

Electronic Supplementary Information

**Hydrogen Evolution from Glycerol Aqueous Solution under
Aerobic Conditions over Pt/TiO₂ and Au/TiO₂ Granular
Photocatalysts**

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Experimental details

[Preparation of photocatalysts by photodeposition method]

To a 50 wt% aqueous solution of methanol (150 mL), TiO₂ powder (P25, Japan Aerosil) (1.5 g) and a 0.1 mol/L aqueous chloroplatinic acid solution (0.24 mL) were added. Argon gas was bubbled into the solution for 30 min to remove dissolved oxygen. The reactor was stirred with a magnetic stirrer at ca. 500 rpm and irradiated with a 100W high pressure Hg lamp (HL100G, SEN Lights Corp.) for about 1.5 h. The precipitate was filtered with suction, washed with water, and dried at 373 K to obtain the Pt/TiO₂ photocatalyst (0.3 wt% Pt loading) as crude aggregates. The Au/TiO₂ photocatalyst (0.3 wt% Au loading) was prepared by the same procedure using chloroauric acid.

[Classification of photocatalyst aggregates by size]

The crude aggregates of the prepared photocatalysts were classified by size into three groups, i.e., 300–710 μm, 125–300 μm, and <125 μm, using three types of metal sieves. Photocatalyst aggregates A and photocatalyst aggregates B were obtained from the largest (300–710 μm) and medium class particles (125–300 μm), respectively, after removal of residual powder particles by sedimentation in water. Photocatalyst aggregates C were obtained from the smallest class (<125 μm) by removing particles smaller than 40 μm by sedimentation in water. A part of aggregates C was subsequently grinded in a mortar to obtain aggregates D (powder form) with size less than 10 μm in diameter.

[Characterization of the photocatalyst samples]

The secondary particle size distribution of the photocatalyst aggregates was measured by means of a laser diffraction-scattering particle size distribution analyser (MT3000 II, Microtrac Inc.). Powder X-ray diffraction (XRD) measurements were performed using a diffractometer Ultima-IV (Rigaku Co., Ltd.) with Cu K α radiation (40 kV, 40 mA). The transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images were recorded on a TECNAI G2 F20 (FEI) at a 200 kV acceleration voltage.

[Photocatalytic reaction (Fig. S1(a))]

A GC vial equipped with an open-top screw cap sealed with a butyl rubber septum (SVG-12, Nichiden-Rika Glass Co., Ltd., internal volume of 15.6 mL) was employed as the reaction vessel. The photocatalyst aggregate (50 mg) and a 0.5 wt% aqueous solution of

glycerol (5.0 mL) were added to the vial, which was then tightly closed. Air was trapped in the 10.6-mL headspace volume. The vessel was kept in a water bath at a constant temperature of 293 K, and different solution mixing conditions were tested, as described in Table 2. A Xe lamp (Optical Modulex SX-UID 501XAMQ, USHIO Co., Ltd.) was used, and the light was filtered through a 320 nm cut-off filter and an infrared cut filter (IRA-25S, Toshiba Co.). In order to start the reaction, the vessel was irradiated from the bottom by bending the output light beam from the horizontal to the upward direction using a mirror (light-irradiated area 3.6 cm²). After 30 min, the headspace gas (0.2 mL) was sampled with a gas-tight syringe and analysed by two gas chromatographs. The results were compared with those of the air before reaction. A TCD gas chromatograph (GC320, GL Sciences Co., Ltd.) equipped with a MS5A column (2 m) and Ar carrier gas was used for H₂, O₂, and N₂ determination. The amounts of evolved H₂ and consumed O₂ were calculated from the molar ratio in the headspace on the basis of the relative molar sensitivity for each gas. A FID gas chromatograph (GC14B, Shimadzu Co., Ltd.) equipped with a methaniser (MT-221, GL Sciences Co., Ltd.) and a G-950 column (40 m length, 25 mm film thickness, and 1.2 mm inner diameter) with He carrier gas was used for CO₂ analysis. The amount of evolved CO₂ was calculated from the absolute peak area of the sampled gas, and the area was compared with that of the standard gas (CO₂ (1%) in air). The photoreaction was continued for at least 1.5 h and the headspace gas was sampled every 30 min.

