Title	Enhancement of UV-responsive photocatalysts aided by visible-light responsive photocatalysts : Role of WO3 for H2 evolution on CuCl
Author(s)	Takagi, Masaki; Kawaguchi, Masayuki; Yamakata, Akira
Citation	Applied Catalysis B: Environmental, 263, 118333 https://doi.org/10.1016/j.apcatb.2019.118333
Issue Date	2020-04
Doc URL	https://hdl.handle.net/2115/84730
Rights	© 2020. This manuscript version is made available under the CC-BY-NC-ND 4.0 license https://creativecommons.org/licenses/by-nc-nd/4.0/
Rights(URL)	https://creativecommons.org/licenses/by-nc-nd/4.0/
Type	journal article
File Information	AppCatB_Yamakata.pdf

Enhancement of UV-responsive photocatalysts aided by visible-light responsive photocatalysts: role of WO_3 for H_2 evolution on CuCl

Masaki Takagi[1a], *Masayuki Kawaguchi*[1b], *Akira Yamakata*[1, 2]*

1 Graduate School of Engineering, Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya 468-8511, Japan

2 Cooperative Research Fellow, Institute for Catalysis, Hokkaido University, Hokkaido 001-0021, Japan.

AUTHOR INFORMATION

***Corresponding Author**

E-mail: yamakata@toyota-ti.ac.jp, TEL: +81-52-809-1828

a: Present Address: Toyoda Gosei Co., Ltd.
1310-128, Mutsumi, Morimachi, Shuchi-gun, Shizuoka 437-0213, Japan

b: Present Address: Daihatsu Motor Co., Ltd.
3000, Yamanoue, Ryuo-cho, Gamo-gun, Shiga 520-2593, Japan

ABSTRACT

WO_3 is one of the most popular materials for visible-light photocatalysts. However, its conduction band minimum is too low for water reduction. Here, we found that WO_3 can assist water reduction by using visible light in a $CuCl_2$ aqueous solution. Photoirradiation of WO_3 in $CuCl_2$ reduces Cu^{2+} to form indissoluble CuCl adducts, and as-produced CuCl/WO_3 was active for H_2 evolution under UV-light. This composite has very low reactivity under visible light (> 400 nm), but visible-light assisted H_2 evolution was observed with simultaneous irradiation with UV light: the activity was increased ~1.7 fold. Transient absorption measurements revealed that Z-schematic recombination initially takes place between photogenerated electrons in WO_3 and holes in CuCl. As a result, the lifetime of electrons in CuCl was increased, enhancing H_2 evolution. These results demonstrate that inactive narrow-band gap materials can be used to enhance the activity of wide-band gap materials under sunlight illumination.

KEYWORDS

Z-Scheme photocatalysis, WO_3, H_2 evolution, CuCl, Charge carrier dynamics

1. INTRODUCTION

Water splitting photocatalysts have attracted considerable attention for their potential application to generating H_2 gas from H_2O by using solar energy. Numerous inorganic materials have been developed for this purpose,[1-8] and some of them have been found to be very active for water splitting reactions. For example, La-doped $NaTaO_3$,[9] Al-doped $SrTiO_3$,[10] and Zn/Ca-co-doped Ga_2O_3[11] can split pure water with >50% quantum efficiency. However, these materials do not work under visible light illumination. A number of visible light responsive photocatalysts have been developed, but the efficiency of visible light responsive photocatalysts is much lower than that of UV-responsive photocatalysts. Rh_xCr_yO-loaded ZnO:GaN[12] exhibits the highest activity under visible light illumination, but has a quantum efficiency of only ~5 % at 405 nm. The effective utilization of visible light is essential for enhancing activity under sunlight illumination.

The main obstacle to obtaining high efficiency for water splitting is the positions of the conduction band (CB) and valence band (VB). In principle, the band gap of these visible-responsive photocatalysts is narrower than that of UV-responsive materials, and hence the positions of the CB and VB are not sufficient to overcome the overpotentials for H_2 and O_2 evolution. Several materials have suitable CBs and are active for H_2 evolution, but they often have higher VBs, and hence the activity for O_2 evolution is low. Conversely, some materials that have lower VBs also possess lower CBs. In this case, the activity for O_2

evolution would be high, but they are less reactive for H_2 evolution. Therefore, the development of Z-scheme photocatalyst systems composed of H_2-active and O_2-active photocatalysts has become a popular approach to overcome the problems.[13-18] Many materials such as metal oxides, metal (oxy)nitrides, and metal (oxy)sulfides, have been employed for Z-scheme water splitting systems, and reasonable photocatalytic activity enhancements have been obtained.[13-18] For these Z-scheme systems, redox couples such as Fe^{3+}/Fe^{2+}, IO_3^-/I_3^-, $[Co(phen)_3]^{3+/2+}$, and $[Co(bpy)_3]^{3+/2+}$ are often used as electron mediators between the two materials.[13-18] However, the direct attachment of the two semiconductors or the use of solid-state electron mediators such as Au[19] and reduced graphene oxide[20] would be more effective and allow for more rapid electron transportation. It has been reported that the conjugation of Rh-doped $SrTiO_3$ and $BiVO_4$ enables H_2 and O_2 evolution from pure water under visible light illumination.[21] However, the behavior of charge carriers in these conjugated catalysts are not well known. Fundamental information on the charge carriers is indispensable for further enhancement of the activity of these materials.

