Electronic Supplementary Material (ESI) for Chemical Communications


Supporting Information

# Improved photocatalytic efficiency for $WO_3$ system by an efficient visible-light-induced hole transfer

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Contents

S. I. [1] Experimental:

Fabrication of Cu (II)-$WO_3/TiO_2$ thin-film:

Initially, the amorphous $TiO_2$ film fabricated on the surface of quartz substrate by sputtering process followed by annealing at 500$^oC$ in the presence of air, results a crystalline $TiO_2$. The thickness of $TiO_2$ film evaluated by cross-section Scanning Electron Microscope analysis is about 200 nm. Field Emission-SEM image of pure $TiO_2$ thin-film is shown in Figure S1. Secondly, Cu (II)-$WO_3$ dispersion is prepared by mixing 0.1 g of Cu (II)-$WO_3$ (Showa Titanium Inc. Japan) particles and 20 g water followed by sonication for 30 min. Then, required amount of Cu (II)-$WO_3$ dispersion discharged over $TiO_2$ film by spin-coating (2000 rpm, 20sec). This Cu (II)-$WO_3$ spin-coated $TiO_2$ film dried at 60$^oC$ for 1 h and its morphology shown in Figure S1. The constructed device is shown in Figure S2 and named as Cu (II)-$WO_3/TiO_2$ thin-film.

Photocatalytic oxidation of $Pb^{2+}$ and reduction of $Ag^+$:

In order to observe the charge transfer, 5 ml of 1mM $Pb(NO_3)_2$ (Wako) or 1mM $AgNO_3$ (Wako) solution and Cu (II)-$WO_3/TiO_2$ thin-film placed in a glass reactor and kept in dark for 1 h to reach adsorption-desorption equilibrium. Then, the sample was illuminated using a 300 W Xe lamp (Hayashi Watch-works Co. Ltd.) in conjunction with an optical fiber coupler, a UV cutoff filter (Y43, Asahi Techno Glass Co. Ltd.), and an IR cutoff filter (C-50S, Asahi Techno Glass Co. Ltd.). A spectro-radiometer (USR-45D, Ushio Co.) employed to measure the visible-light intensity which was adjusted to100 $mW.cm^{-2}$. The hole transfer and reduction reaction in Cu (II)-$WO_3/TiO_2$ thin-film monitored by two photochemical reactions: the oxidation of lead[1] by photo-generated holes ($Pb^{2+} + 2H_2O + 2h^+ \rightarrow PbO_2 + 4H^+$) and the reduction of silver[2] ($Ag^+ + e^- \rightarrow Ag^0$) by photo-generated electrons. After irradiation for an hour, Cu (II)-$WO_3/TiO_2$ thin-film was washed with water to remove

the un-reacted $AgNO_3$ or $Pb(NO_3)_2$. The deposition of Ag or $PbO_2$ on Cu (II)-$WO_3$/$TiO_2$ thin-film was measured by various analytical techniques.

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Sample characterization:

A Hitachi S-4800 field emission scanning electron microscope (FE-SEM, Hitachi Co. Ltd. S-4800) used to investigate the morphology of Cu (II)-$WO_3$/$TiO_2$ thin-film before and after photocatalytic oxidation/reduction. X-ray photoelectron spectroscopy (XPS) analysis conducted using a Quantum 2000 microprobe system (Physical Electronics, Inc.) to analyze various elements present in $Pb^{2+}$ oxidized or $Ag^{+}$ reduced Cu (II)-$WO_3$/$TiO_2$. The crystal phases were evaluated by X-ray diffraction with Cu Ka X-rays (XRD model Ultima-3, Rigaku Co., Tokyo, Japan). The XRD patterns for $PbO_2$ deposited Cu (II)-$WO_3$/$TiO_2$ thin films were measured by in-plane methods. In this method, the incident angle was fixed at $0.5^o$ and 2θ was scanned in the range from $20^o$ to $80^o$. Auger Electron- Scanning Electron Microscope analysis (AE-SEM) was used to measure the morphology and elemental mapping of $PbO_2$ deposited Cu (II)-$WO_3$/$TiO_2$ thin-film. Fluorescence lifetime measurement for Cu (II)-$WO_3$ and $TiO_2$ modified Cu (II)-$WO_3$ performed using time correlated single photon counting setup by Quantaurus Tau C11367-01 (Model: Hamamatsu Compact Fluorescence Lifetime Spectrometer), using external semiconductor laser PLP-10 as an excitation source (excitation wavelength: 470 nm, power: 30mW, pulse width:130 p.sec., frequency: 5MHz, Time range:10 ns). Detected fluorescence wavelength was 780 nm.

