Hydrothermal synthesis of visible light-sensitive conduction band-controlled tungsten-doped titanium dioxide photocatalysts with copper ion-grafts

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We prepared titanium dioxide (TiO₂) photocatalysts sensitive to visible light, namely copper(II) [Cu(II)]-grafted tungsten and gallium co-doped TiO₂ (Tiₓ₋ₓWₓGaₓO₂, x value is up to 0.12), based on the concept of narrowing the band gap of TiO₂ by positively shifting its conduction band (CB) edge to a lower energy level and the catalytic multi-electron reduction of oxygen by Cu(I) ions. [H. Yu, H. Irie, K. Hashimoto, J. Am. Chem. Soc., 132, 6898 (2010)]. Using this approach, the optical band-gap energy of TiO₂ was decreased to ~2.8 eV, and band-gap narrowing was confirmed by measuring the action spectrum for oxygen evolution from water in the presence of iron ions [Fe(III), from FeCl₃]. The Cu(II)-grafted Ti₁₋ₓWₓGaₓO₂ (x = 0.12) photocatalyst effectively decomposed 2-propanol to carbon dioxide (CO₂) via acetone under visible light (400–530 nm, 1 mW/cm²) with a CO₂-generation rate of 0.30 μmol/h. Grafting Cu(II) ions after the hydrochloric acid treatment of Ti₁₋ₓWₓGaₓO₂ (x = 0.12) increased the CO₂-generation rate to 0.40 μmol/h.

1. Introduction

The development of titanium dioxide (TiO₂) photocatalysts with high sensitivity to visible light is needed to allow incoming light energy to be used more effectively, particularly for indoor applications. The main approaches for increasing the efficiency of light-energy conversion of TiO₂ have involved either doping foreign elements into TiO₂(1–7) or modifying TiO₂ with absorbed molecules, such as the Ru complex(8,9) and platinum chloride (PtCl₄ or H₂[PtCl₆])(10,11). Recently, we demonstrated that TiO₂ powder with grafted metal ions (copper(II) [Cu(II)] or iron(III) [Fe(III)]) is sensitive to visible light.(12–14) This system functions photocatalytically, because the interfacial charge transfer (IFCT)-induced holes in the valence band (VB) of TiO₂ decompose organic substances, while the Cu(I) [or Fe(II)] ions produced by IFCT appear to reduce adsorbed oxygen (O₂) through a multi-electron reduction process.(12–14) The induction of O₂ reduction by photo-generated Cu(I) [or Fe(II)] ions grafted on TiO₂ enables the conduction band (CB) of TiO₂ to be controlled, which led to the successful development of a visible light-sensitive CB-controlled Cu(II)/Ti₁₋ₓWₓGaₓO₂ photocatalyst.(15) In this system, W⁶⁺ (W 5d) contributes to the electronic structure of the TiO₂ CB bottom, which is mainly composed of Ti 3d, meaning that the CB consists of W 5d and Ti 3d hybrid orbitals, leading to band-gap narrowing. In addition, Ga³⁺ acts as a counter dopant to maintain charge neutrality, but the Ga 3d orbital does not contribute to either the CB bottom or VB top. In a previous study,(15) Ti₁₋ₓWₓGaₓO₂ was prepared using a pseudo-solid solution method; however, the highest x value achieved was only 0.05. To further enhance the visible-light absorption of this photocatalyst, further optimization of the preparation method is required to introduce larger amounts of W⁶⁺ and Ga³⁺ ions.

In the present study, we attempted to enhance the visible-light absorption capability of Ti₁₋ₓWₓGaₓO₂ using a hydrothermal method to increase the x values of this photocatalyst. Using this approach, Ti₁₋ₓWₓGaₓO₂ photocatalysts with x values up to 0.12 were prepared and characterized. Specifically, the photocatalytic oxidation activities of the prepared photocatalysts were assessed using 2-propanol decomposition reaction after the grafting of Cu(II) ions and by measuring the action spectrum of bare Ti₁₋ₓWₓGaₓO₂ for O₂ evolution in the presence of a sacrificial agent [Fe(III)].