In this work, we found that WO_3 can assist the H_2 evolution reaction in the presence of a $CuCl_2$ aqueous solution. After 1–2 hours of photo-illumination, H_2 gas started to be evolved. During the induction period, indissoluble CuCl were deposited on WO_3. CuCl is active for H_2 gas generation under UV light, but the activity of bare CuCl gradually decreases. However, the photocatalytic activity and its stability was greatly improved by the combination with WO_3. It is well known that WO_3 is inactive for H_2 evolution, but we found that photoexcitation of WO_3 enhances the activity of H_2 evolution of CuCl. Time-resolved absorption measurements revealed that the lifetime of electrons in CuCl becomes longer in combination with WO_3. The detailed behavior of photogenerated charge carriers was also investigated.

2. EXPERIMENTAL SECTION

The steady-state photocatalytic activity measurements were performed in a 50-mM $CuCl_2$ (Kanto Chemical Co., Inc.) aqueous solution with 10-vol% MeOH (Kanto Chemical Co., Inc.). WO_3 powder (500 mg, Kojundo Co., Ltd.) was added to the solution (200 mL) and deaerated by Ar gas bubbling in a Pyrex reactor. The catalysts were irradiated by a 300-W Xe lamp (Excelitas Technologies Co., Ltd., Cermax PE300BUV) equipped with a short-pass filter for UV irradiation (< 400 nm, Edmund Optics, #84-715) and a long-pass filter for visible irradiation (> 420 nm, Sigma-Koki Co., Ltd., SCF-50S-42L; > 400 nm, Edmund Optics, #84-754). The amount of evolved H_2 gas was analyzed by gas chromatography (Shimadzu, GC8A). Diffuse reflectance absorption spectra were measured using a Jasco V-670 spectrometer equipped with an integrating sphere. The size and shape of the powder catalysts were measured by transmission electron microscopy (TEM; JEOL, JEM-2100). The concentration change of Cu^{2+} in the solution was evaluated by measuring the absorption of

Cu^{2+} at 817 nm. After the reaction, the weight of the catalysts increased from 500 mg (bare WO_3) to >1400 mg. This corresponds to >90% of Cu^{2+} changed to CuCl as will be described later.

Transient absorption spectra were measured using custom-built spectrometers, as described previously.[22; 23] The powder photocatalyst was fixed on a CaF_2 plate at a density of 2 mg cm^{-2}, and photoexcited by a 355-nm pulse from an Nd:YAG laser (Continuum Surelite I, 6-ns duration, 0.1–10 Hz, 0.5-mJ $pulse^{-1}$). In the IR region (6000–1000 cm^{-1}), the probe light from a MoSi coil was focused on the sample and transmitted light was dispersed by a spectrometer (Acton, SP-2300). The monochromated light was detected by an MCT detector, and the output electrical signal was amplified using an AC-coupled voltage amplifier (SRS, SR560). The transient absorption change was recorded using a digital oscilloscope. In the visible and NIR regions (25000–6000 cm^{-1}), the probe light from a halogen lamp was focused on the sample and diffuse reflected light was dispersed by the spectrometer. The monochromated output was detected using a Si-photodiode or InGaAs detector. The time-resolution was limited to ~ 2 μs by the response of the voltage amplifier.

3. RESULTS AND DISCUSSION

3.1 H_2 gas evolution from WO_3 powders in the presence of $CuCl_2$ solution

We found that the photocatalytic H_2 gas evolution reaction proceeds in WO_3

powders in 0.05-M $CuCl_2$ with 10% MeOH aqueous solution. As shown in Figure 1, after the induction period of 1–2 hours, H_2 gas started to be evolved by the full arc illumination from a xenon lamp. During the induction period, the color of the WO_3 changed from green-yellow to dark gray with some adducts (inset of Figure 1). The concentration of Cu^{2+} gradually decreased and H_2 evolution started after the concentration of Cu^{2+} became lower than ~10 mM. Furthermore, the induction period became longer as the initial concentration of Cu^{2+} was increased (Figure S1A). These results suggest that H_2 evolution starts after the disappearance of Cu^{2+} from the solution. The activity gradually increases as the concentration of $CuCl_2$ increased from 0 to 50 mM and started to decrease at 100 mM (Figure S1B). Since WO_3 is inactive for H_2 evolution, the compounds formed from Cu^{2+} should be responsible for the H_2 gas evolution.