Evaluation of photocatalytic activities:

Photocatalytic activities of $TiO_2$, Cu (II)-$WO_3$, $TiO_2$ modified Cu (II)-$WO_3$ was evaluated by gaseous acetaldehyde decomposition. For the photocatalytic measurements, 0.1 g of photocatalyst uniformly dispersed on a circular glass dish, and the sample pre-treated for 3 h using black light irradiation in air to

clean the surface. The resulting sample then mounted in a cylindrical glass air-filled static reactor (500 mL total volume) with quartz window. The $O_2$ (20%) - $N_2$ mixture adjusted to a relative humidity of 50% was used to fill the reaction vessel. Then, a certain amount of the gas-phase acetaldehyde was introduced into the reactor by syringe until the concentration reached about 500 ppmv. Before illumination, the catalyst and acetaldehyde kept in the dark for 3 h to ensure the establishment of adsorption-desorption equilibrium among catalyst and acetaldehyde. The wavelength of visible-light between 400-550 nm blue-green LED used as a light source. The light intensity of LED measured by a spectro-radiometer (USR-40D, Ushio Ltd), was 20 $mW.cm^{-2}$. The concentration of acetaldehyde and the generation of $CO_2$ monitored using a gas chromatograph (Shimadzu, GC-8A) equipped with a 2 m Propak-Q column, a flame ionization detector, and a methanizer.

S. I. [2] Field Emission- Scanning Electron Microscope (FE-SEM) images of Cu (II)-$WO_3$ and $TiO_2$ thin-film before $PbO_2$ deposition.

