## ChemComm

Cite this: Chem. Commun., 2012, 48, 4323-4325

## COMMUNICATION

## Improved photocatalytic efficiency of a $WO_3$ system by an efficient visible-light induced hole transfer<sup>†</sup>

Srinivasan Anandan and Masahiro Miyauchi\*

Received 16th February 2012, Accepted 8th March 2012 DOI: 10.1039/c2cc31162c

Amorphous Cu(II) nanoclusters grafted WO<sub>3</sub> particles were coated on a smooth TiO<sub>2</sub> film, and site selective depositions of PbO<sub>2</sub> and metal Ag particles by photocatalytic processes were observed on TiO<sub>2</sub> and WO<sub>3</sub> due to transfer of holes to TiO<sub>2</sub>, and accumulation of electrons in WO<sub>3</sub> respectively. As a result, the photocatalytic activity of TiO<sub>2</sub> modified Cu(II)–WO<sub>3</sub> increased  $\sim$  3.5 fold higher than that of Cu(II)–WO<sub>3</sub>.

Although N-doped TiO<sub>2</sub> is considered as an efficient visible-light photocatalyst;<sup>1a</sup> its quantum yield (QE) under visible light is 1-2 orders of magnitude smaller than those under UV light due to slower hole mobility and lower oxidation power of holes.1b Recently, Irie et al.<sup>2</sup> succeeded in fabricating an efficient visiblelight responsive photocatalyst through high oxidation power of holes in the valence band (VB) of photocatalysts induced by interfacial charge transfer (IFCT) and multi-electron reduction via Cu(II)-ions. The efficiency of Cu(II)-grafted WO<sub>3</sub> photocatalysts is  $\sim 16$  times higher than that of N-doped TiO<sub>2</sub>. Based on this report, extensive research studies<sup>3</sup> have been carried out such as (i) varying co-catalysts,  $3^{a,b}$  or (ii) varying other metal oxides, 3c-e or (iii) using nanotubes/nanosheets, 3fg to improve the performance. These previous works optimized the conduction band (CB) side to improve its reduction reaction of electrons, but the performance becomes saturated. The oxidation pathway is also very important in WO<sub>3</sub> based photocatalysts, but the optimization of the VB side for Cu(II)-WO<sub>3</sub> is still challenging. Recently in water splitting systems, RuO<sub>2</sub> or IrO<sub>2</sub> act as a co-catalyst for oxygen evolution.<sup>4</sup> Previous studies also reported heterogeneous semiconductor systems like CdS–TiO<sub>2</sub>,  ${}^{5a}$  TiO<sub>2</sub>–SnO<sub>2</sub>,  ${}^{5b}$  TiO<sub>2</sub>–ZnO,  ${}^{5c}$  TiO<sub>2</sub>–WO<sub>3</sub>,  ${}^{5d}$  but the UV light irradiation to excite the TiO<sub>2</sub> side was indispensable to proceed photocatalytic reactions. Especially under the indoor environment, a light source like an incandescent lamp or LED does not emit any UV light, thus the visible-light-sensitive photocatalyst is very important for the practical use in the indoor environment. Herein, we report a simple and effective strategy to improve the efficiency of photocatalysts (Cu(II)-WO<sub>3</sub>) by the modification of TiO<sub>2</sub>. Hole transfer

Department of Metallurgy and Ceramic Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan. from VB of WO<sub>3</sub> to TiO<sub>2</sub> upon visible-light illumination has been observed by thermodynamic and kinetic analysis. And the visible-light activity was improved much more than the reported Cu( $\pi$ )–WO<sub>3</sub>.

