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Conduction Band Energy Level Control of Titanium Dioxide: Toward an Efficient Visible-Light-Sensitive Photocatalyst

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TiO_2 is well-known as an efficient photocatalyst, but it can only be activated under UV-light irradiation because of its band gap of 3.2 eV (anatase).[1] Therefore, the modification of TiO_2 to make it sensitive to visible light is one of the most important objectives in photocatalyst studies. There have been several studies of the sensitization of TiO_2 with absorbed molecules, such as a Ru complex[2] and $H_2[PtCl_6]$ (or $PtCl_4$).[3] However, the main approaches involve either introducing an isolated impurity state into the forbidden band or narrowing the band gap by doping a foreign element into TiO_2. Doping is usually performed using transition-metal cations (e.g., Cr, V, Fe, Ni) at Ti sites[4] and anions (e.g., N, S, C) at O sites.[5] With the latter approach, anion-doped TiO_2 has been widely studied and regarded as a promising candidate for practical applications, as anion doping into TiO_2 (anatase) can be used to control the density of states (DOS) of its valence band (VB) (the potential of the top of the VB is ca. 3.0 V vs SHE at pH 0). In fact, N doping into TiO_2 forms an isolated state originating from N 2p above the top of the VB (the potential of the N 2p state is ca. 2.3 V vs SHE at pH 0).[5g] Upon irradiation with visible light, electrons in the N 2p states are excited to the conduction band (CB) (the potential of the bottom of the CB is ca. -0.2 V vs SHE at pH 0), and holes are produced simultaneously in the N 2p states. The produced holes decompose organic substances, and the electrons in the CB are consumed by oxygen molecules through a one-electron reduction reaction ($O_2 + H^+ + e^- \rightarrow HO_2$, -0.046 V vs SHE).[6] It should be noted, however, that anion-doped TiO_2 usually shows a lower photocatalytic activity under visible light than UV light, and the quantum efficiency (QE) of N-doped TiO_2 under visible light is 1−2 orders of magnitude smaller than that under UV light. This is due to the oxidation power and mobility of the photogenerated holes in the isolated state, which are lower than those in the VB of TiO_2.[5b] However, if the DOS of the CB can be controlled either to form the isolated state below the CB or to narrow the band gap by shifting the CB bottom positively, allowing TiO_2 to absorb visible light, it is self-evident that the photoexcited electrons will accumulate in either the isolated state or the newly constructed CB, as they rarely reduce oxygen through a one-electron reduction on TiO_2 surface. Subsequently, the photoexcited holes will recombine with the accumulated electrons.

Very recently, we reported that Cu(II)-grafted TiO_2 powders are sensitive to visible light.[7] In this system, we proposed that visible light initiates interfacial charge transfer (IFCT), following suggestions made in the literature concerning the photoinduced IFCT between the continuous energy levels of solids and the discrete ones of molecular species on the surface, as theoretically formulated by Creutz et al.[8] That is, electrons in the VB of TiO_2 are transferred directly to Cu(II), forming Cu(I). The holes produced in the VB are then capable of decomposing organic substances. Although the reduction reaction mechanism is not clearly understood, it may possibly proceed by multielectron reduction [two-electron reduction ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$; 0.68 V vs SHE) or four-electron reduction ($O_2 + 2H_2O + 4H^+ + 4e^- \rightarrow 4H_2O$; 1.23 V vs SHE)].[6] Consequently, this system functions catalytically and exhibits oxidative decomposition activity.

The discovery that O_2 reduction can be induced by the photoproduced Cu(I) on TiO_2 releases the TiO_2 photocatalyst from the restriction that VB control is required to gain visible-light sensitivity, enabling one to control the CB of TiO_2 for this purpose. On the basis of this concept, we attempted to develop a novel and efficient visible-light-sensitive TiO_2-based photocatalyst.