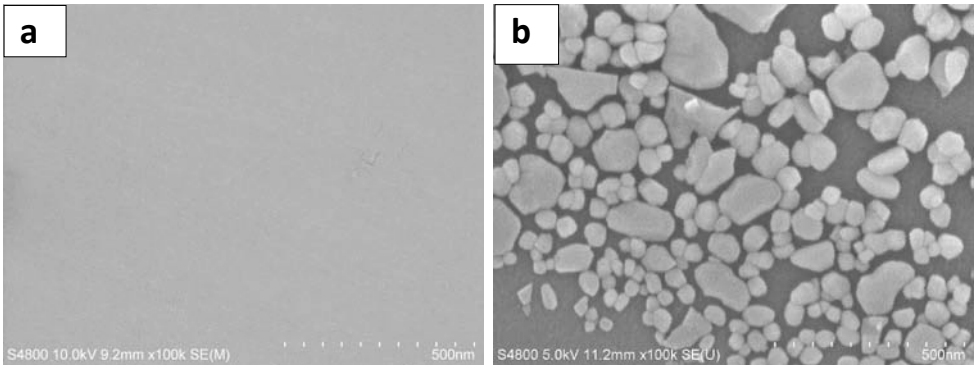


***Figure S1.*** FE-SEM images of a) $TiO_2$ film, and b) Cu (II)-$WO_3$ dispersed $TiO_2$ film.

S. I. [3] Construction of Cu (II)-$WO_3$/$TiO_2$ thin-film

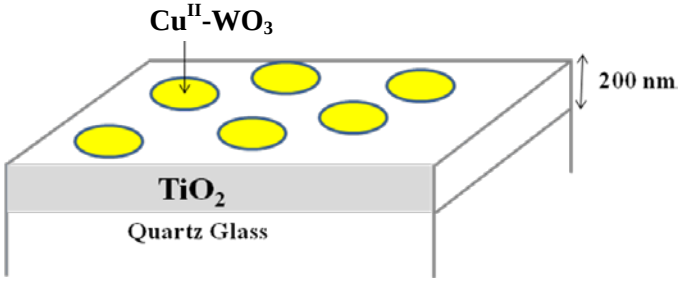


***Figure S2.*** Fabrication of Cu (II)-$WO_3$/$TiO_2$ thin-film

S. I. [4] Field Emission- Scanning Electron Microscope (FE-SEM) images of $TiO_2$ thin-film after $PbO_2$ deposition.

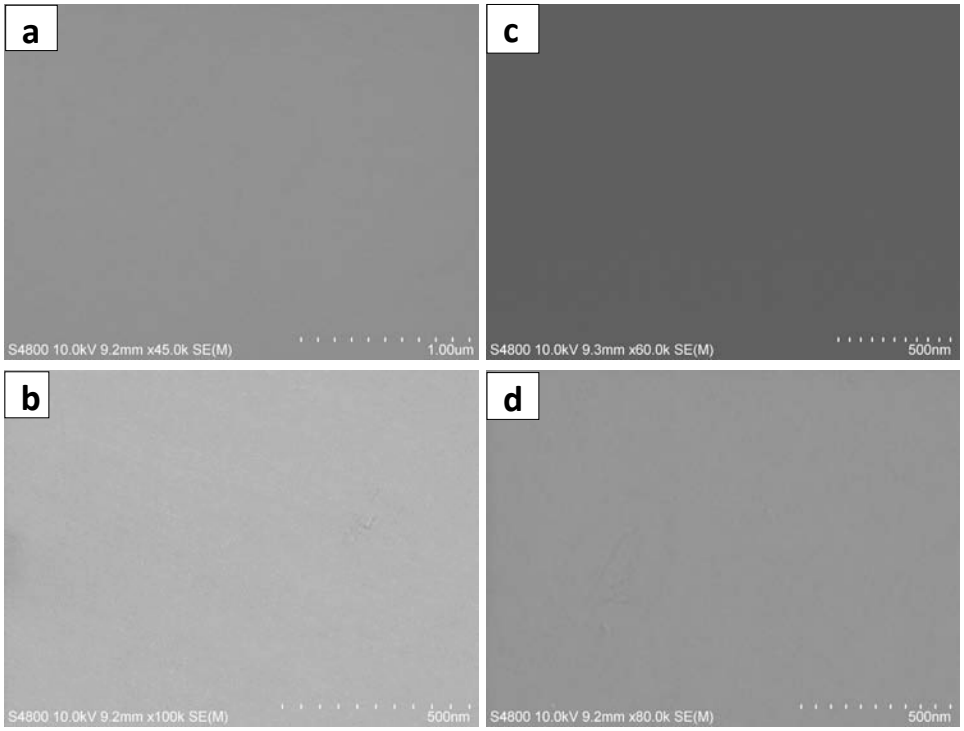


***Figure S3.*** (a, c)Scattering Electron (SE) and (b, d) Back Scattering Electron (BSE) mode FE-SEM images of $PbO_2$ deposited $TiO_2$ thin-film after 1 hour (a, b), and 12 hour (c, d) visible-light illumination. (Reaction condition: 1mM Pb $(NO_3)_2$ = 5ml; Light source: xenon lamp with Y-43 and c-50s cut-off filters; Light intensity: 100 mw. $Cm^{-2}$)

S. I. [5] Field Emission- Scanning Electron Microscope (FE-SEM) images of Cu (II)-$WO_3/TiO_2$ thin-film after $PbO_2$ deposition.

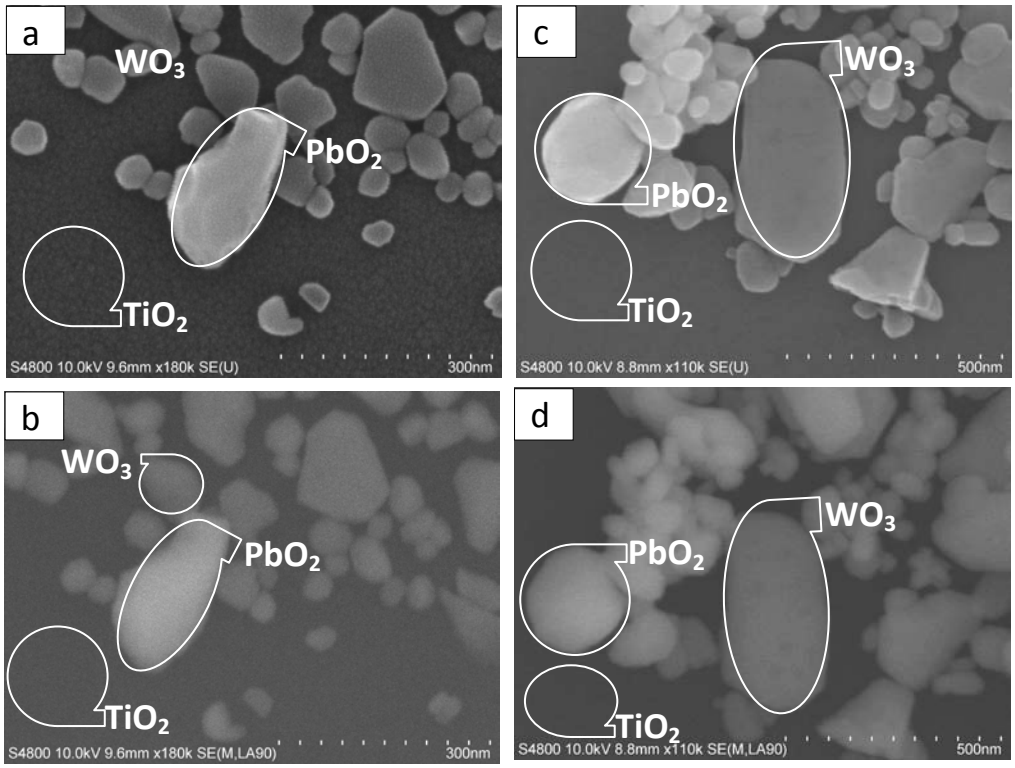


***Figure S4.*** (a, c)Scattering Electron (SE) and (b, d) Back Scattering Electron (BSE) mode FE-SEM images of $PbO_2$ deposited Cu (II)-$WO_3/TiO_2$ thin-film. (Reaction condition: 1mM Pb $(NO_3)_2$ = 5ml; Light source: xenon lamp with Y-43 and c-50s cut-off filters; Light intensity: 100 mw. $cm^{-2}$; Adsorption in dark = 1 hour; Irradiation time = 1 hour.)

