Solar-light-driven photocatalytic production of peroxydisulfate over noble-metal loaded WO₃

Zeai Huang, Yugo Miseki, Kazuhiro Sayama*

Advanced Functional Materials Team, Research Center for Photovoltaics

(RCPV), National Institute of Advanced Industrial Science and Technology

(AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565 Japan.

Corresponding author e-mail: *k.sayama@aist.go.jp*; Fax: +81-29-861-4760;

Tel: +81-29-861-4760

Experimental section

Preparation of noble-metal loaded WO$_3$

An amount corresponding to 1.0 wt% of the noble metal precursor (H$_2$PtCl$_6$, Pd(NO$_3$)$_2$, HAuCl$_4$, RuCl$_3$, or RhCl$_3$ solution) was added to a mixture of 45 mL ultrapure water and 5 mL methanol. 1.0 g WO$_3$ (99.99%, Kojundo Chemical Laboratory Co., Ltd) was then added under strong stirring. After 10 min of adsorption-desorption equilibration, an AM 1.5G solar simulator (SAN-EI Electric Co., XES-151S) was started for the photodeposition of the noble metal onto WO$_3$. After 2 h of photoirradiation, the stirring was stopped, the mixture was filtered, washed to a natural pH, and dried at 333 K overnight. The other catalysts, H$_2$WO$_4$,[1] BiVO$_4$,[2] and g-C$_3$N$_4$,[3] were prepared following literature methods. Degussa P25-TiO$_2$ was purchased from Evonik Company.

Characterization

The WO$_3$ and noble-metal-loaded WO$_3$ was characterized using X-ray diffraction (XRD, PANalytical, EMPYREAN), UV–vis diffuse reflectance (UV–vis DR, JASCO V-670 spectrometer equipped with an integrating sphere), X-ray fluorescence spectroscopy (XRF, Rigaku, Supermini200), X-ray photoelectron spectroscopy (XPS, Ulvac-Phi, XPS-1800), scanning probe microscopy (SEM, SHIMADZU, SPM–9700), and scanning transmission electron microscopy (STEM, Hitachi High-Technologies Co., Ltd., HD-2700) with EDX mapping.

Photocatalytic reaction test

50 mg of the photocatalyst was dispersed in 50 mL of a 1.0 M H$_2$SO$_4$ or NaHSO$_4$ aqueous solution in a 100 mL beaker. 100 mL min^{-1} of O$_2$ was flowed into the mixture under strong stirring, and the beaker was placed in an ice bath to maintain a temperature below 278 K. Prior to photoirradiation, O$_2$ was flowed for at least 30 min to achieve an

equilibrium of dissolved O_2 and was kept flowing during the reaction. The photoirradiation was then started using an AM 1.5G solar simulator (SAN-EI Electric Co., XES-151S); the intensity of the irradiation was about 100 mW cm^{-2}. The recycle test was performed under the same conditions, excepted that the stirring was performed at the first 30 min and stopped before irradiation, the solution was directly replaced by 50 mL of fresh 1.0 M H_2SO_4 aqueous solution after 3 h irradiation, then started the next cycle.

The quantum efficiency (QE) of $S_2O_8^{2-}$ formation at 420 nm was measured using a 300 W Xe lamp with monochromatic light through a bandpass filter (ASAHI SPECTRA Co., MAX-302).

Since the $S_2O_8^{2-}$ formation is a two-electron process, therefore the QE can be defined as follows (Eq. S1);

$$QE\% = (M(S_2O_8^{2-}) \times 2 \times n)/N \times 100 \qquad \text{S1}$$

where $M(S_2O_8^{2-})$, n, and N denote the amount of $S_2O_8^{2-}$ formation at 420 nm (2.9 μmol), the number of molecules per molar (6.0×10^{23} mol^{-1}), the number of incident photons, respectively. N was calculated from the listed Eq. S2;

$$N = E_\lambda/E_0 = (E_\lambda \times \lambda)/(h \times c) = (P \times S \times t \times \lambda)/(h \times c) \qquad \text{S2}$$

whereas, E_λ, E_0, P, S, t, λ, h, and c denote the incident energy, the energy of per photons ($E_0 = h\nu = hc/\lambda$), the intensity of irradiation (0.4 mW cm^{-2}), the irradiated area (10 cm^2), the irradiation time (3 h), the wavelength of light (420 nm), Plank constant (6.6×10^{-34} J·s), the speed of light (3.0×10^8 m s^{-1}), respectively.

