Electronic supplementary information for

Rapid production of 38 mM H_2O_2 in an alcoholic suspension of a WO_3 photocatalyst under visible light

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Experimental

1. Chemicals

2-Propanol (guaranteed reagents, FUJIFILM Wako Pure Chemical, Osaka, Japan) was used without further purification. Commercial WO_3 (Kojundo Chemical Lab., Saitama, Japan) was used without any additional treatment.

2. Photocatalytic H_2O_2 production

Fifty mg of WO_3 powder was suspended in a 2-propanol-water solvent (5 cm^3) in a Pyrex test tube (volume of gas phase: 30 cm^3). The test tube was sealed with a rubber septum under O_2, set in a water bath kept at various temperatures, and then irradiated with a xenon (Xe) lamp (LA-410UV, Hayashi-Repic, Tokyo, Japan) equipped with an L-42 cut filter (light intensity of 114 mW cm^{-2}). The temperature of the water bath was changed in the range of 27-60℃. The boiling point of 2-propanol is 82°C, and the total pressure of O_2 and 2-propanol in the test tube is 140 kPa even at 60°C. The reactor employed in this experiment is a Pyrex test tube, which is sealed with a rubber septum. For reasons of safety, it is not possible to operate the photocatalytic reaction at temperatures exceeding 60°C. The amount of O_2 in the gas phase was measured by gas chromatography (GC) under the conditions specified in Table S1. Acetone in the liquid phase was measured by GC under the conditions specified in Table S2. For the acetone measurement, a solution of 2-propanol (50 cm^3) plus toluene (1 cm^3) was used as an internal standard. By using a potassium iodide reagent (WAK-H_2O_2(C), Kyoritsu Chemical-Check Lab., Kanagawa, Japan), H_2O_2 in the liquid phase was colored and then analyzed spectrophotometrically. To assess the precision of data obtained via a photoabsorption method using potassium iodide, a 0.35%H_2O_2 solution was prepared by hundred-fold dilution of a 35%H_2O_2 solution (guaranteed reagents, FUJIFILM Wako Pure Chemical). The concentration was determined to be 0.12 mol dm^{-3} by a titration

method using 0.04 mol dm^{-3} $KMnO_4$ solution (for volumetric analysis, FUJIFILM Wako Pure Chemical), while the concentration was determined to be 0.12 mol dm^{-3} by the photoabsorption method. The agreement between the two concentrations indicates that the concentration determined by the photoabsorption method is accurate and reliable.

3. Action spectrum measurement

To investigate the efficiency of light energy utilization at specific wavelengths in photocatalytic reactions, we calculated the apparent quantum efficiency (AQE) and measured action spectra. We used 50 mg of WO_3 powder in a Pyrex test tube, suspended it in a 90 vol% 2-propanol solution (5 cm^3), replaced the gas phase with O_2, and sealed it with a rubber septum. The suspension was irradiated with visible light from a Xe lamp equipped with band-pass filters (Asahi Spectra, Tokyo, Japan). The reaction temperature was controlled by placing the test tube in a water bath controlled at 60℃. The amount of H_2O_2 was determined by using the same method as that described in 2-2 and then AQE was calculated using Equation S1.

$$\mathrm{AQE} = \frac{2 \times amount\ of\ H_2O_2}{number\ of\ incident\ photons} \times 100. \quad \text{(S1)}$$

Table S1 GC condition for analysis of O_2 in the gas phase

GC	GC-8A (Shimadzu, Kyoto, Japan)
Detector type	TCD
Injection temperature	120°C
Detector temperature	120°C
Column temperature	100°C
Current	60 mA
Carrier gas	Ar
Column	MS5A

Table S2 GC condition for analysis of acetone in the liquid phase

GC	GC-2014s (Shimadzu, Kyoto, Japan)
Detector type	FID
Injection temperature	150°C
Detector temperature	180°C
Column temperature	80°C
Carrier gas	N_2
Column	PEG20M