S. I. [6] Grazing angle x-ray diffraction analysis of $PbO_2$ deposited Cu (II)-$WO_3$/$TiO_2$ thin-film

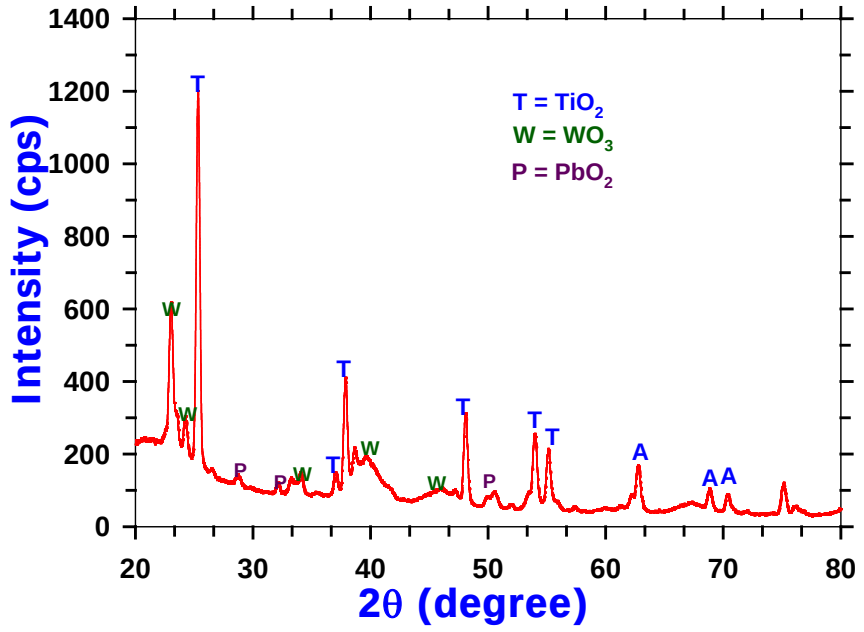


***Figure S5***. XRD patterns of Cu (II)-$WO_3$/$TiO_2$ thin-film after $PbO_2$ deposition. (Photocatalytic reaction condition: 1mM Pb $(NO_3)_2$ = 5ml; Light source: xenon lamp with Y-43 and c-50s cut-off filters; Adsorption in dark = 1 hour; Irradiation time = 1 hour.)

Grazing angle X-ray diffraction pattern $PbO_2$ photo-irradiated Cu (II)-$WO_3$/$TiO_2$ is shown in *Figure S5*. The diffraction peaks at 2θ= 28.41, 32.88, and 49.5 indexed to $PbO_2$ with lattice constants a = 4.071 Å, and C= 5.438Å (JCPDS 45-1416), which is consistent previous studies.[1] The peaks at 2θ= 25.32, 37.82, 48.02, 53.9, 55.06, 62.66, 68.76, 770.31 and 75.1 corresponds with anatase $TiO_2$ with lattice constants a = 3.7852 Å and c = 9.5139 Å. The remaining peaks of XRD pattern other than $TiO_2$ and $PbO_2$ reveals the presence of monoclinic $WO_3$ (JCPDS = 43-1035).