Quantitative analysis of products

The total content of the oxidants of $S_2O_8^{2-}$ and H_2O_2 was first measured by colorimetry using the color change from Fe^{2+} to Fe^{3+}, as shown in Eq. S3 and S4, using a microplate reader (Tecan Japan Co., Ltd., infinite M200PRO).

$$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^- \qquad \text{S3}$$

$$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-} \qquad \text{S4}$$
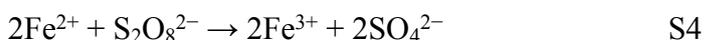
To differentiate the H_2O_2 content from the total oxidant content, the reduction of Ce^{4+} to

Ce^{3+} was used. $E_0(Ce^{4+}/Ce^{3+})$ is 1.61 V, which is higher than $E_0(O_2/H_2O_2) = 0.68$ V. Therefore, H_2O_2 can be oxidized by Ce^{4+} (Eq. S5); however, $S_2O_8^{2-}$ cannot be oxidized due to its higher oxidation potential.

$$2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + O_2 + 2H^+ \qquad\qquad \text{S5}$$
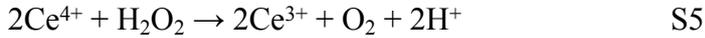
Subsequently, the amount of $S_2O_8^{2-}$ can be calculated from the difference between the two measurements; a similar concept has been reported.[4]

   In detail, 1.7 mL 1.0 M H_2SO_4, 100 μL reaction solution, and 200 μL 0.01 M $FeSO_4$ in 1.0 M H_2SO_4 were mixed together. After 30 min, the solution was measured using Fe^{3+} colorimetry at 330 nm. Finally, the total oxidant content could be calculated. To determine the amount of H_2O_2, the 0.01 M $FeSO_4$ was replaced by 0.0025 M $Ce(SO_4)_2$ in 1.0 M H_2SO_4. After 30 min, the solution was measured using Ce^{4+} colorimetry at 360 nm.

Electrochemical properties

   The electrochemical performance of noble-metal loaded fluorine doped tin oxide (noble-metal/FTO) was measured using an electrochemical analyzer (BAS. Inc., ALS660B). The noble-metal/FTO electrode was prepared as follows: FTO (2.4 cm × 6 cm) was pretreated in O_3 for 30 min. and loaded with a 0.03 M aqueous solution of the noble-metal precursor by the spin coating method (2000 rpm, 15 s). The electrodes were then calcined at 823 K for 30 min to obtain the noble-metal loaded FTO.