[Photocatalytic reaction with dissolved oxygen (DO) measurement (Fig. 1S(b))]

A DO meter (HI-2040, Hanna Instruments) was used for measuring the dissolved oxygen concentration during the photocatalytic reaction, as shown in Fig. 1S(b). A DO electrode HI-764080 was inserted through the rubber septum of the GC vial (SVG-100, Nichiden-Rika Glass Co., Ltd.). The Pt/TiO₂ photocatalyst (Pt 0.3 wt%) aggregate A (100 mg) and a 10 wt% aqueous solution of glycerol (85 mL) were added to the vial, and a glass plate (51 × 19 mm) was placed in order to avoid direct contact of the tip of the electrode with the hydrogen bubbles. The glycerol solution was mixed using a small magnetic stirrer (CC 301; AS One Co., Ltd.) fixed on the side of the vial. The headspace was filled with air, and the volume was 15.6 mL after tightly closing the vial. The vial was kept in a water bath at a constant temperature of 293 K. The output light from the Xe lamp (SX-UID 501XAMQ) was guided by a quartz optical fibre, and the reaction vessel was irradiated from the bottom (light-irradiated area: 9.6 cm²). Gas sampling and GC analysis were carried out as described in the previous section.

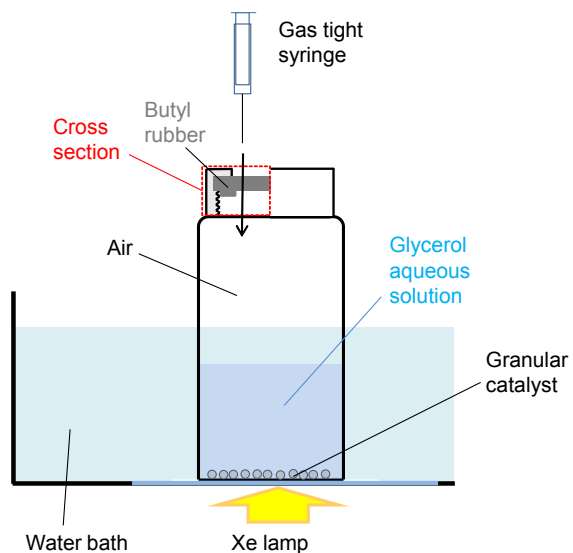
[Photocatalytic reaction using solar simulator (AM 1.5G)]

The same GC vial (SVG-12) described in the previous section was employed as the reaction vessel. The photocatalyst aggregate (100 mg) and a 10.0 wt% aqueous solution of glycerol (5.0 mL) were added to the vial, which was then tightly closed. The vessel was kept in a water bath at a constant temperature of 293 K, without mixing. A solar simulator (XES-502S, SAN-EI Co., Ltd.) was used, and the output light was reflected by a pair of mirrors so that the reaction vessel was irradiated from the bottom (light-irradiated area 3.6 cm²), providing a 24.2 mW/cm² illumination, as measured by a Nova Display equipped with a calibrated 2A-SH thermopile head (Ophir Optronics, USA). Gas sampling and GC analysis were carried out as described in the previous section.

[Turbidity measurement of the reaction mixture]

A turbidity sensor (TCR-30, Kasahara Chemical Instruments Corp.) based on absorption spectrophotometry was used for measuring the turbidity of the photocatalytic reaction mixture caused by the suspension of the photocatalyst aggregates. After completion of the photocatalytic reaction, the mixture was mixed under the same conditions used during the reaction, while opening the vial. The reaction mixture (1 mL) was sampled, transferred into the vessel of the sensor, and diluted to 150 mL with distilled water. The reading of the sensor was multiplied by 150 to obtain the turbidity of the original reaction mixture.

(a)



(b)