We selected W^{6+} and Ga^{3+} ions to be substituted at Ti^{4+} sites in order to control the CB of TiO_2 for the following reasons. First, W^{6+} (W 5d) possibly contributes to the electronic structure of the CB of TiO_2, which is mainly composed of Ti 3d, leading to band-gap narrowing. Second, Ga^{3+} acts as a counterdopant to maintain the charge neutrality. Third, the effective ionic radii of W^{6+} and Ga^{3+} (six-coordinate) are 0.058 and 0.062 nm, respectively, which are similar to that of Ti^{4+} (0.061 nm).[9] Finally, W^{6+} and Ga^{3+} have closed electronic shell configurations of W $5d^0$ and Ga $3d^{10}$, respectively.

We first calculated the DOSs of rutile TiO_2 and $Ti_{1-3x}W_xGa_{2x}O_2$ ($x = 0.125$) (section S. I. 1 in the Supporting Information). It is well-known that the CB and VB of TiO_2 mainly consist of Ti 3d and O 2p, respectively (Figure 1a). Figure 1b indicates that the W 5d does not contribute to the top of the VB in $Ti_{1-3x}W_xGa_{2x}O_2$ ($x = 0.125$) but does contribute to its CB. Therefore, the CB consists of the W 5d and Ti 3d hybrid orbitals, and the bottom of the CB is shifted to the low-energy side, leading to a decrease in the band-gap energy. The Ga 3d orbital contributes to neither the bottom of the CB nor the top of the VB, as shown in Figure 1b. It should be noted that the top of the VB is not affected by the dopants, indicating that the its potential is likely to be unchanged.

$Ti_{1-3x}W_xGa_{2x}O_2$ powders were prepared using TiO_2 (rutile form), WCl_6 and $Ga(NO_3)_3 \cdot nH_2O$. The grafting of Cu(II) ions onto $Ti_{1-3x}W_xGa_{2x}O_2$ was performed by the same impregnation method reported previously (S. I. 2).[7]

Figure 1c shows UV−vis absorption spectra of $Ti_{1-3x}W_xGa_{2x}O_2$ obtained using the diffuse reflection method. These spectra clearly indicate that the doping of W^{6+} (and Ga^{3+}) at the Ti^{4+} sites narrows the band gap of rutile TiO_2 and that the absorption edges shift to longer wavelength with increasing x. It should be noted that the photocatalysts maintained a tetragonal crystal system with a homogeneous rutile TiO_2 crystallinity until at least $x = 0.05$ (section S. I. 3). From the DOS calculations shown in Figure 1b, we can conclude that the band-gap narrowing is derived from the shift of

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the bottom of the CB to lower energy while potential of the top of the VB is maintained. The potentials at the CB bottoms for $x = 0.02$, 0.03, and 0.05 were calculated to be 0.04, 0.07, and 0.10 V (vs SHE at pH 0), respectively, on the basis of the reported value of the potential of the top of the TiO_2 VB (3.0 V vs SHE at pH 0; section S. I. 4).

Figure 1d displays the absorption spectra of Cu(II)-grafted $Ti_{1-3x}W_xGa_{2x}O_2$ (hereafter, Cu(II)/$Ti_{1-3x}W_xGa_{2x}O_2$). A comparison of the corresponding absorption spectra in Figure 1c,d clearly shows that the grafting of Cu(II) increases the absorption intensities in the 420−550 and 700−800 nm wavelength regions. The slight increase in the former region can be assigned to IFCT of VB electrons to surface-grafted Cu(II), as we reported previously in the Cu(II)/TiO_2 system,[7] although the latter is due to a simple d−d transition of Cu(II).[10]

