This indicates homogeneous incorporation of the added cations into the TiO_2 lattice. The TiO_2 (101) peak was shifted by Ta_2O_5 doping despite the presence of crystalline Ta_2O_5. This suggests that a part of Ta^{5+} was doped in TiO_2 lattice. The slight shift in TiO_2 (101) peak was also observed for TiO_2 doped with ZrO_2.

Table 1 shows the XRF results and BET specific surface area of the doped TiO_2 particles. XRF elemental analysis revealed the presence of added metal oxides in the particles. The BET specific surface area was approximately 0.2 $m^2\ g^{-1}$ owing to the sintering by high temperature calcination. The TiO_2 doped with Ta_2O_5, Nb_2O_5, and GeO_2 exhibited relatively high BET specific surface area. SEM images show that the particles with larger surface area were composed of particles smaller