## References:

1. T. Ohno, K. Sarukawa, M. Matsumura, *New J. Chem.*, 2002, **26,** 1167.

S. I. [7] x-ray photoelectron spectroscopic analysis of $PbO_2$ deposited Cu (II)-$WO_3/TiO_2$.

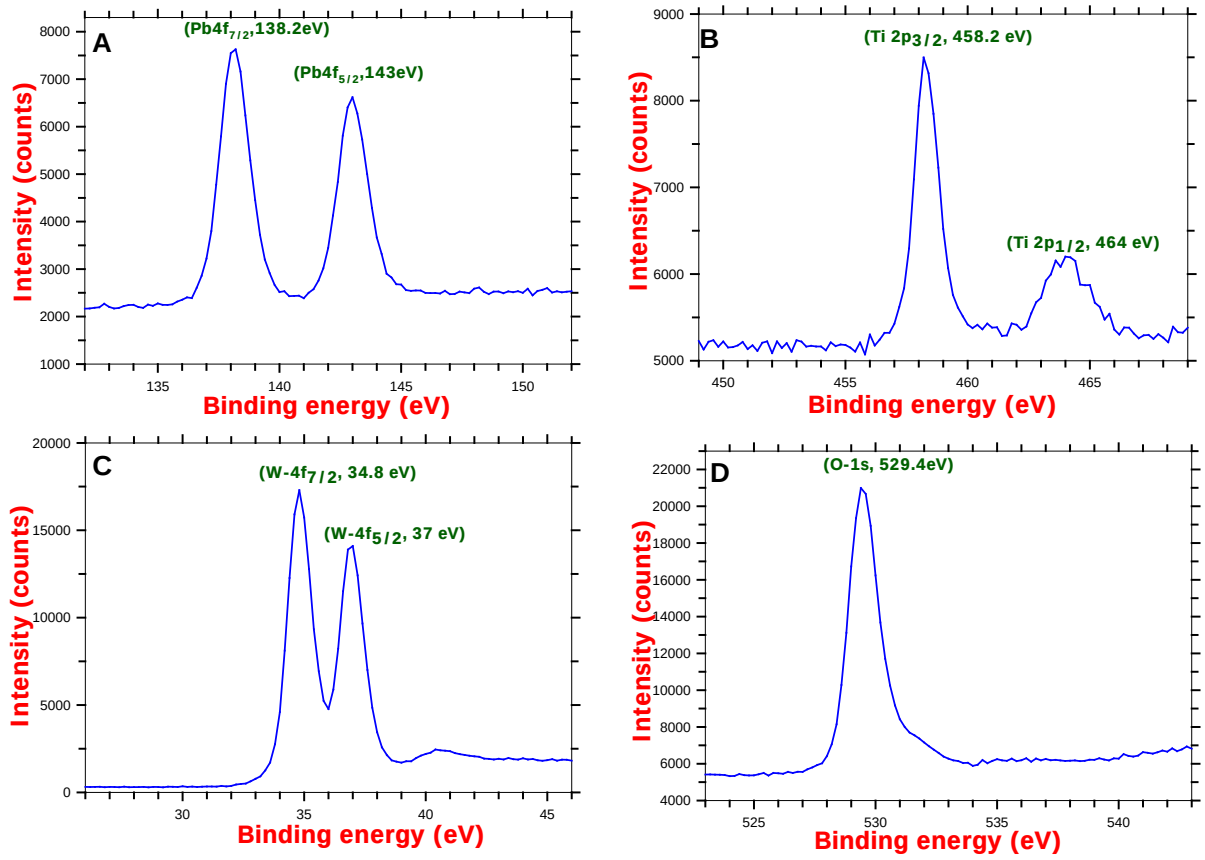


***Figure S6***. XPS spectra of a) Pb-4f, b) Ti-2p, c) W-4f, and d) O-1s for Cu (II)-$WO_3/TiO_2$ after $PbO_2$ deposition. (Photocatalytic reaction condition: 1mM Pb $(NO_3)_2$ = 5ml; Light source: xenon lamp with Y-43 and c-50s cut-off filters; Adsorption in dark = 1 hour; Irradiation time = 1 hour.)

**Figure S6** shows the XPS spectrum of Pb-4f (Figure S6 A), Ti-2p(Figure S6 B), W-4f (Figure S6 C), and O1s(Figure S6 D) orbital. The XPS spectrum of Pb-4f deconvoluted into two doublets like Pb-$4f_{7/2}$ at 138.2 eV and Pb-$4f_{5/2}$ at143 eV (Figure S6 A), corresponding to $Pb^{4+}$ oxidation state of $PbO_2$. This result is consistent with the XPS spectra of $PbO_2$ reported previously.[1] The peaks locates at 458.2 eV and 464 eV, (see Figure S6 B) related to $Ti2p_{3/2}$ and Ti $2p_{1/2}$ binding energies of $Ti^{4+}$ in $TiO_2$.[2] Figure S6 C shows the corresponding W-4f XPS spectrum. Two W-4f peaks located at 34.8 eV (W-$4f_{7/2}$) and 37 eV

($W\text{-}4f_{5/2}$) assigned to $W^{6+}$ as reported in previous studies.[3] The spectra of O-1s shows peak at 529.4 eV (Figure S6 D) corresponds with lattice oxygen in either $TiO_2$ or $WO_3$. XPS analysis concludes the existence of not only $TiO_2$, and $WO_3$, but also $PbO_2$ in Cu (II)-$WO_3$/$TiO_2$.

## References:

1. L. Lubenov, M. Bojinov, T. Tzvetkoff, *J. Solid State Electrochem.* 2007, **11**, 1613.

2. J. Wang, X .Ni, *J. Appl. Poly. Sci*, 2008, **108**, 3552.

3.M. Miyauchi, Y. Li, S. Yanai, K. Yotsugi, *Chem. Commun.* 2011, **47**, 8596.