2. Experimental

Ti₁₋ₓWₓGaₓO₂ (x = 0, 0.03, 0.05, 0.07, 0.08, 0.10, and 0.12) was synthesized using a hydrothermal method. Stoichiometric amounts of Ti(SO₄)₂ (Kanto Kagaku) and Na₂WO₄ (Kanto Chemical), and an excess amount of Ga(NO₃)₃·nH₂O (n = 7–9; n was assumed to be 8, which is 1.5 times larger than the stoichiometric amount; High Purity Chemicals) were mixed in 180 mL distilled water, stirred for 0.5 h, and then heated at 140°C for 12 h in a 300-mL Teflon-lined stainless steel autoclave. The suspension was then centrifuged and the obtained yellowish precipitates were washed with a sufficient amount of distilled water. The centrifugal and washing steps were repeated four times.

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DOI http://dx.doi.org/10.2109/jcersj2.121.563
times, and the obtained precipitates were dried at 80°C in a drying oven. The resulting powders were heated at 600°C for 2 h, and then further heated either at 780 or 900°C for 24 h. In the case of Ti$_{1-x}$W$_x$Ga$_2$O$_5$ \((x = 0.12\), the dried powder was further washed with dilute HCl once and distilled water repeatedly four times, and then dried at 80°C in a dry oven.

Cu(II)/Ti$_{1-x}$W$_x$Ga$_2$O$_5$ photocatalyst was prepared by the same impregnation method used in our previous report\(^{12,13}\) using copper chloride \((\text{CuCl}_2 \cdot 2\text{H}_2\text{O}, \text{Aldrich})\) as the source of Cu(II). Briefly, 1 g of Ti$_{1-x}$W$_x$Ga$_2$O$_5$ powder was dispersed in 10 mL distilled water. CuCl$_2 \cdot 2\text{H}_2\text{O}$ was added to the aqueous Ti$_{1-x}$W$_x$Ga$_2$O$_5$ suspension at a weight fraction of Cu relative to Ti$_{1-x}$W$_x$Ga$_2$O$_5$ of 1.0 $\times 10^{-3}$, as this fraction displayed the highest activity for the decomposition of 2-propanol in the case of Cu(II)/TiO$_2$ in our preliminary tests.\(^{15}\) The resulting suspension was heated to 90°C under stirring for 1 h in a vial reactor. The suspension was then filtered twice through a 0.025-$\mu$m membrane filter (Millipore) and washed with copious amounts of distilled water. The residues were dried at 110°C for 24 h and then ground into a fine powder using an agate mortar.

The crystal structures of the prepared Ti$_{1-x}$W$_x$Ga$_2$O$_5$ powders were determined by X-ray diffraction (XRD; Panalytical PW-1700). The morphology of the Ti$_{1-x}$W$_x$Ga$_2$O$_5$ samples was investigated by field emission scanning electron microscopy (FE-SEM; S-4500, Hitachi). UV–visible absorption spectra were measured by a diffuse reflection method using a V-650 spectrometer (JASCO). Brunauer–Emmett–Teller (BET) surface areas were determined using a Microtrics TriStar 3000 nitrogen adsorption apparatus (Shimadzu).

O$_2$ evolution was measured in the presence of bare Ti$_{1-x}$W$_x$Ga$_2$O$_5$ \((x = 0 \text{ and } 0.10, \text{ 30 mg})$ with the aid of Fe(III) \([\text{iron chloride (FeCl}_3]; \text{Kanto Kagaku, } 0.01 \text{ mol/} \text{L}]\) as a sacrificial agent. The measurements were performed in 3 mL water, without adjusting the solution pH, while stirring using a magnetic stirrer under monochromatic light (360, 390, 420, 430, 450, 480 $\pm$ 5 nm) from an Xe lamp (C2578-02, Hamamatsu Photonics). Higher-order diffracted light was cutoff with an appropriate optical filter.

The photocatalytic activity of the prepared powders was evaluated by monitoring 2-propanol gas decomposition under visible-light irradiation, as described in our previous report.\(^{12,13}\) Briefly, visible light (1 mW cm$^{-2}$, 400–530 nm) from an Xe lamp (Luminar Ace 210, Hayashi Tokei Works) and a combination of optical filters (B-46, L-42, and C-40C, Hoya) was used to irradiate a 300-µg sample of each prepared Cu(II)/Ti$_{1-x}$W$_x$Ga$_2$O$_5$ photocatalyst, which was uniformly spread over the irradiation area (5.5 cm$^2$) in a 500-µL quartz vessel. Prior to irradiation, the vessel was evacuated and filled with synthetic air. To eliminate organic contaminants on the sample surface, the sample was irradiated with visible light until the rate of CO$_2$ generation was less than 0.02 µmol/day. The vessel was then evacuated and filled with synthetic air, followed by the injection of 6.1 µmol (300 ppm) of the reactant gas. The samples were kept in the dark until the gas concentration reached a constant level, as this indicated that the adsorption of 2-propanol gas onto the powder surface was complete. Visible-light irradiation was then started, and the concentrations of produced acetone and CO$_2$ were monitored using a gas chromatograph (GC-8A, Shimadzu).