   The current-voltage (*I-V*) characteristics were studied with a three-electrode system using a one-compartment cell consisting of noble-metal/FTO as the working electrode, a Ag/AgCl electrode as the reference electrode, and a Pt mesh as the counter electrode at a low scan rate (50 mV s^{-1}) in 50 mL of 1.0 M H_2SO_4 with flowing O_2.
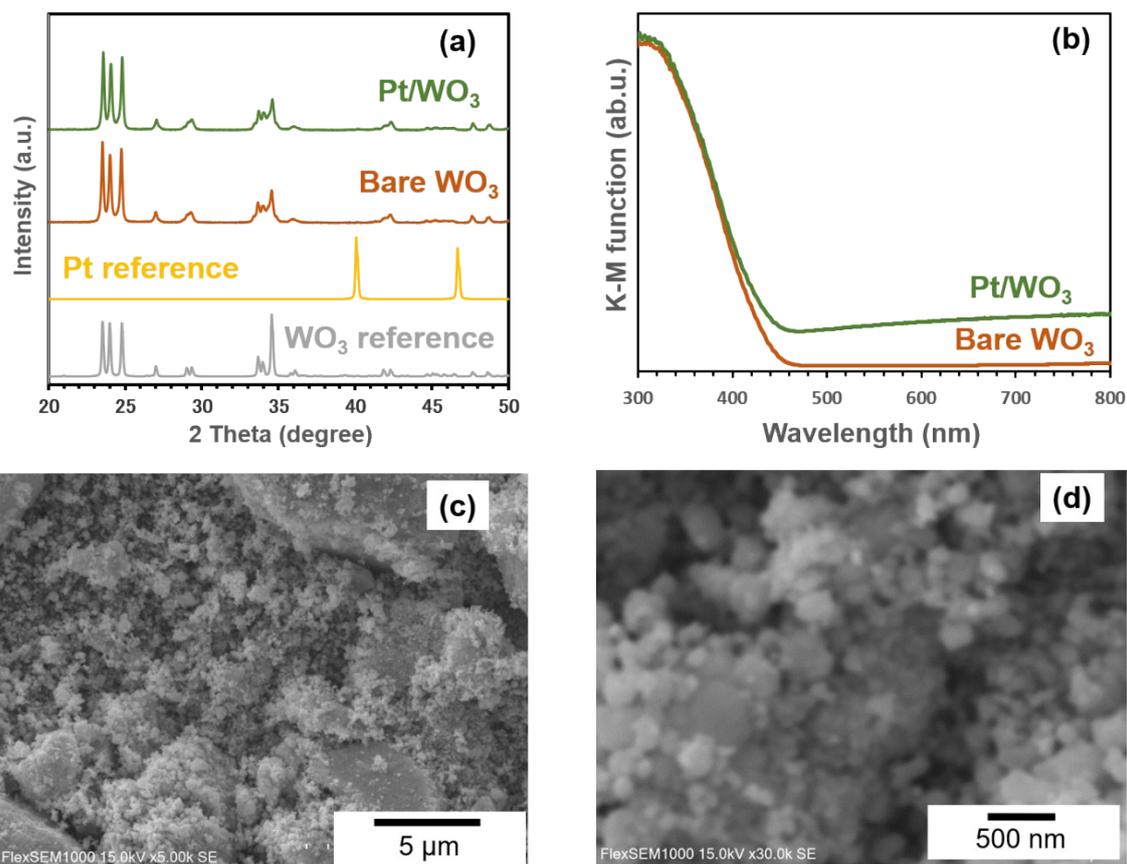