S. I. [8] x-ray photoelectron spectroscopic analysis of Ag deposited Cu (II)-$WO_3/TiO_2$.

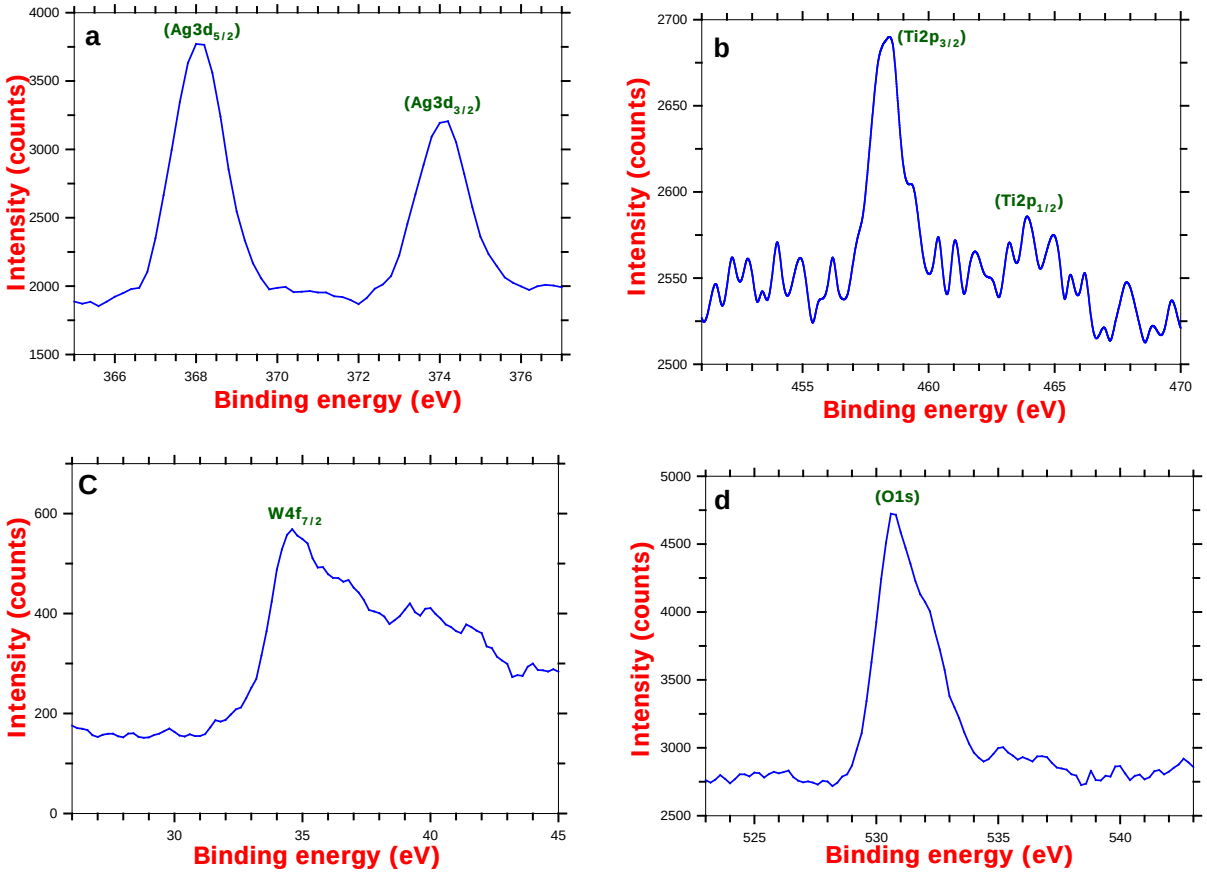


***Figure S7.*** XPS spectra of a) Ag-3d, b) Ti-2p, c) W-4f, and d) O-1s for Cu (II)-$WO_3/TiO_2$ after Ag deposition. (Photocatalytic reaction condition: 1mM $AgNO_3$ = 5ml; Light source: xenon lamp with Y-43 and c-50s cut-off filters; Light intensity: 100 mw. $cm^{-2}$; Adsorption in dark = 1 hour; Irradiation time = 1 hour.)