### 3. Results and discussion

Figure 1(a) shows the XRD patterns of the prepared Ti$_{1-x}$W$_x$Ga$_2$O$_5$ \((x = 0, 0.03, 0.05, 0.07, \text{ and } 0.08)$ powders after calcination at 900°C. The powders with $x = 0, 0.03, \text{ and } 0.05$ displayed a tetragonal crystal system with rutile TiO$_2$ crystalinity. However, in the $x = 0.07 \text{ and } 0.08$ samples, a trace amount of Ga$_2$O$_3$ as an impurity was observed. At a lower calcination temperature (780°C), the XRD patterns of the Ti$_{1-x}$W$_x$Ga$_2$O$_5$ \((x = 0.05, 0.07, 0.08, 0.10, \text{ and } 0.12)$ powders revealed that the rutile and anatase phases increased and decreased, respectively, with increasing $x$ values [Fig. 1(b)] and that a rutile phase was obtained in photocatalysts with $x = 0.10 \text{ and } 0.12$ [Fig. 1(b)]. Note that all powders contained a small amount of polymorphous titanium oxide (either TiO$_2$ or Ti$_2$O$_3$). However, the existence of such titanium oxide would be negligible because of its trace amount. The phase compositions of the prepared photocatalysts are summarized in Table 1.

**Table 1.** Phases of the prepared photocatalysts with increasing $x$ value after calcination at 780 and 900°C

| $x$   | 780°C       | 900°C        |
|-------|-------------|--------------|
| 0     | —           | R            |
| 0.03  | —           | R            |
| 0.05  | R $\gg$ A   | R + Ga$_2$O$_3$ |
| 0.07  | R $\gg$ A   | R + Ga$_2$O$_3$ |
| 0.08  | R $\gg$ A   | R + Ga$_2$O$_3$ |
| 0.10  | R           | —            |
| 0.12  | R           | —            |

A and R denote anatase and rutile phases, respectively. All photocatalysts contain a trace amount of either Ti$_2$O$_3$ or Ti$_2$O$_5$.

The visible–ultraviolet absorption spectra of the prepared Ti$_{1-x}$W$_x$Ga$_2$O$_5$ powders \((x = 0.05 \text{ and } 0.12)$ after calcination at 900 and 780°C are shown in Figs. 2(a) and 2(b), respectively. The particles of Ti$_{1-x}$W$_x$Ga$_2$O$_5$ \((x = 0.05)$ ranged in size from 1–3 µm and appeared rounded with dull edges, and were well crystallized with a surface step structure. In contrast, those of $x = 0.12$ were more slender in shape with sizes of $\sim$0.5 µm $\times$ 3 µm. Calcination decreased the surface area of the Ti$_{1-x}$W$_x$Ga$_2$O$_5$ \((x = 0.12)$ powder from 107 to 2.56 m$^2$/g.

The UV–visible absorption spectra of the prepared Ti$_{1-x}$W$_x$Ga$_2$O$_5$ photocatalysts were measured by the diffuse reflection method (Fig. 3). The spectra for the photocatalysts calcined at 900°C indicated that the doping of W$^{6+}$ (and Ga$^{3+}$) at Ti$^{4+}$ sites narrowed the band-gap of rutile TiO$_2$ and shifted the absorption edges to a longer wavelength region [Fig. 3(a)]. Notably, the
photocatalysts maintained rutile TiO$_2$ crystallinity until $x = 0.05$. However, the spectra for the photocatalysts calcined at 780°C did not exhibit any marked changes up to $x = 0.12$ [Fig. 3(b)]. A small amount of anatase was present in the photocatalysts with $x = 0.07$ and 0.08; however, because the band-gap of anatase (3.2 eV) is larger than that of rutile TiO$_2$ (3.0 eV), the effect of anatase on the UV-visible absorption spectrum would be negligible. Rutile TiO$_2$ is an indirect gap semiconductor, the bandgap of Ti$_{1-x}$W$_x$Ga$_2$O$_2$ can be estimated from the tangent lines in plots of the square root of the Kubelka-Munk function against the photon energy, as shown in Figs. 3(c) and 3(d). Using this approach, the band-gap energies of Ti$_{1-x}$W$_x$Ga$_2$O$_2$ determined from the tangent lines, which were extrapolated to $(h\nu)^{1/2} = 0$, remained constant at approximately 2.8 eV (Fig. 4).