We constructed a Cu(II)–WO<sub>3</sub>/TiO<sub>2</sub> thin-film by dispersing Cu(II)–WO<sub>3</sub> particles on a smooth TiO<sub>2</sub> film (thickness  $\approx$  200 nm) (see Fig. S1 and S2, ESI<sup>†</sup>), which is an ideal setup to observe charge transfer experimentally by an electron microscope analysis. We photocatalytically oxidized 1 mM Pb(NO<sub>3</sub>)<sub>2</sub> solution by employing the Cu(II)–WO<sub>3</sub>/TiO<sub>2</sub> thin-film under visible-light irradiation, and tried to observe PbO<sub>2</sub> which formed by the oxidation of lead<sup>6</sup> (Pb<sup>2+</sup> + 2H<sub>2</sub>O + 2h<sup>+</sup>  $\rightarrow$  PbO<sub>2</sub> + 4H<sup>+</sup>) by holes. The surface morphology of photo-irradiated Cu(II)–WO<sub>3</sub>/TiO<sub>2</sub> is measured by an Auger electron, and scanning electron microscope coupled with an energy dispersive X-ray spectroscope (SEM-EDX), and the results are shown in Fig. 1. Fig. 1a and b show that PbO<sub>2</sub> particles (diameter  $\approx$  400 nm) generate on both surfaces of TiO<sub>2</sub> and WO<sub>3</sub>. TiO<sub>2</sub>, WO<sub>3</sub> and PbO<sub>2</sub> are indicated in Fig. 1b as blue, green, and red color respectively.



**Fig. 1** (a) Auger electron image, (b) Auger elemental mapping, (c) SEM image, and (d) EDX patterns of PbO<sub>2</sub> deposited Cu(II)–WO<sub>3</sub>/TiO<sub>2</sub>. (Photocatalytic oxidation conditions: 1 mM Pb  $(NO_3)_2 = 5$  ml; light source: xenon lamp with Y-43 and c-50s cut-off filters; adsorption in dark = 1 hour; irradiation time = 1 hour.)

E-mail: mmiyauchi@ceram.titech.ac.jp

<sup>†</sup> Electronic supplementary information (ESI) available. See DOI: 10.1039/c2cc31162c

It is interesting to note that  $PbO_2$  mainly appears on the  $TiO_2$ surface near the interface between TiO<sub>2</sub> and WO<sub>3</sub>, though some PbO<sub>2</sub> particles deposit on WO<sub>3</sub>. In contrast, PbO<sub>2</sub> particles were not observed in the bare TiO2, even after long-time photoirradiation of Pb(NO<sub>3</sub>)<sub>2</sub> solutions (see Fig. S3, ESI<sup>+</sup>), revealing that TiO<sub>2</sub> cannot be excited by visible-light illumination. SEM observation at various portions of the Cu(II)-WO3/TiO2 thin film reveals the uniform deposition of PbO<sub>2</sub> on the surface of the TiO<sub>2</sub> film (see Fig. S4, ESI<sup>+</sup>). SEM-EDX results of the Cu(II)-WO<sub>3</sub>/ TiO<sub>2</sub> thin film are shown in Fig. 1c and d. The EDX patterns represented in red, blue, and green in Fig. 1d correspond to the spectrum I, II, and III of Fig. 1c respectively. The EDX pattern for point I reflects the presence of TiO<sub>2</sub> alone, while point II displays the existence of TiO<sub>2</sub> and PbO<sub>2</sub>. Point III exhibits the presence of not only WO<sub>3</sub>, but also TiO<sub>2</sub> and PbO<sub>2</sub>. These results instruct that the holes generated initially on WO3 are responsible for the deposition of PbO<sub>2</sub> on WO<sub>3</sub> particles, while migration of holes from  $WO_3$  to  $TiO_2$  is the reason for the formation of  $PbO_2$  on  $TiO_2$ . We compared the peak intensities of  $PbO_2$  (Fig. 1d) on the WO<sub>3</sub> with that on the interface between TiO<sub>2</sub> and WO<sub>3</sub>. Then, the PbO<sub>2</sub> particles deposited more on the interface than on WO<sub>3</sub>. Moreover, we investigated the SEM-EDAX analysis on several portions of particles, then a similar trend has been observed. The grazing angle X-ray diffraction (GXRD) pattern (see Fig. S5, ESI<sup>†</sup>), and X-ray photoelectron spectroscopic (XPS) results (Fig. S6, ESI<sup>†</sup>) of photo-irradiated Cu(II)-WO<sub>3</sub>/TiO<sub>2</sub> revealed the presence of crystalline PbO<sub>2</sub> particles.<sup>7</sup>