Results

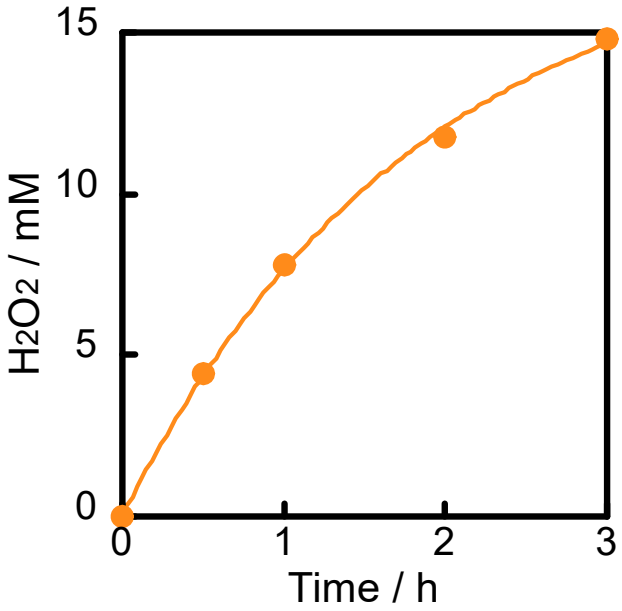


Figure S1 Time courses of photocatalytic H_2O_2 production by O_2 reduction in a 2-propanol-water (9:1) suspension of Au-WO_3 at 60°C under irradiation of visible light.

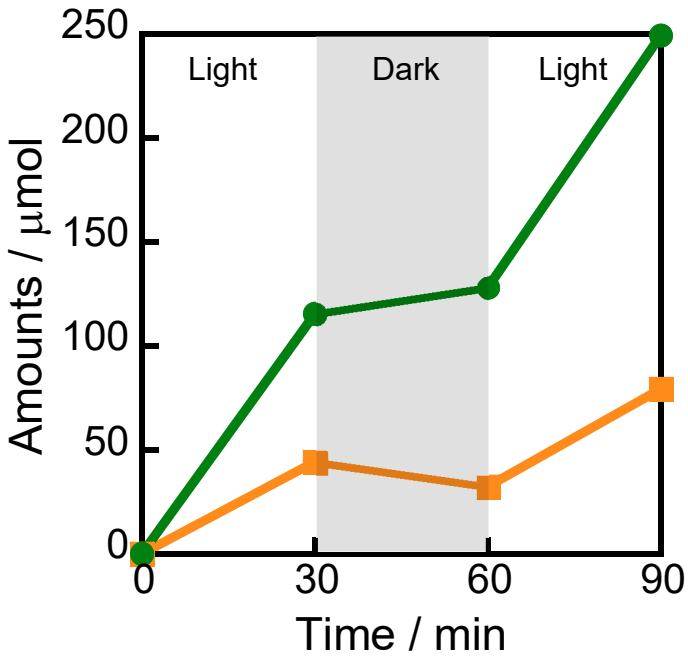


Figure S2 Time courses of photocatalytic H_2O_2 production by O_2 reduction in a 2-propanol-water (9:1) suspension of WO_3 under irradiation of visible light and in the dark.