To confirm the grafting of Cu(II) ions, the UV-vis diffuse reflectance spectra of $x = 0$ and 0.12 in Cu(II)/Ti$_{1-x}$W$_x$Ga$_2$O$_2$ were also shown as examples [Figs. 3(e) and 3(f), respectively], as the spectra of all other prepared photocatalysts were similar to that of the $x = 0.12$ photocatalyst. The corresponding spectra of ungrafted (bare) samples in Figs. 3(a) and 3(b) are also shown as a comparison. The slight increase in the 420–550-nm wavelength region in the spectrum of Cu(II)/Ti$_{1-x}$W$_x$Ga$_2$O$_2$ ($x = 0$) can be assigned to IFCT of VB electrons to surface-grafted Cu(II), as we reported previously for Cu(II)/TiO$_2$.[12],[13],[15] In contrast, the absorption slightly increased above ~440 nm in the spectrum of Cu(II)/Ti$_{1-x}$W$_x$Ga$_2$O$_2$ ($x = 1.2$), a result that may reflect
Experimental error. A slight increase was expected in the 440–550-nm region on comparison with the spectra of Ti$_{1-x}$W$_x$Ga$_2$O$_5$ ($x = 0$) with and without Cu(II) grafts because it is reasonable to assume that the absorption due to IFCT at 420–440 nm was masked by interband transition.

The action spectrum for O$_2$ evolution by Ti$_{1-x}$W$_x$Ga$_2$O$_5$ ($x = 0.10$) photocatalyst in aqueous Fe(III) solution (Fig. 5) confirmed that the photocatalyst was able to utilize visible light up to ~480 nm. Importantly, the apparent quantum efficiency (QE) values for this material under irradiation with both UV (360 and 390 nm) and visible light (420–480 nm) coincided with the UV–visible spectrum, indicating that Ti$_{1-x}$W$_x$Ga$_2$O$_5$ ($x = 0.10$) certainly underwent band-gap narrowing. The spectrum for O$_2$ evolution by Ti$_{1-x}$W$_x$Ga$_2$O$_5$ ($x = 0$) was also measured (Fig. 5). As rutile TiO$_2$ has a band gap of 3.0 eV, it is reasonable that the photocatalyst was inactive upon irradiation with visible light at wavelengths longer than 430 nm.

Figure 6 shows the changes in the amounts of acetone and CO$_2$ of 2-propanol oxidation tests for Cu(II)/Ti$_{1-x}$W$_x$Ga$_2$O$_5$ ($x = 0$, 0.07, 0.10, and 0.12) under visible-light irradiation. In all of the tests, including those with Cu(II)/Ti$_{1-x}$W$_x$Ga$_2$O$_5$, the profiles of acetone and CO$_2$-generation were characterized by initial increases in the acetone concentration, which then began to decrease, accompanied by CO$_2$ production. This behavior is plausible, as 2-propanol decomposes into CO$_2$, which is the final product, via acetone, the intermediary product.

The number of absorbed photons, CO$_2$-generation rates, and QE values for the decomposition of 2-propanol by the photocatalysts are presented in Table 2. The QE value was estimated based on the assumption that six photons are required to produce one CO$_2$ molecule, as represented in the formula: C$_3$H$_8$O + 5H$_2$O + 18h$^+$ → 3CO$_2$ + 18H$^+$. The QE value for CO$_2$-generation was calculated using the equation: QE = $6 \times$ CO$_2$-generation rate/absorption rate of incident photons, where the CO$_2$-generation rate was obtained from the slope of the CO$_2$-generation curve, which was calculated using the conventional least-squares method, as employed in previous reports.

The QE value for Cu-grafted photocatalysts decreased with increasing $x$ values from 0 to 0.05. This phenomenon is frequently encountered for photocatalysts because dopants can act as impurities that negatively impact hole and electron transports. As dopants typically serve as recombination centers for holes and electrons, the efficiency of utilization of photogenerated electron–hole pairs, which is reflected in the QE, decreases. In contrast, dopants increase visible-light absorption capability compared to non-doped materials. For the Cu(II)/Ti$_{1-x}$W$_x$Ga$_2$O$_5$ photocatalysts, the positive influence of the dopants dominated up to $x = 0.03$, whereas the negative effect was more significant up to $x = 0.05$. For this reason, the overall photocatalytic activity of the material increased up to $x = 0.03$ and then decreased up to $x = 0.05$.