Next, to investigate reduction reaction,  $Cu(II)-WO_3/TiO_2$  in AgNO<sub>3</sub> solution was irradiated by visible-light, and the results of microscopic analysis are shown in Fig. 2. Fig. 2a and b show SEM images of the surfaces of the  $Cu(II)-WO_3/TiO_2$  thin-film after Ag deposition. Ag particles (inside black line in Fig. 2a and b) having sizes of about 2–5 nm deposit only on WO<sub>3</sub> rather than on TiO<sub>2</sub>. The EDX pattern (Fig. 2d) represented in green and red corresponds with points I and II of Fig. 2c, revealing that photoreduction of Ag<sup>+</sup> ions takes place only on WO<sub>3</sub>. XPS results



**Fig. 2** (a and b) FE-SEM images, (c and d) SEM-EDX analysis of Ag deposited Cu(II)–WO<sub>3</sub>/TiO<sub>2</sub>. (Photocatalytic reduction conditions: 1 mM AgNO<sub>3</sub> = 5 ml; light source: xenon lamp with Y-43 and c-50s cut-off filters; adsorption in dark = 1 hour; irradiation time = 1 hour.)

(see Fig. S7, ESI<sup>†</sup>) confirm the presence of metallic Ag on photo-deposited Cu(II)–WO<sub>3</sub>/TiO<sub>2</sub>. These results indicate the accumulation of electrons in WO<sub>3</sub> particles. It is also important to consider the electron transfer from the CB of WO<sub>3</sub> to Cu(II) ions. As reported by Irie *et al.*,<sup>2</sup> a visible-light excited electron in CB of WO<sub>3</sub> is consumed by Cu(II) ions, which reduces oxygen through multi-electron reduction.

The CB potential of WO<sub>3</sub> is +0.3 to +0.5 V (vs. SHE,  $pH = 0^{8a}$ ) more positive than that of TiO<sub>2</sub> (0.04 V vs. SHE, pH = 0) and it is not sufficient for single-electron reduction of an oxygen molecule ( $O_2 + H^+ + e^- \rightarrow HO_2$ , -0.046 V vs. SHE at pH = 0).<sup>8b</sup> The VB potential of WO<sub>3</sub> is 3.1–3.2 V (vs. SHE,  $pH = 0^{8c}$ ) positive than that of TiO<sub>2</sub> (3.04 V vs. SHE,  $pH = 0^{8b}$ ). When visible-light is irradiated on Cu(II)-WO<sub>3</sub>/TiO<sub>2</sub> the charge carriers (holes and electrons) are generated on WO3 as shown in Fig. 3. Holes in the VB of WO<sub>3</sub> transfer to TiO<sub>2</sub>, since the VB positions of  $TiO_2$  is more negative than that of  $WO_3$ .<sup>9</sup> The holes in the VB of TiO<sub>2</sub> have sufficient life-time to initiate photocatalytic oxidation either in solution (oxidation of  $Pb^{2+}$  in to Pb<sup>4+</sup>) or under aerobic conditions (oxidation of acetaldehyde into carbon dioxide) as shown in Fig. 3. The electron in the CB of  $WO_3$  transfers to either  $Cu^{2+}$  or  $Ag^+$  ions as per thermodynamic consideration, since their redox potentials  $\{Cu^{2+}/Cu^{+}, E^{0}\}$ 0.16 V);  $Ag^+/Ag$  (0.77 V)} are more positive than that of CB of WO<sub>3</sub>. The electron transfer to Cu(II) ions may reduce oxygen into hydrogen peroxide through multi-electron reduction reaction.<sup>9</sup> Due to this charge transfer, holes and electrons generated in WO<sub>3</sub> efficiently separated, so that Cu(II)-WO<sub>3</sub>/TiO<sub>2</sub> can utilize visible-light efficiently to decompose organic pollutants.

Based on our experimental analysis for the visible-light induced charge transfer between WO<sub>3</sub> and TiO<sub>2</sub>, a highly active visible-light sensitive powder system has been developed. We prepared TiO<sub>2</sub> modified Cu(II)-WO<sub>3</sub> by physical mixing of Cu(II)-WO<sub>3</sub> and commercial TiO<sub>2</sub> particles. Since small size particles are beneficial for hole mobility,<sup>10</sup> we used TiO<sub>2</sub> nanoparticles (MT-150A, grain size 15 nm, TAYCA, Japan) for the modification of Cu(II)-WO<sub>3</sub>. We investigate the photocatalytic efficiency for the decomposition of gaseous acetaldehyde under visible-light illumination ( $\lambda$  > 400 nm), and the changes in generated  $CO_2$  concentration by oxidation reaction are shown in Fig. 4. For comparison, the results of TiO<sub>2</sub> and Cu(II)-WO<sub>3</sub> are also included in Fig. 4. Pure TiO<sub>2</sub> shows negligible visible-light activity due to lack of visible-light absorption. Cu(II)-WO<sub>3</sub> showed visible light activity, whereas pure WO<sub>3</sub> without Cu(II) co-catalysts was inactive.<sup>3a</sup> In contrast, it is noted that the addition of TiO<sub>2</sub> particles onto Cu(II)-WO<sub>3</sub> abruptly