The chemical properties of the Cu-containing adducts produced by the photoirradiation were examined. A TEM image of the WO_3 (Figure S2) shows that chemical compounds were deposited on the WO_3. Diffuse reflectance absorption spectra show that the pristine WO_3 absorbs visible light shorter than 480 nm, but the WO_3 powders after the reactions exhibited absorption up to 600 nm with a background increase at 600–900 nm (Figure 2A). Cu_2O and CuCl exhibit absorption at < 630 nm and 600–900 nm, respectively (Figure 2A); therefore it is suggested that Cu_2O and CuCl were deposited on the WO_3 particles. The X-ray diffraction (XRD) patterns (Figure 2B) clearly suggest the formation of

Cu_2O and CuCl. However, Cu_2O is a minor component of the catalysts relative to CuCl, based on the intensity of the XRD pattern. Therefore, CuCl[24; 25] and/or Cu_2O[26; 27] would be responsible for the H_2 evolution, since they can produce H_2 gas by water reduction. In addition, we performed the same experiments in $CuSO_4$ and $Cu(NO_3)_2$ solutions to evaluate the effects of adsorbed Cu^{2+}. In these cases, H_2 gas was evolved under UV light ($\lambda >$ 300 nm) irradiation, but the rate was much smaller than that in $CuCl_2$ solution (Figure S3). The low activity in these solutions would be ascribed to the low amount of the Cu-containing precipitates: the color as well as the weight of WO_3 did not change so much. For the formation of Cu_2O on WO_3, more strong reducing reagents are necessary [26; 27]. In addition, it has been reported that the adsorption and doping of Cu-ions sensitizes the UV-responsible photocatalysts,[28-30] but these sensitization effects was negligibly small. The effects of mechano-catalytic water splitting reactions[31] can also be excluded.

In order to identify the species responsible for the H_2 gas evolution, the wavelength dependence of the photocatalytic activity was examined. The band gap of Cu_2O is ~2.0 eV (630 nm) [32] but that for CuCl is 3.3 eV (376 nm): [24; 25] the visible absorption of CuCl at > 400 nm are ascribed to d-d transition of Cu^{2+} mixed as impurities in CuCl. [25] Therefore, to cut out the UV light, a long pass filter of 420 nm (~ 3.0 eV) was used with the xenon lamp. Figure S4 clearly shows that visible light (> 420 nm) irradiation induces very little H_2 evolution. It is hence evident that UV-excitation of CuCl is responsible for the H_2 evolution.

We also confirmed that bare CuCl powder is active for photocatalytic H_2 evolution from a 10% MeOH solution under UV light illumination (Figure S5A). However, the activity gradually decreased over tens of hours due to the degradation of CuCl.[24; 25] However, in the case of CuCl/WO_3 conjugated photocatalysts, the photocatalytic activity does not decrease for a period longer than 100 h (Figure S5B). This result reveals that WO_3 protects CuCl from degradation.

3.2 Photocatalytic activity of CuCl/WO_3 conjugated photocatalysts

To further examine the role of WO_3 in the photocatalytic H_2 evolution on CuCl, the conjugated CuCl/WO_3 photocatalysts were simultaneously excited by UV and visible light. We expected that the UV light would excite both the CuCl and WO_3, but that the visible light would excite only the WO_3. Therefore, comparing the activity of H_2 generation with and without visible light illumination would give information about the role of WO_3 photoexcitation. In this experiment, two xenon lamps were used, equipped with a short pass filter (< 400 nm) and a long pass filter (> 400 nm). As shown in Figure 3, the adducts show H_2 evolution activity even in dark (0.2 μmol h^{-1}). This corresponds to the mechano-catalytic water splitting reaction which proceeds on Cu-containing compounds as reported by Prof. Ikeda et al. [31]. Under the visible light irradiation, the activity is 1.0 μmol h^{-1}, which is responsible to the photoexcitation of Cu_2O [26; 27]. However, more large activity (9.3 μmol

h^{-1}) was observed under UV light irradiation. When both UV and visible light were simultaneously used, the activity increased 1.7-fold compared to only UV light irradiation: it increased from 9.3 μmol h^{-1} to 15.8 μmol h^{-1}. These results confirm that additional photoexcitation of WO_3 by visible light enhances the H_2 generation on CuCl, although the quantum efficiency is still much lower than < 0.01. Photogenerated holes in WO_3 can oxidize water and MeOH, but photogenerated electrons in WO_3 cannot reduce water. Therefore, it is deduced that the electrons excited in WO_3 were transferred to CuCl. The electrons in CuCl can reduce water to H_2, but CuCl can be excited only by UV light. Hence, the enhancement of the H_2 evolution by visible light strongly suggests that some charge transfer takes place between WO_3 and CuCl.