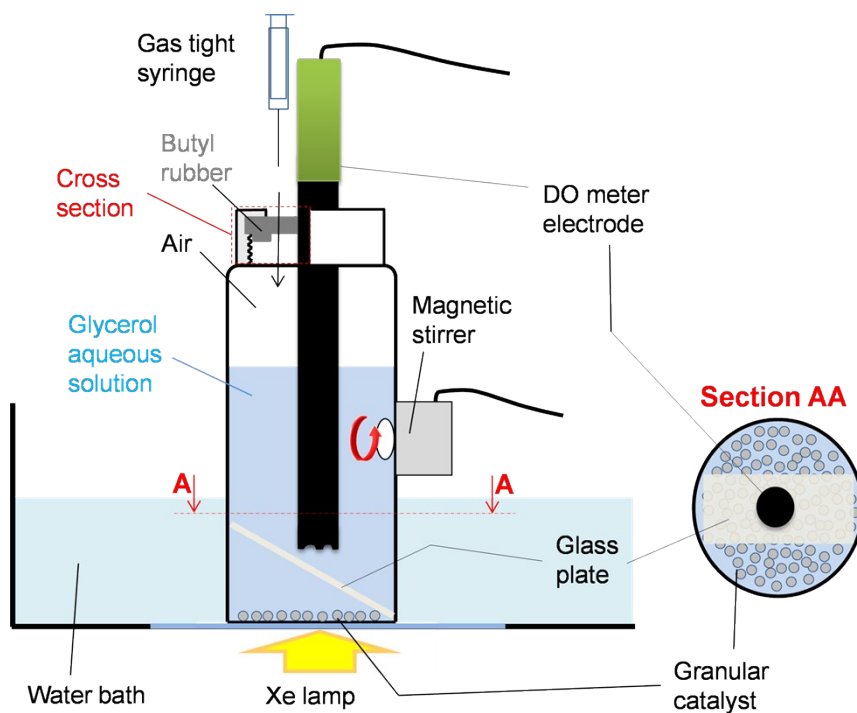


Fig. S1 Experimental setup for the photocatalytic reaction. (a) Standard experimental setup and (b) setup with DO measurement.

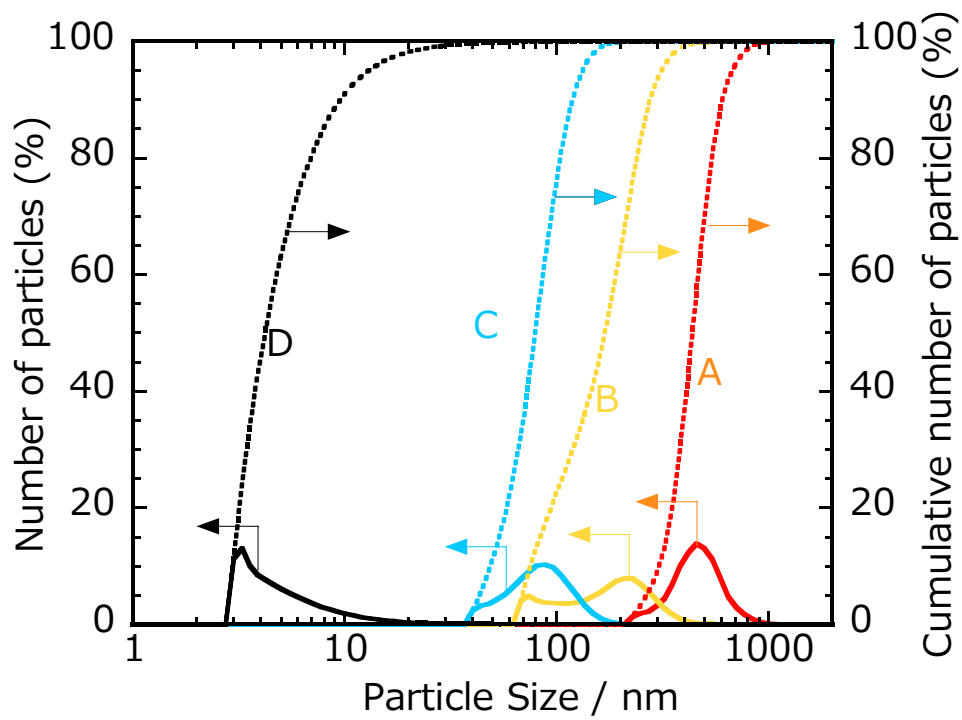
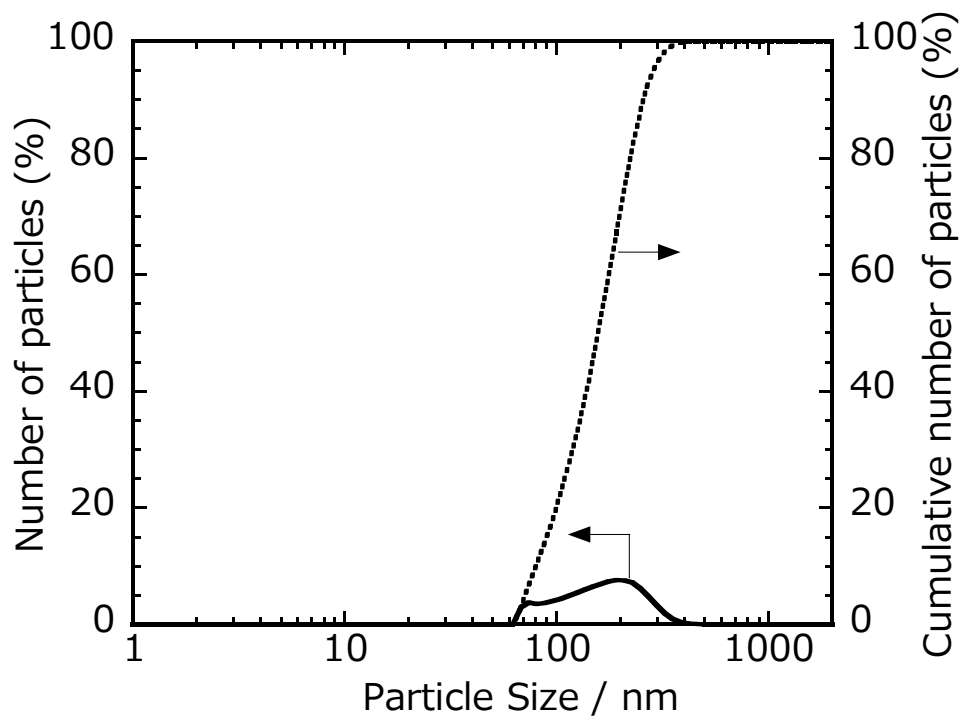