Fig. 3 Mechanism of charge separation over  $TiO_2$  modified Cu(1)–WO<sub>3</sub>. The aerobic phase reaction and the solution phase reaction take place independently in this system.





**Fig. 4** Initial reaction rate of  $CO_2$  generation over  $TiO_2$ , Cu(1)– $WO_3$ , and  $TiO_2$  modified Cu(1)– $WO_3$ .

enhances the photocatalytic activity of WO<sub>3</sub>. It shows  $\sim 3.5$  fold higher reaction rates than Cu(II)-WO<sub>3</sub>. The photocatalytic activity as a function of TiO<sub>2</sub> loading in TiO<sub>2</sub> modified Cu(II)-WO<sub>3</sub> can be found in the ESI<sup>+</sup> (Fig. S8). Since we carried out the photocatalytic reactions under light-limited conditions,11 the photocatalytic efficiency largely depends on the charge separation. High visiblelight sensitivity of TiO<sub>2</sub> modified Cu(II)-WO<sub>3</sub> is due to its efficient charge separation for both holes and electrons. TiO<sub>2</sub> nanoparticles act as co-catalysts for oxidation reaction by the extraction of holes from WO3, while the Cu(II) nanoclusters act as cocatalysts for reduction reaction through the multi-electrons reduction for adsorbed oxygen molecules.<sup>9</sup> Kinetic fluorescence lifetime analysis (Fig. 5), revealing that TiO<sub>2</sub> modified Cu(II)-WO<sub>3</sub> shows a slow decay curve with long-lived (382 ps) charge carriers, whereas Cu(II)-WO<sub>3</sub> exhibits fast decay with short-lived (188 ps) carriers. The high photocatalytic activity of TiO2 modified Cu(II)-WO3 is assigned to its slow recombination rate. The trade off relation observed between photocatalytic activity and fluorescence analysis is consistent with the previous studies<sup>12</sup> (detailed discussion can be found in ESI<sup>†</sup>). Long-lived photo-generated charge carriers in the present study are mainly due to the addition of TiO<sub>2</sub> on Cu(II)-WO<sub>3</sub>.

In conclusion, the visible-light induced charge transfer is successfully investigated in the Cu(II)– $WO_3/TiO_2$  thin-film. Hole transfer



Fig. 5 Time resolved fluorescence decay analysis of Cu(n)–WO<sub>3</sub>, and  $TiO_2$  modified Cu(n)–WO<sub>3</sub>.

has been confirmed by site-selective photo-deposition of PbO<sub>2</sub> on the surface of TiO<sub>2</sub> by the excitation of WO<sub>3</sub> alone. This charge transfer ensures the efficient separation of charge carriers generated on WO<sub>3</sub>. TiO<sub>2</sub> nanoparticles modification drastically improved the visible-light activity of Cu(II)–WO<sub>3</sub>. Its visible light activity showed ~3.5 fold higher reaction rate than Cu(II)–WO<sub>3</sub>, which was reported as one of the best efficient visible-light photocatalysts to date. Here TiO<sub>2</sub> plays an important role as a co-catalyst and is used for the accumulation of holes from WO<sub>3</sub>. We have investigated the effect of TiO<sub>2</sub> addition to Cu(II)–WO<sub>3</sub> for other commercial TiO<sub>2</sub> particles, then this commercial TiO<sub>2</sub> also enhanced the photocatalytic activity of Cu(II)–WO<sub>3</sub> (see Fig. S9, ESI†). The simple strategy, *i.e.* modification of TiO<sub>2</sub> onto Cu(II)–WO<sub>3</sub> used in this study promises to be very valuable for designing more efficient visible-light-active photocatalysts using other semiconductors.