Interestingly, the QE values of Cu-grafted photocatalysts increased with increasing $x$ above $x = 0.07$, while the visible-light absorption capability of the material was maintained. Thus, the overall photocatalytic activity increased. At present, we are unable to explain this phenomenon; however, it is possible that the density of states of the W 5d orbital increased, thereby enhancing the contribution of the W 5d orbital to the CB, which is composed of W 5d and Ti 3d hybrid orbitals, and increasing the mobility of the photo-excited electrons in the CB. This would allow the electrons to more easily diffuse to the surface, where they would be captured effectively by Cu(II). As a result, the possibility of hole-electron recombination decreased and generated holes could be effectively utilized to oxidize 2-propanol. Thus, the CB control of TiO$_2$ contributed to the increase in both QE and visible-light absorption, leading to the enhanced overall photocatalytic activity of Cu(II)/Ti$_{1-x}$W$_x$Ga$_2$O$_5$.

Table 2. Number of absorbed photons, CO$_2$-generation rate, and QEs for 2-propanol decomposition by Cu(II)/Ti$_{1-x}$W$_x$Ga$_2$O$_5$ and Cu(II)/WO$_3$

| $x$  | Flux of absorbed photons/s$^{-1}$ | CO$_2$-generation rate/μmol h$^{-1}$ | QE (%) |
|-----|---------------------------------|-------------------------------------|--------|
| 0   | $1.0 \times 10^{15}$           | $1.6 \times 10^{-7}$                | 16     |
| 0.03 | $2.0 \times 10^{15}$           | $2.1 \times 10^{-7}$                | 10     |
| 0.05 | $2.0 \times 10^{15}$           | $1.3 \times 10^{-7}$                | 6.5    |
| 0.07 | $1.8 \times 10^{15}$           | $1.2 \times 10^{-7}$                | 6.7    |
| 0.08 | $1.9 \times 10^{15}$           | $2.3 \times 10^{-7}$                | 12     |
| 0.10 | $1.8 \times 10^{15}$           | $2.5 \times 10^{-7}$                | 14     |
| 0.12 | $1.8 \times 10^{15}$           | $3.0 \times 10^{-7}$                | 17     |
|      |                                 | $4.0 \times 10^{-7}$ ($x = 0.10$)  |        |

WO$_3$ $4.2 \times 10^{15}$ $4.8 \times 10^{-7}$ 11

a) Average values for two photocatalytic decomposition tests.
b) Cu(II) ions were grafted after HCl treatment of the photocatalyst.

Fig. 5. Action spectra for O$_2$ evolution by Ti$_{1-x}$W$_x$Ga$_2$O$_5$ ($x = 0.10$, closed circles; and $x = 0$, open circles) in an aqueous Fe(III) solution. UV–visible absorption spectra for $x = 0.10$ (black line) and $x = 0$ (broken line) are also shown.

Fig. 6. Changes in acetone and CO$_2$ amounts as a function of time during 2-propanol oxidation by Ti$_{1-x}$W$_x$Ga$_2$O$_5$ ($x = 0$, 0.07, 0.10, and 0.12).
The observed action spectrum for O₂ evolution confirmed that the band gap of the prepared materials underwent narrowing. Ti₁₋₃ₓGa₂O₅ photocatalysts grafted with Cu(II) effectively decomposed 2-propanol to CO₂ under visible light. Our findings clearly demonstrate that the CB control of TiO₂ contributes to an increase in both QE and visible-light absorption, leading to a marked increase in overall photocatalytic activity. In addition, HCl treatment enhanced the photocatalytic activity of Ti₁₋₃ₓGa₂O₅ (x = 0.12). To further enhance the visible light-induced activity of this system, optimization of the calcination conditions is necessary to increase the surface area of Ti₁₋₃ₓGa₂O₅.

Acknowledgements This work was mainly performed under the management of the Project to Create Photocatalyst Industry for Recycling-oriented Society supported by NEDO. This study was partially supported by the Cooperative Research Program of Catalysis Research Center, Hokkaido University (Grant #11IC3002) and JST, CREST. We express gratitude to Mr. G. Newton for the careful reading of the manuscript.

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