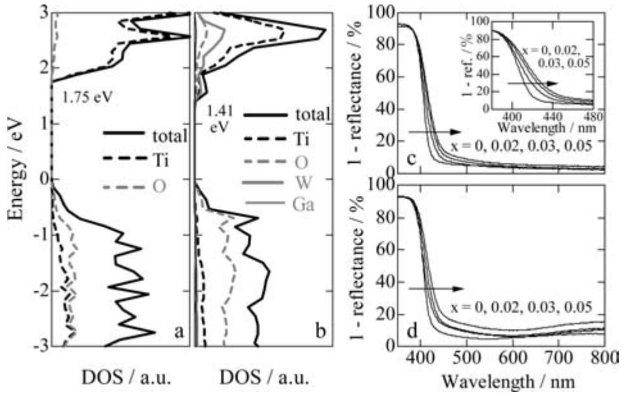

Figure 1. (a, b) DOS for (a) rutile TiO_2 and (b) $Ti_{1-3x}W_xGa_{2x}O_2$ ($x = 0.125$). The values 1.75 and 1.41 eV denote the energies of the bottom of the CB in TiO_2 and $Ti_{1-3x}W_xGa_{2x}O_2$ ($x = 0.125$), respectively, when the tops of the VBs are assigned as 0 eV. (c) UV−vis absorption spectra of $Ti_{1-3x}W_xGa_{2x}O_2$ ($x = 0$, 0.02, 0.03, 0.05). The inset shows an enlargement of the region from 380 to 480 nm. (d) UV−vis absorption spectra of Cu(II)/$Ti_{1-3x}W_xGa_{2x}O_2$ ($x = 0$, 0.02, 0.03, 0.05).

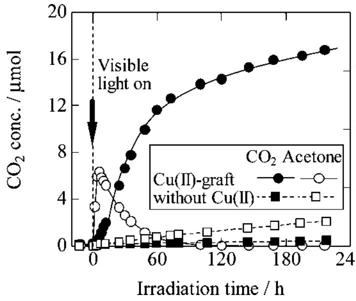

Figure 2. Changes in acetone and CO_2 concentrations due to the decomposition of gaseous 2-propanol as a function of time in the presence of $Ti_{1-3x}W_xGa_{2x}O_2$ and Cu(II)/$Ti_{1-3x}W_xGa_{2x}O_2$ ($x = 0.03$) photocatalysts under visible-light irradiation at 400−530 nm (1 mW cm^{-2}).

Figure 2 shows the photocatalytic activities of $Ti_{1-3x}W_xGa_{2x}O_2$ and Cu(II)/$Ti_{1-3x}W_xGa_{2x}O_2$ ($x = 0.03$) evaluated by monitoring the acetone and CO_2 concentrations generated by the gaseous decomposition of 2-propanol under visible light (400−530 nm, 1 mW/cm^2) (section S. I. 2). With respect to $Ti_{1-3x}W_xGa_{2x}O_2$, CO_2 was scarcely detectable, although very low levels of acetone were generated. In contrast, Cu(II)/$Ti_{1-3x}W_xGa_{2x}O_2$ produced both acetone and CO_2 at much higher rates (section S. I. 5). The QE for CO_2 generation by Cu(II)/$Ti_{1-3x}W_xGa_{2x}O_2$ ($x = 0.03$) was calculated to be ca. 13% using the following equation, assuming that six photons are required to produce one CO_2 molecule: QE = 6 × (CO_2 generation rate)/(absorption rate of incident photon) $= 6 \times (0.25 \times 10^{-6})/(3.6 \times 10^3)$ mol $s^{-1} \times (6.0 \times 10^{23}$ quanta $mol^{-1})/(1.9 \times 10^{15}$ quanta $s^{-1}) = 1.3 \times 10^{-1}$ (13%) (Table S1 in the Supporting Information). Similarly, the QE of $Ti_{1-3x}W_xGa_{2x}O_2$ ($x = 0.03$) was 0.093% (section S. I. 5).

The drastic increase in photocatalytic activity produced by grafting Cu(II) on the surface may be dominated by the catalytic activity of photoproduced Cu(I) over O_2 reduction, similar to the case for Cu(II)-grafted TiO_2.[7] In the present case, however, visible-light irradiation could induce band-to-band excitation, and thus, the electrons produced in the CB could also contribute to the reduction of Cu(II) in addition to the direct charge transfer from the VB (IFCT process). As a result, the light absorption capability of Cu(II)/$Ti_{1-3x}W_xGa_{2x}O_2$ ($x = 0.03$) in the 400−530 nm region increased ca. 1.7 times relative to Cu(II)/TiO_2. These photosensitization processes are illustrated schematically in section S. I. 6.