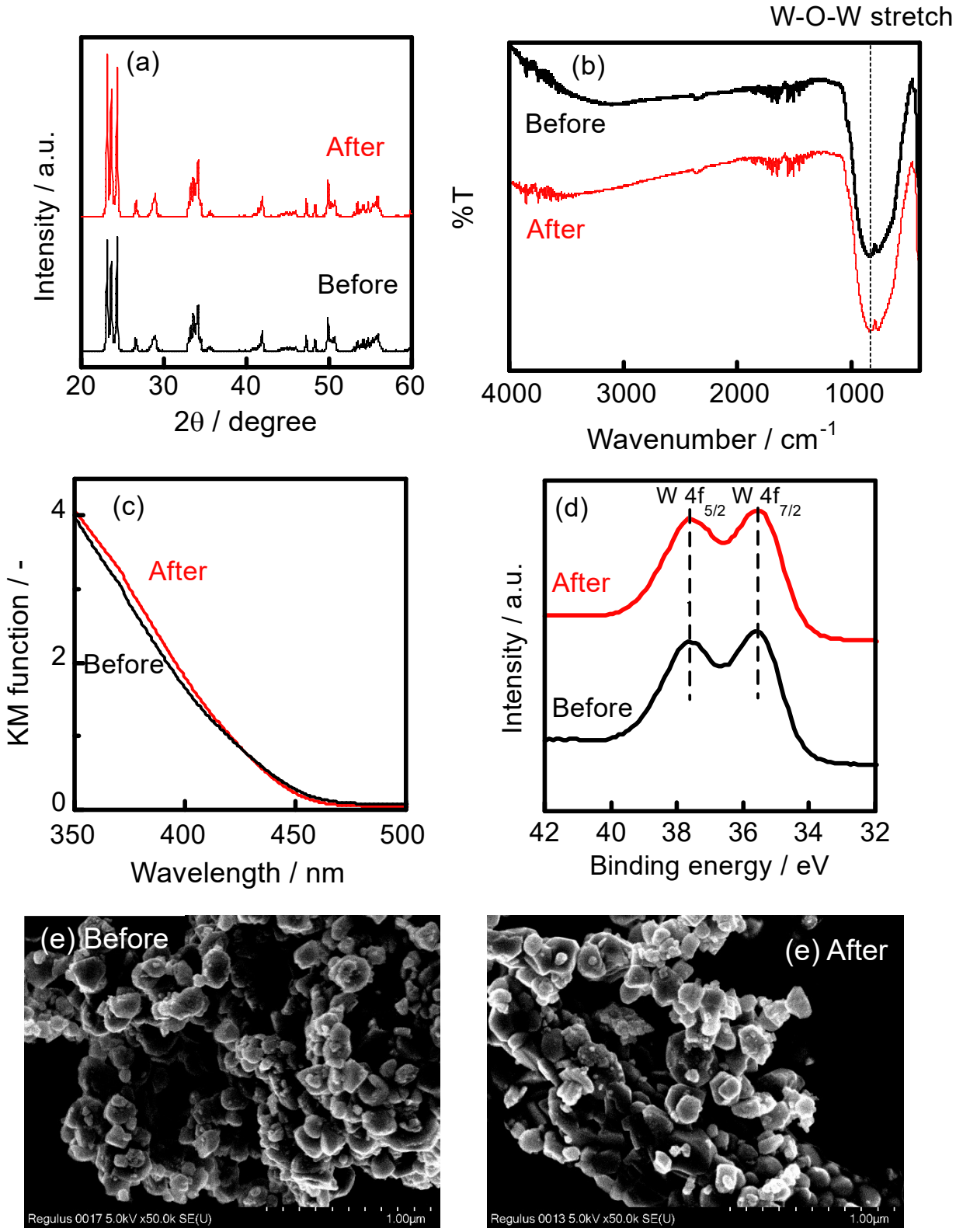
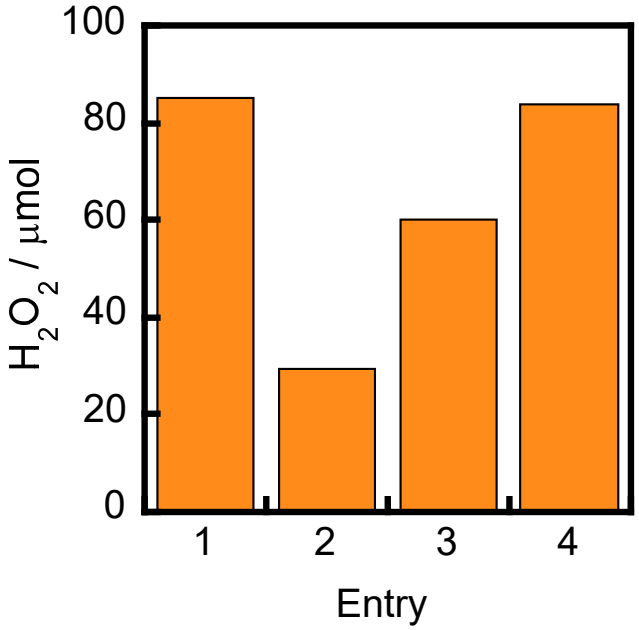


Figure S3 (a) XRD patterns, (b) FT-IR spectra, (c) UV-vis spectra, (d) XPS spectra, and (e) SEM photographs of WO_3 samples before and after the reaction.



Entry	Cycling count	Calcination temp. / °C
1	0（Fresh）	-
2	1	-
3	1	200
4	1	300

Figure S4　Re-used tests of the WO_3 photocatalyst after thermal treatment in air at various temperatures.