This work is supported by the New Energy and Industrial Technology Development Organization (NEDO) in Japan. We would like to thank the Japan Society for the Promotion of Science (JSPS) for providing the JSPS fellowship. This work was initiated by the discussion with Mr K. Yotsugi and Mr S. Yanai in Sekisuijushi Technical Research Corporation.

## Notes and references

- (a) R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki and Y. Taga, Science, 2001, 293, 269–271; (b) H. Irie, Y. Watanabe and K. Hashimoto, J. Phys. Chem. B, 2003, 107, 5483–5486.
- 2 H. Irie, S. Miura, K. Kamiya and K. Hashimoto, *Chem. Phys. Lett.*, 2008, **457**, 202–205.
- (a) R. Abe, H. Takami, N. Murakami and B. Ohtani, J. Am. Chem. Soc., 2008, 130, 7780–7781; (b) H. Yu, H. Irie, Y. Shimodaira, Y. Hosogi, Y. Kuroda, M. Miyauchi and K. Hashimoto, J. Phys. Chem. C, 2010, 114, 16481–16487; (c) X. Qiu, M. Miyauchi, H. Yu, H. Irie and K. Hashimoto, J. Am. Chem. Soc., 2010, 132, 15259–15267; (d) S. Anandan, N. Ohashi and M. Miyauchi, Appl. Catal., B, 2010, 100, 502–509; (e) S. Anandan and M. Miyauchi, Phys. Chem. Chem. Phys., 2011, 13, 14937–14945; (f) Z. G. Zhao and M. Miyauchi, Angew. Chem., Int. Ed., 2008, 47, 7051–7055; (g) A. Nakajima, Y. Akiyama, S. Yanagida, T. Koike, T. Isobe, Y. Kameshima and K. Okada, Mater. Lett., 2009, 63, 1699–1701.
- 4 M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. X. Mi, E. A. Santori and N. S. Lewis, *Chem. Rev.*, 2010, **110**, 6446–6473.
- 5 (a) N. Serpone, E. Borgarello and M. Gratzel, J. Chem. Soc., Chem. Commun., 1984, 342–344; (b) H. Tada, A. Hattori, Y. Tokihisa, K. Imai, N. Tohge and S. Ito, J. Phys. Chem. B, 2000, 104, 4585–4587; (c) G. Marci, V. Augugliaro, M. J. Lopez-Munoz, C. Martin, L. Palmisano, V. Rives, M. Schiavello, R. J. D. Tilley and A. M. Venezia, J. Phys. Chem. B, 2001, 105, 1026–1032; (d) M. Miyauchi, A. Nakajima, T. Watanabe and K. Hashimoto, Chem. Mater., 2002, 14, 4714–4720.
- 6 (a) K. Tanaka, K. Harada and S. Murata, Sol. Energy, 1986, 36, 159–161; (b) J. M. Hermann, J. Disdier and P. Pichat, J. Catal., 1988, 113, 72–81.
- 7 T. Ohno, K. Sarukawa and M. Matsumura, New J. Chem., 2002, 26, 1167–1170.
- 8 (a) G. R. Bamwenda, K. Sayama and H. Arakawa, J. Photochem. Photobiol., A, 1999, 122, 175–183; (b) T. Torimoto, N. Nakamura, S. Ikeda and B. Ohtani, Phys. Chem. Chem. Phys., 2002, 4, 5910–5914; (c) M. Miyauchi, A. Nakajima, K. Hashimoto and T. Watanabe, Adv. Mater., 2000, 12, 1923–1927.
- 9 Y. Nosaka, S. Takahashi, H. Sakamoto and A. Y. Nosaka, J. Phys. Chem. C, 2011, 115, 21283–21290.
- 10 J. M. Coronado, A. J. Maira, J. C. Conesa, K. L. Yeung, V. Augugliaro and J. Soria, *Langmuir*, 2001, **17**, 5368–5374.
- 11 H. Gerischer, Electrochim. Acta, 1993, 38, 3-9.
- (a) H. N. Ghosh and S. Adhikari, *Langmuir*, 2001, **17**, 4129–4130;
  (b) Z. Zhang, Q. Lin, D. Kurunthu, T. Wu, F. Zuo, S. T. Zheng, C. J. Bardeen, X. Bu and P. Feng, *J. Am. Chem. Soc.*, 2011, **133**, 6934–6937.