Figure S1 XRD (a), and UV-vis DR spectra (b) of bare WO_3 and 1.0 wt% Pt loaded WO_3 by a photodeposition method. (c) and (d) are SEM images of 1.0 wt% Pt loaded WO_3.
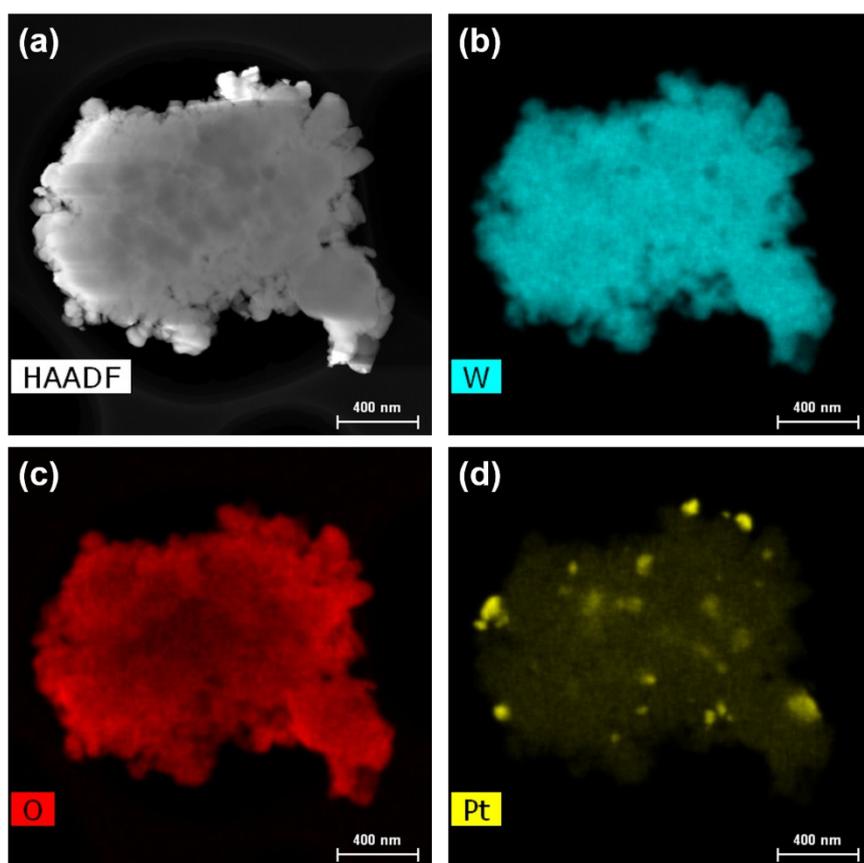
Figure S2 HAADF image (a) and the related element mapping of W (b), O(c) and Pt (d) of 1.0 wt% Pt/WO$_3$.
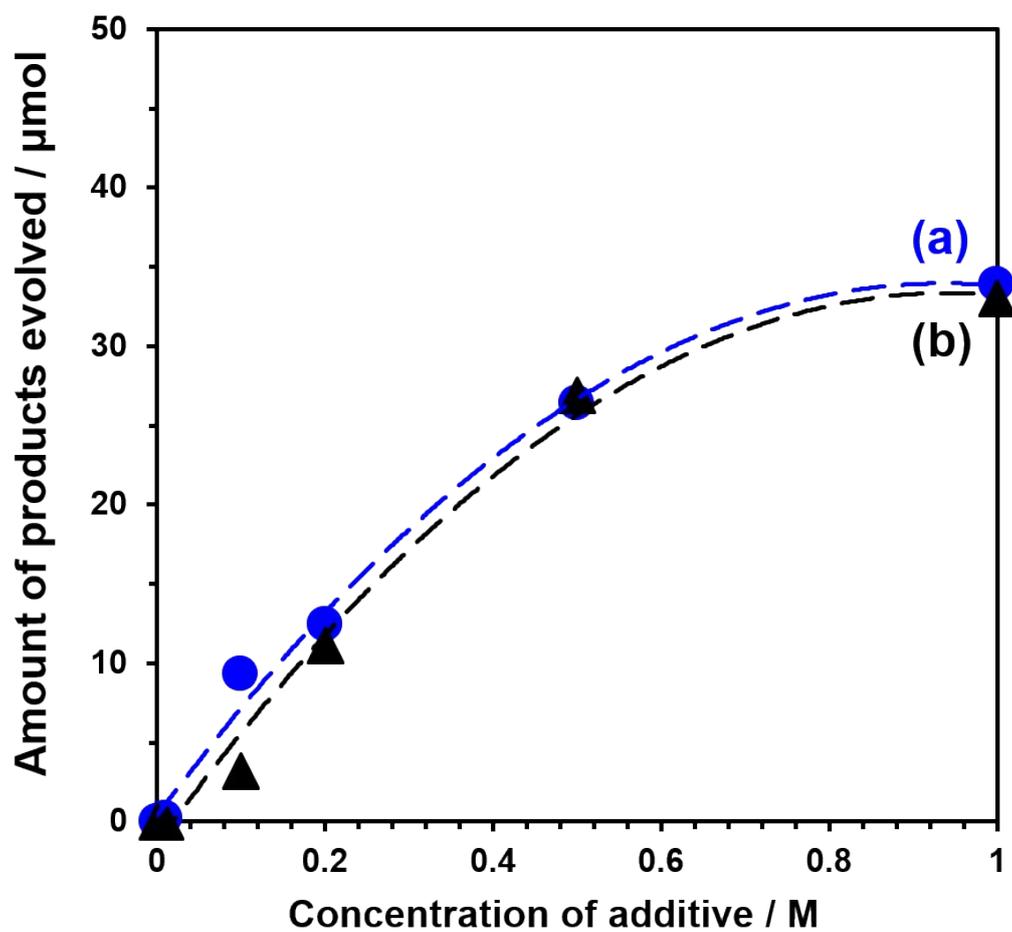
Figure S3 Effect of concentration of H_2SO_4(a) and $NaHSO_4$(b) on the formation of $S_2O_8^{2-}$ over 1.0 wt% Pt/WO_3.