3.3 Electron and hole transfer between CuCl and WO_3 by time-resolved study

To study the charge transfer processes at the CuCl/WO_3 interface, time-resolved visible to mid-IR absorption studies were performed. This spectroscopy provides detailed information about the individual behavior of electrons and holes.[23; 33; 34] Figure 4 shows the transient absorption spectra of the catalysts measured after UV laser pulse irradiation. In the case of bare WO_3, positive absorption peaks appeared at 25000–20000 cm^{-1} and 3000–1000 cm^{-1} (Figure 4A). It has been reported that trapped holes and electrons give absorption in the visible to IR region, and so the peaks are assigned to trapped holes and electrons, respectively.[23; 33-37] The spectral shape of CuCl is different from that of WO_3. A broad absorption of trapped holes was similarly observed at 25000–20000 cm^{-1}, but the absorption of trapped electrons was absent at ~ 2600 cm^{-1} (Figure 4B). Instead, a very broad absorption of trapped electrons was observed at 15000–4000 cm^{-1}. The difference in the absorption of trapped electrons is due to the difference in the depth of the electron traps from the CB.[33; 38] These results suggest that trapped holes in WO_3 and CuCl give similar absorption in the visible region, but the electrons surviving in WO_3 and CuCl can be distinguished by observing the spectral shapes of the transient absorption in the NIR and mid-IR region.

Transient absorption spectra of the CuCl/ WO_3 conjugated photocatalysts were next measured (Figure 4C). The spectral shape from the visible to NIR region (25000–4000 cm^{-1}) closely resembles that for bare CuCl, where broad absorptions due to trapped holes and trapped electrons were observed at 25000–20000 cm^{-1} and 15000–4000 cm^{-1}, respectively. It is notable that the absorption peak for shallow trapped electrons observed for WO_3 (~ 2400 cm^{-1}) was absent in the conjugated catalysts, but the signal intensity for the trapped electrons at ~ 12000 cm^{-1} was stronger than in bare CuCl. This result suggests that electrons are mainly located in CuCl rather than in WO_3 in the conjugated catalysts.

It is noted that the absorption intensity associated with surface OH at ~ 3600 cm^{-1} was greatly increased by the band-gap excitation (Figure 4B). This phenomenon is not observed for many metal oxides such as TiO_2[33; 39] and $LaTiO_2N$.[23] We noticed that the intensity associated with surface OH usually decreases by the desorption of H_2O by laser pulse irradiation. The increase of the intensity of surface OH group on CuCl is not by the increase of the number of surface OH groups, but the increase of the absorption co-efficient of the surface OH groups since the absorption co-efficient is very sensitive to the charge density of O-H [39]. Furthermore, it has been proposed that OH groups capture holes,[1; 2; 39] the increase in the O-H band intensity could be ascribed to hole transfer to surface OH groups. By the combination with WO_3, the intensity change of OH decreases (Figure 4C). This result might be supporting the conclusion that the trapped holes are mainly located in the WO_3 rather than in the CuCl.

The detailed decay behavior of the photogenerated charge carriers at the CuCl/ WO_3 heterojunctions was studied by measuring the temporal profiles of the transient absorption. Figure 5B clearly shows that the lifetime of electrons in CuCl (12000 cm^{-1}) is increased by the formation of CuCl/WO_3 over the entire region from 0 to 1 ms. However, the absorption intensity for electrons in WO_3 (2400 cm^{-1}, Figure 5A) and the total number of holes in CuCl/WO_3 (22000 cm^{-1}, Figure 5C) at 0 ms was decreased by the formation of the heterojunction. These results suggest that the Z-scheme recombination shown in Scheme 1 takes place between electrons in WO_3 and holes in CuCl within the time resolution of our spectrometer (~ 2 μs). As a result, the electrons in CuCl and holes in WO_3 are spatially separated and hence the lifetime of electrons in CuCl becomes longer. The lifetime of holes in WO_3 should also be increased, but the absorption intensity at 20000 cm^{-1} is due to a mixture of holes in WO_3 and CuCl, so it is difficult to distinguish them. However, the total number of holes in CuCl/WO_3 at 0 ms is smaller than that in bare WO_3 and becomes larger after 100 μs. This result is consistent with the Z-scheme rapid consumption of holes in CuCl, resulting in an increase of the hole lifetime in WO_3. A similar Z-scheme type recombination is proposed to take place for $BiVO_4$/Rh-$SrTiO_3$. [21]

In general, recombination decreases the light-conversion efficiency. However, the photogenerated electrons surviving in WO_3 cannot participate in water reduction. The present result revealed that by the combination with CuCl, these non-useful electrons in WO_3 can increase the lifetime of electrons in CuCl and indirectly enhance the H_2 evolution reaction by consuming the holes in CuCl. In this way, the H_2 evolution activity is enhanced by the simultaneous photoexcitation of CuCl and WO_3. WO_3 can absorb visible light, but CuCl cannot. The present work has demonstrated that by the combination of two different band-gap materials, we can effectively utilize solar light. This finding, that the activity of visible-light responsive photocatalysts can be further enhanced by forming a heterojunction with NIR-responsive materials, can be applied to many other systems.