It should be noted that the QEs of commercially available N-doped TiO_2 (anatase form, HP-N08, Showa Denko K.K.) and Cu(II)/N-doped TiO_2 are 3.9 and 0.94%, respectively (section S. I. 5).

In summary, we have demonstrated that CB-controlled TiO_2 ($Ti_{1-3x}W_xGa_{2x}O_2$) can serve as an efficient visible-light-sensitive photocatalyst when its surface is grafted with Cu(II). This strategy for the design of visible-light-sensitive TiO_2 is a novel and promising approach for applying photocatalysts for indoor use, possibly serving air-purifying, self-cleaning, bactericidal, and virucidal functions. However, it is necessary to further enhance the visible-light absorption capability, which will require the optimization of the preparation method in order to introduce larger amounts of W^{6+} and Ga^{3+}.

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Supporting Information Available: Details of DOS calculations, preparations, and characterizations; XRD, UV−vis, and photocatalytic data; and an illustration of photosensitization processes. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Gerischer, H.; Heller, A. *J. Electrochem. Soc.* **1992**, *139*, 113. (b) Linsebigler, A. L.; Lu, G. Q.; Yates, J. T. *Chem. Rev.* **1995**, *95*, 735.
(2) (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (b) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49. (c) Cho, Y.; Choi, W.; Lee, C.-H.; Hyeon, T.; Lee, H.-I. *Environ. Sci. Technol.* **2001**, *35*, 966.
(3) (a) Kisch, H.; Zang, L.; Lange, C.; Maier, W. F.; Antonius, C.; Meissner, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 3034. (b) Ishibai, Y.; Sato, J.; Akita, S.; Nishikawa, T.; Miyagishi, S. *J. Photochem. Photobiol., A* **2007**, *188*, 106.
(4) (a) Borgarello, E.; Kiwi, J.; Grätzel, M.; Pelizzetti, E.; Visca, M. *J. Am. Chem. Soc.* **1982**, *104*, 2996. (b) Anpo, M.; Takeuchi, M. *J. Catal.* **2003**, *216*, 505.
(5) (a) Asahi, R.; Morikawa, T.; Ohwaki, T.; Aoki, K.; Taga, Y. *Science* **2001**, *293*, 269. (b) Irie, H.; Watanabe, Y.; Hashimoto, K. *J. Phys. Chem. B* **2003**, *107*, 5483. (c) Umebayashi, T.; Yamaki, T.; Itoh, H.; Asai, K. *Appl. Phys. Lett.* **2002**, *81*, 454. (d) Ohno, T.; Akiyoshi, M.; Umebayashi, T.; Asai, K.; Mitsui, T.; Matsumura, M. *Appl. Catal., A* **2004**, *265*, 115. (e) Sakthivel, S.; Kisch, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4908. (f) Mrowetz, M.; Balcerski, W.; Hoffmann, M. R. *J. Phys. Chem. B* **2004**, *108*, 17269. (g) Nakamura, R.; Tanaka, T.; Nakato, Y. *J. Phys. Chem. B* **2004**, *108*, 10617.
(6) (a) Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solution*; Marcel Dekker: New York, 1985; pp 49−66. (b) Torimoto, T.; Nakamura, N.; Ikeda, S.; Ohtani, B. *Phys. Chem. Chem. Phys.* **2002**, *4*, 5910.
(7) (a) Irie, H.; Miura, S.; Kamiya, K.; Hashimoto, K. *Chem. Phys. Lett.* **2008**, *457*, 202. (b) Irie, H.; Kamiya, K.; Shibanuma, T.; Miura, S.; Tryk, D. A.; Yokoyama, T.; Hashimoto, K. *J. Phys. Chem. C* **2009**, *113*, 10761.
(8) (a) Creutz, C.; Brunschwig, B. S.; Sutin, N. *J. Phys. Chem. B* **2005**, *109*, 10251. (b) Creutz, C.; Brunschwig, B. S.; Sutin, N. *J. Phys. Chem. B* **2006**, *110*, 25181.
(9) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925.
(10) Filho, N. L. D. *Mikrochim. Acta* **1999**, *130*, 233.

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