In order to investigate the chemical states of silver, the surface of Cu (II)-$WO_3/TiO_2$ after Ag deposition was analyzed by XPS. The XPS spectrum of Ag-3d is shown in Figure S7a. It can be seen from the spectrum that two peaks locate at 368.2eV and 374.2eV, correspond with Ag $3d_{5/2}$ and $Ag3d_{3/2}$ respectively. These binding energies are assigned to metallic silver (Ag $3d_{5/2}$:368.3eV and

$Ag3d_{3/2}$:374.3eV) which is consistent with the results in the literature.[1] Ti2p spectrum displays two peaks for $Ti2p_{3/2}$ and Ti $2p_{1/2}$ at 458.4 eV and 464 eV respectively (Figure S7b). These results good agreement with $Ti^{4+}$ of $TiO_2$.[2] The spectra of W-4f (Figure S7c) shows broad peak and the peak shifted to lower binding energy compared to W-$4f_{7/2}$ ($W^{6+}$) of $WO_3$ notify that tungsten exist as either $W^{5+}$ or $W^{4+}$ after visible-light irradiation.[3] The spectra of O1s (Figure S7d) exhibits peak at 530.8 eV, assigned to the lattice oxygen in either $TiO_2$ or $WO_3$. The results of Ag-3d and W-4f clearly reveal that both silver and tungsten in Cu (II)-$WO_3$/$TiO_2$ reduced by electron reduction reaction.

***References:***

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2. J. Wang, X .Ni, *J. Appl. Poly. Sci*, 2008, **108**, 3552.
3. W. Grunert, E. S. Shpiro, R. Feldhaus, K. Anders, G. V. Antoshin, and K.M. Minachev, *J. Catal.* 1987, **107**, 522.

S. I. [9] The photocatalytic activity as a function of $TiO_2$ loading in $TiO_2$ modified Cu (II)-$WO_3$

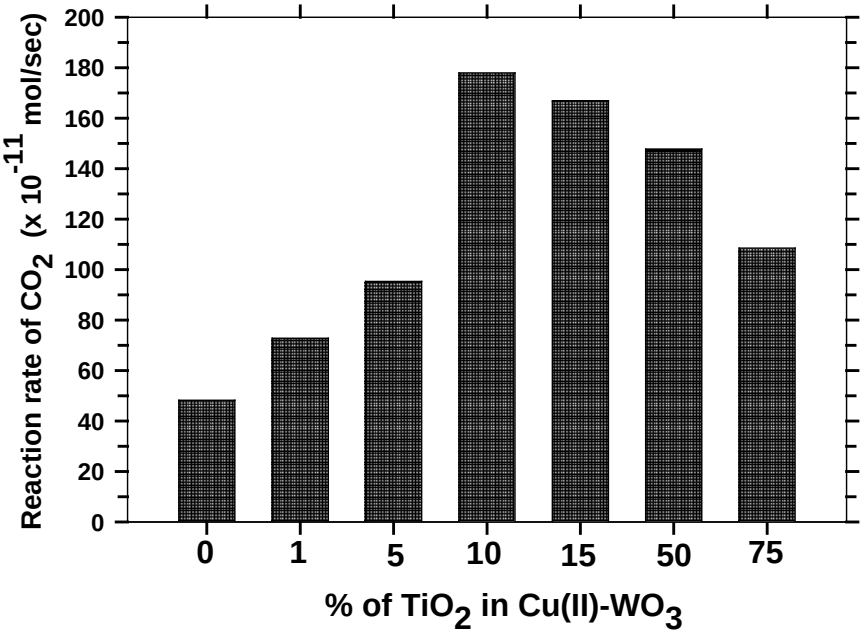


***Figure S8.*** Reaction rate of $CO_2$ generation as a function of $TiO_2$ loading in $TiO_2$ modified Cu (II)-$WO_3$.

The reaction rate of $CO_2$ increased with increasing loading of $TiO_2$ on Cu(II)-$WO_3$ with the maximum reaction rate at 10%, and further loading (15, 50, 75%) resulted in the decrease of reaction rate as shown in Figure S8. In this study, $WO_3$ is fundamental photocatalyst, while $TiO_2$ acts as co-catalyst. When the amount of co-catalyst increase, the absorbed photon numbers of $WO_3$ decrease in visible-region. As a result, it restricts the diffusion of gaseous acetaldehyde and oxygen molecules to the surface of $WO_3$, and decrease the photocatalytic activity.

S. I. [10] Kinetic time resolved fluorescence life-time analysis:

In the present study, $WO_3$ is the responsible for fluorescence emission, which shows a broad emission spectrum between 600 and 800 nm.[1] In detail, the fluorescence spectrum of $WO_3$ is originated from a self-trapped exciton on the $d^0$-ion octahedron.[2] Time-resolved fluorescence measurements was carried out for Cu (II)-$WO_3$ and $TiO_2$ modified Cu (II)-$WO_3$ by the excitation of laser pulse of 470 nm. Detected fluorescence wavelength was 780 nm. $Cu^{II}$-$WO_3$ exhibits fast fluorescence decay with a fluorescence life time of 188 ps, whereas $TiO_2$ modified Cu (II)-$WO_3$ shows a slow decay with life-time of 382 ps. Recently, Pradhan et al.[3] observed a enhanced photocatalytic performance for Au-$TiO_2$ and studied the enhancement by fluorescence life time analysis. Fluorescence analysis of Au-$TiO_2$ showed a slow decay curve which is due to the efficient charge separation of photo-generated electrons at the Au-$TiO_2$ interface by transfer of electrons from the conduction band to Au. Rothenberger et al.[4] and Ghosh et al.[5] studies are consistent with the above discussion and conclude that slow recombination of photo-generated charge carriers correspond to decay curve with long fluorescence life time. Further, Zhang et al.[6] observed a tradeoff relationship between photocatalytic activity and fluorescence life time, and concludes that slow decay curve led to high photocatalytic activity. Long-lived photo-generated charge carriers in the present study are mainly due to the addition of $TiO_2$ on Cu (II)-$WO_3$, which contribute enhanced efficiency of photocatalysts.