4. CONCLUSION

In this work, we found that the photocatalytic activity of UV-responsive photocatalysts can be enhanced by combining visible-light responsive photocatalysts. In our example, CuCl can produce H_2 gas from water by UV-light exposure, but its activity can be further enhanced by a combination with WO_3. WO_3 absorbs visible light, but is inactive for H_2 evolution since its CB is too low. Transient absorption measurements showed that photogenerated electrons in WO_3 recombine with holes in CuCl via Z-scheme type recombination. We found that the lifetime of electrons in CuCl becomes longer, so enhancing H_2 evolution. Furthermore, the self-oxidation of CuCl is prevented. This heterojunction exhibits enhanced activity of UV-photocatalysts through the aid of visible-light photocatalysts. Several visible-light responsive photocatalysts have no reactivity for H_2 evolution, but can assist H_2 evolution in other materials. This method can be applied to many other visible- and IR-light responsive photocatalysts. The present work demonstrates that a combination of several photocatalysts with different band gap materials is beneficial for the effective use of solar light from the UV to IR region.

ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid for Basic Research (B) (19H02820) and Scientific Research on Innovative Areas (Mixed Anion: 19H04708), the Strategic Research Infrastructure Project of MEXT, and the Cooperative Research Program of Institute for

Catalysis, Hokkaido University (17A1001).

REFERENCES

[1] M.R. Hoffmann, S.T. Martin, W.Y. Choi, D.W. Bahnemann, Chem. Rev. 95 (1995) 69-96.

[2] A.L. Linsebigler, G.Q. Lu, J.T. Yates, Chem. Rev. 95 (1995) 735-758.

[3] T.L. Thompson, J.T. Yates, Chem. Rev. 106 (2006) 4428-4453.

[4] P.G. Hoertz, T.E. Mallouk, Inorg. Chem. 44 (2005) 6828-6840.

[5] K. Maeda, K. Domen, J. Phys. Chem. C 111 (2007) 7851-7861.

[6] A. Kudo, Y. Miseki, Chem. Soc. Rev. 38 (2009) 253-278.

[7] Y. Inoue, Energy Environ. Sci. 2 (2009) 364-386.

[8] T. Hisatomi, J. Kubota, K. Domen, Chem. Soc. Rev. 43 (2014) 7520-7535.

[9] H. Kato, K. Asakura, A. Kudo, J. Am. Chem. Soc. 125 (2003) 3082-3089.

[10] Y. Goto, et al., Joule 2 (2018) 509-520.

[11] Y. Sakata, T. Hayashi, R. Yasunaga, N. Yanaga, H. Imamura, Chem. Commun. 51 (2015) 12935-12938.

[12] K. Maeda, T. Takata, M. Hara, N. Saito, Y. Inoue, H. Kobayashi, K. Domen, J. Am. Chem. Soc. 127 (2005) 8286-8287.

[13] R. Abe, J. Photochem. Photobiol. C-Photochem. Rev. 11 (2010) 179-209.

[14] R. Abe, K. Sayama, K. Domen, H. Arakawa, Chem. Phys. Lett. 344 (2001) 339-344.

[15] K. Maeda, ACS Catal. 3 (2013) 1486-1503.

[16] Y. Tachibana, L. Vayssieres, J.R. Durrant, Nat. Photonics 6 (2012) 511-518.

[17] H.J. Li, W.G. Tu, Y. Zhou, Z.G. Zou, Adv. Sci. 3 (2016) 12.

[18] P. Zhou, J.G. Yu, M. Jaroniec, Adv. Mater. 26 (2014) 4920-4935.

[19] H. Tada, T. Mitsui, T. Kiyonaga, T. Akita, K. Tanaka, Nat. Mater. 5 (2006) 782-786.

[20] Y.H. Ng, A. Iwase, A. Kudo, R. Amal, J. Phys. Chem. Lett. 1 (2010) 2607-2612.

[21] Q.X. Jia, A. Iwase, A. Kudo, Chem. Sci. 5 (2014) 1513-1519.

[22] A. Yamakata, T. Ishibashi, H. Onishi, Chem. Phys. Lett. 333 (2001) 271-277.

[23] A. Yamakata, M. Kawaguchi, N. Nishimura, T. Minegishi, J. Kubota, K. Domen, J. Phys. Chem. C 118 (2014) 23897-23906.

[24] K. Tennakone, S. Wickramanayake, J. Chem. Soc. Faraday Trans. 82 (1986) 1475-1479.

[25] C. Eisel, M.W. Tausch, J. Photochem. Photobiol. A-Chem. 128 (1999) 151-154.

[26] K. Lalitha, G. Sadanandam, V.D. Kumari, M. Subrahmanyam, B. Sreedhar, N.Y. Hebalkar, J. Phys. Chem. C 114 (2010) 22181-22189.