Catalyst	×	O	O	O	O	O
Photoirradiation	O	×	O	O	O	O
O$_2$ flow	O	O	×※	O	O	O
Pt cocatalyst	O	O	O	×	O	O
H$_2$SO$_4$ additive	O	O	O	O	×	O

※with N$_2$ flowing
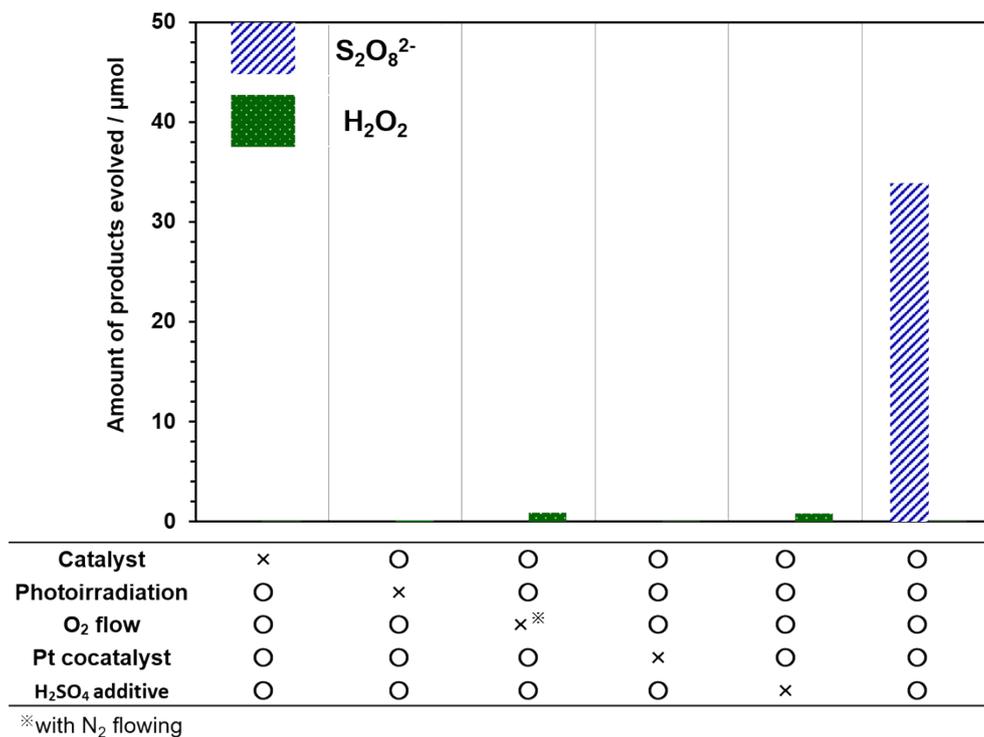
Figure S4 Formation amounts of products in the absence of each component during the photocatalytic production of over 1.0 wt% Pt loaded WO$_3$.
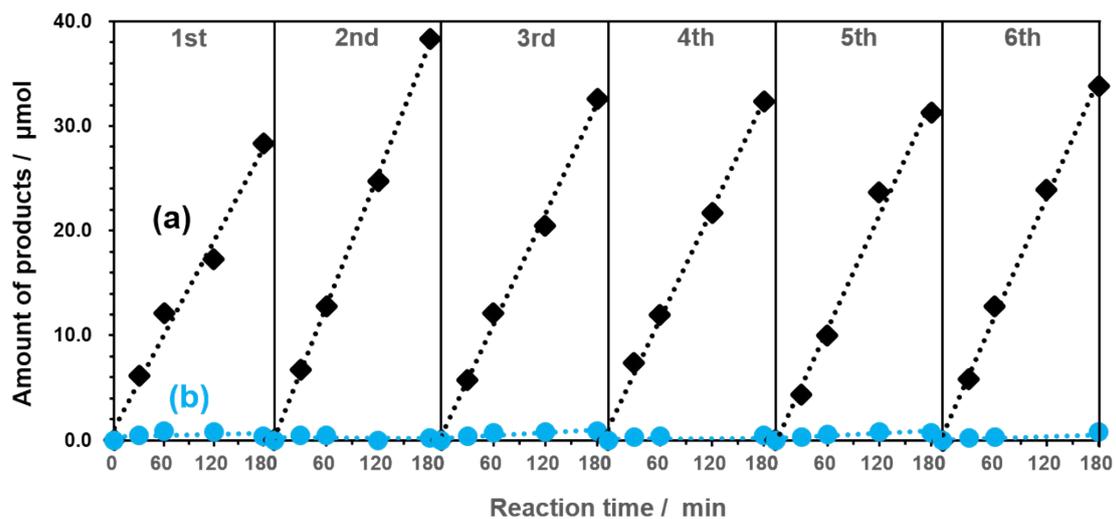
Figure S5 Time course of $S_2O_8^{2-}$(a) and H_2O_2(b) formation amount during 6-cycle of 3 h photoirradiation over 1.0 wt% Pt/WO$_3$ in 1.0 M H$_2$SO$_4$ under flowing O$_2$.
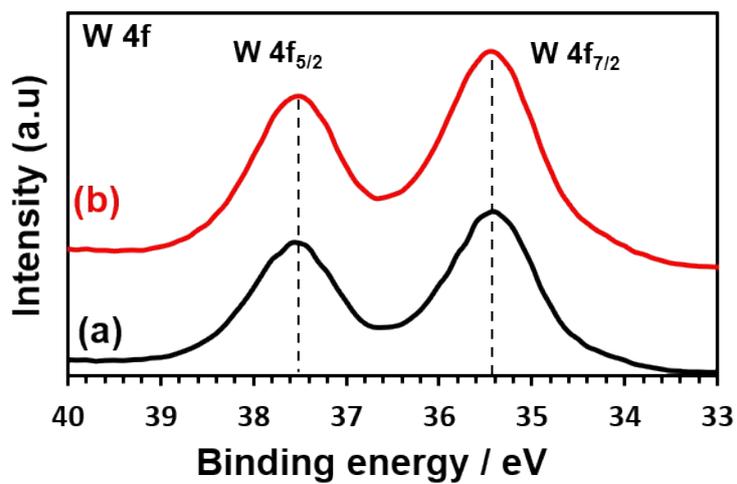
Figure S6 XPS spectra of as-prepared(a) and after 6-cycle reaction(b) of W 4f in 1.0 wt% Pt/WO$_3$ photocatalyst.

References

1. Suzuki, H., Tomita, O., Higashi, M., Abe, R. Tungstic acids H_2WO_4 and H_4WO_5 as stable photocatalysts for water oxidation under visible light. *Journal of Materials Chemistry A*, **2017**, 5(21), 10280-10288.

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4. Liang, C., He, B. A titration method for determining individual oxidant concentration in the dual sodium persulfate and hydrogen peroxide oxidation system. *Chemosphere*, **2018**, 198, 297-302.