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4. G. Rothenberger, J. Moser, M. Gratzel, N. Serpone, D. K. Sharma, *J. Am. Chem. Soc.*, 1985, **107**, 8054.

5. H.N. Ghosh, S. Adhikari, *Langmuir*, 2001, **17**, 4129.

6. 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.

S. I. [11] Comparison of photocatalytic activity of commercial $TiO_2$ nanoparticles modified Cu (II)-$WO_3$ with $TiO_2$, and Cu (II)-$WO_3$.

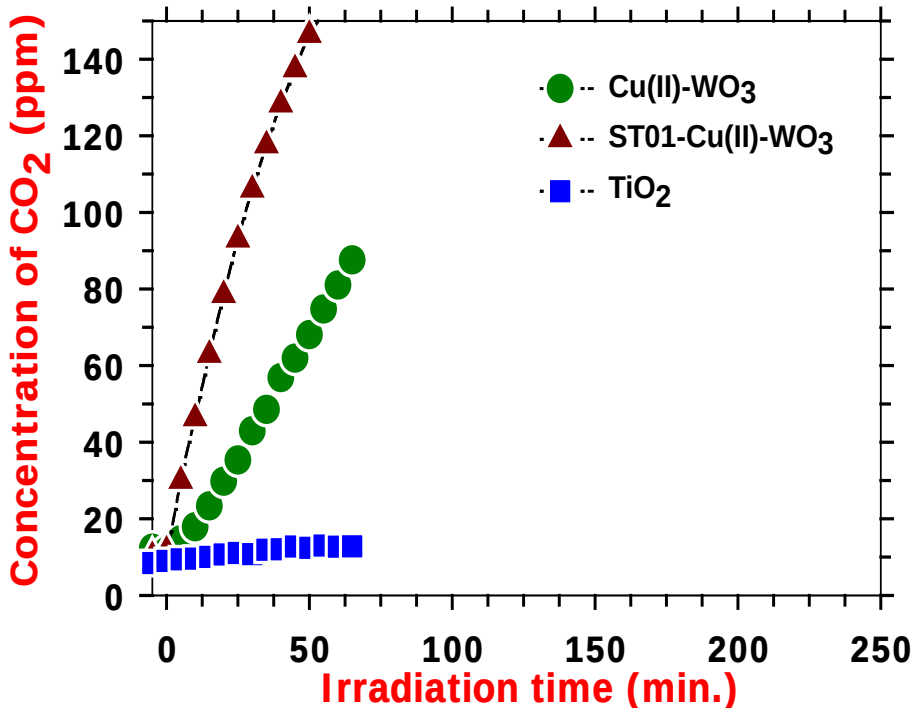


***Figure S9.*** Reaction rate of $CO_2$ generation over $TiO_2$, Cu(II)-$WO_3$, and $TiO_2$ (ST01) nanoparticles modified Cu(II)-$WO_3$.

S. I. [12] The stability of $TiO_2$ modified Cu (II)-$WO_3$ photocatalysts.

The photocatalyst used in the present study is very stable under light irradiation. Irie et al carefully investigated the chemical state of Cu(II)–ion before and after photocatalytic reaction by X-ray absorption fine structure (XAFS) analysis.[1] In situ XAFS measurements revealed that the Cu(II) ions were stable even after the photocatalytic oxidative reaction, and the turnover numbers of the photocatalytic reaction is more than 4. $TiO_2$[2]and $WO_3$[3] are also very stable in aerobic or aqueous media, even under the UV irradiation with photocatalytic oxidative condition. Hence, we can safely conclude that the $TiO_2$ modified Cu(II)-$WO_3$ developed in the present study is very stable for long term light irradiation.

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**2.** (a) A. Heller, *Acc. Chem. Res.* 1995, **28**, 141; A. L. Linsebigler, G. Q. Lu, J. T. Yates, *Chem. Rev.* 1995, **95**, 735; A. Fujishima, K. Hashimoto, T. Watanabe, *$TiO_2$ Photocatalysis, Fundamentals and Applications*; BKC, Inc.: Tokyo, 1999.

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