[27] C.C. Hu, J.N. Nian, H. Teng, Solar Energy Materials and Solar Cells 92 (2008) 1071-1076.

[28] H. Irie, S. Miura, K. Kamiya, K. Hashimoto, Chem. Phys. Lett. 457 (2008) 202-205.

[29] K. Iwashina, A. Iwase, A. Kudo, Chem. Sci. 6 (2015) 687-692.

[30] T. Morikawa, Y. Irokawa, T. Ohwaki, Appl. Catal., A 314 (2006) 123-127.

[31] S. Ikeda, T. Takata, M. Komoda, M. Hara, J.N. Kondo, K. Domen, A. Tanaka, H. Hosono, H. Kawazoe, Phys. Chem. Chem. Phys. 1 (1999) 4485-4491.

[32] H.Q. Pan, S. Chowdhury, D. Premachandra, S. Olguin, M.D. Heagy, ACS Sustain. Chem. Eng. 6 (2018) 1872-1880.

[33] A. Yamakata, J.J.M. Vequizo, H. Matsunaga, J. Phys. Chem. C 119 (2015) 24538-24545.

[34] A. Yamakata, J.J.M. Vequizo, M. Kawaguchi, J. Phys. Chem. C 119 (2015) 1880-1885.

[35] D.W. Bahnemann, M. Hilgendorff, R. Memming, J. Phys. Chem. B 101 (1997) 4265-4275.

[36] T. Yoshihara, R. Katoh, A. Furube, Y. Tamaki, M. Murai, K. Hara, S. Murata, H. Arakawa, M. Tachiya, J. Phys. Chem. B 108 (2004) 3817-3823.

[37] M. Barroso, A.J. Cowan, S.R. Pendlebury, M. Gratzel, D.R. Klug, J.R. Durrant, J. Am. Chem. Soc. 133 (2011) 14868-14871.

[38] J.J.M. Vequizo, H. Matsunaga, T. Ishiku, S. Karnimura, T. Ohno, A. Yamakata, ACS Catal. 7 (2017) 2644-2651.

[39] A. Yamakata, T. Ishibashi, H. Onishi, Bull. Chem. Soc. Jpn. 75 (2002) 1019-1022.

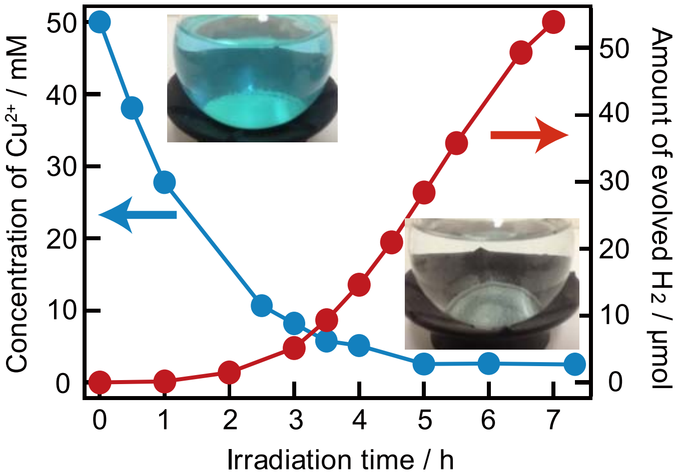


Figure 1. Time courses of photocatalytic H_2 evolution from 0.05-M $CuCl_2$ aqueous solution with 10% MeOH over WO_3 powder. The concentration of Cu^{2+} is also shown. Reaction conditions: catalyst, 200 mg; solution, 200 mL; light source, xenon lamp (300 W, $\lambda > 300$ nm) at 300 K.

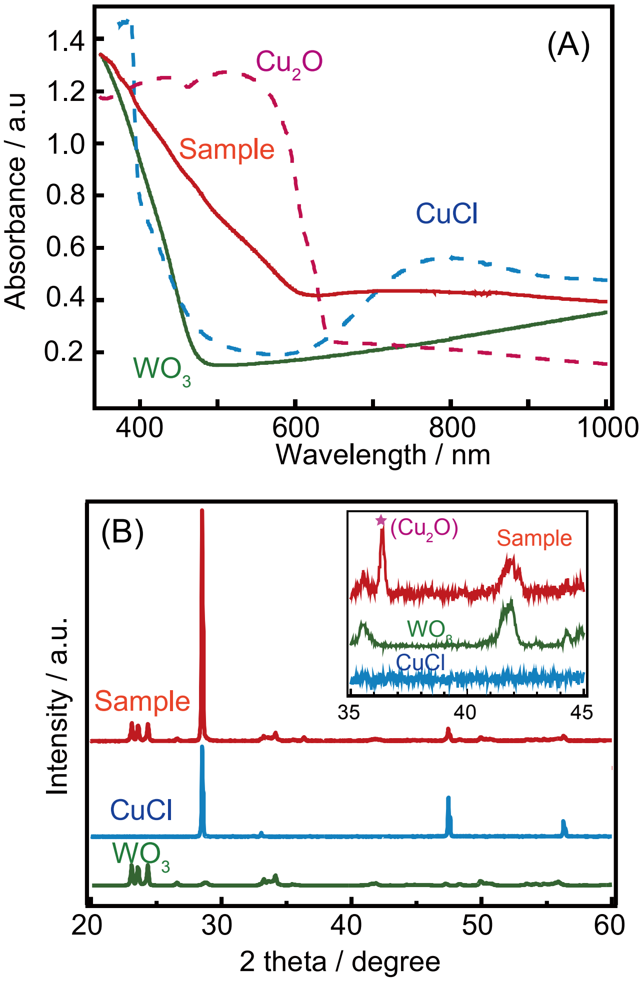


Figure 2. Diffuse reflectance absorption spectra (A) and XRD patterns (B) for WO_3, CuCl, and the WO_3 sample after photocatalytic reaction in $CuCl_2$ solution.

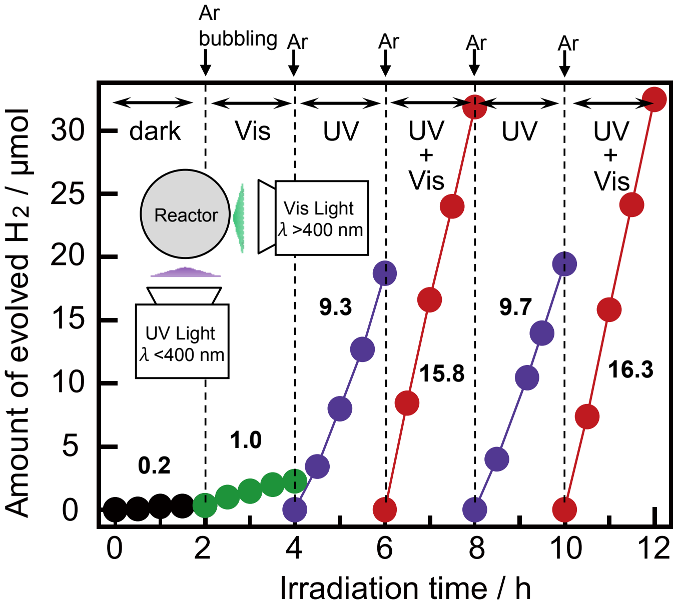


Figure 3. Progress of H_2 evolution from CuCl/WO_3 conjugates in 10 vol% MeOH aqueous solution. Samples were irradiated with UV (300 nm < λ < 400 nm) and visible light (λ > 400 nm) from a xenon lamp (300 W) at 300 K. The numbers shown in the panels represent the rate of H_2 evolution (μmol h^{-1}).

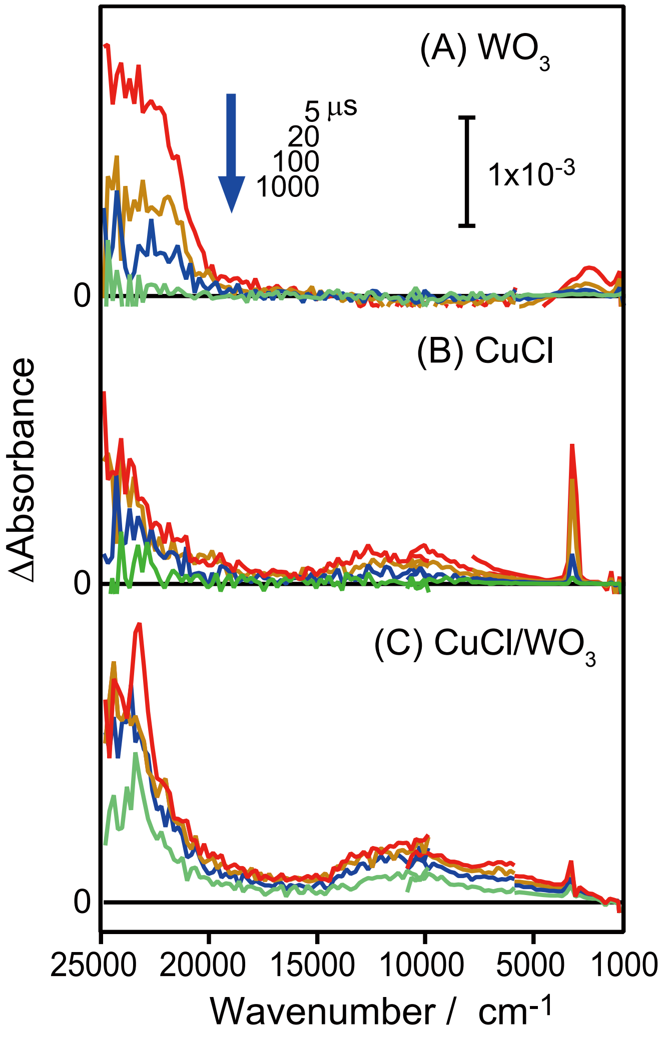


Figure 4. Time-resolved absorption spectra of (A) bare WO$_3$, (B) bare CuCl, and (C) WO$_3$/CuCl conjugated catalysts, measured in vacuum after 355-nm UV laser pulse irradiation (0.5 mJ pulse^{-1}, 6-ns duration, 5 Hz).

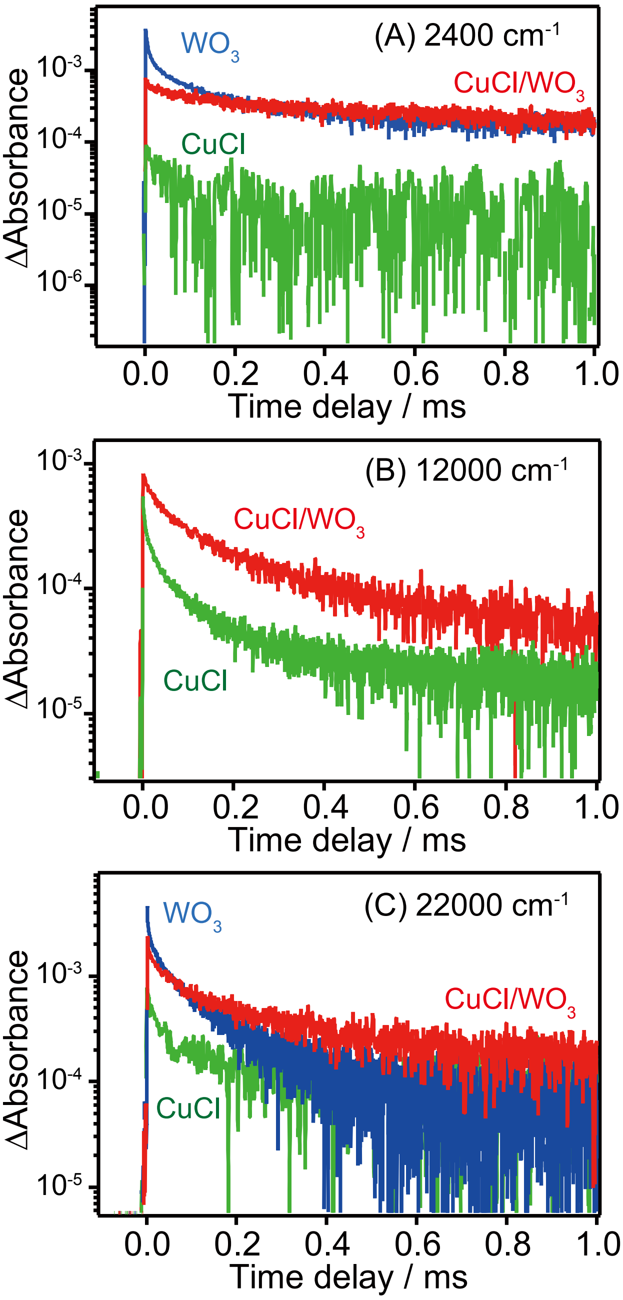
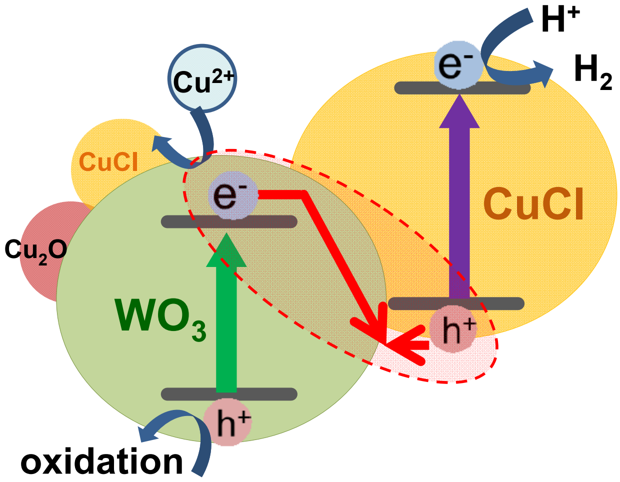


Figure 5. Decay curves for transient absorption by WO_3, CuCl, and WO_3/CuCl measured in vacuum at 2400 cm^{-1} (A), 12000 cm^{-1} (B), and 22000 cm^{-1} (C). The catalysts were irradiated by 355-nm UV laser pulses (0.5 mJ $pulse^{-1}$, 6-ns duration, 1 Hz).



Scheme 1. Proposed mechanism for enhancement of H_2 evolution by visible photoexcitation of WO_3 on WO_3/CuCl conjugated catalysts