Fig. S2 Number-based particle size distribution of Pt/TiO₂ (A), (B), (C), and (D).



Photocatalyst aggregates	Nominal size range / μm	$d_{\text{avr.}}$ / μm	$d_{10\%}$ / μm	$d_{90\%}$ / μm	Sedimentation rate / mm s^{-1}
Au/TiO ₂ (B)	125-300	164	79.0	257	24

Fig. S3 Number-based particle size distribution of Au/TiO₂ (B)

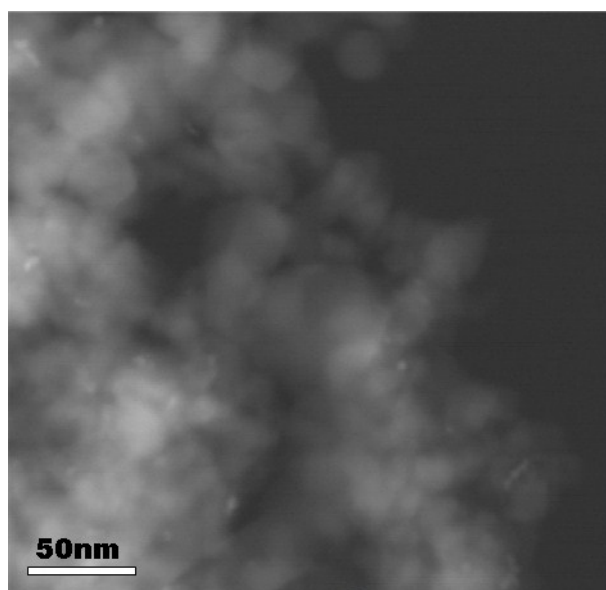
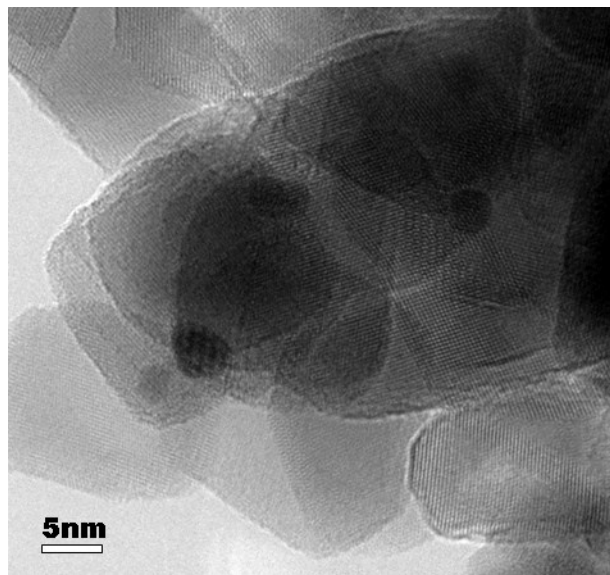


Fig. S4 TEM and HAADF-STEM images of Pt/TiO₂ (B)

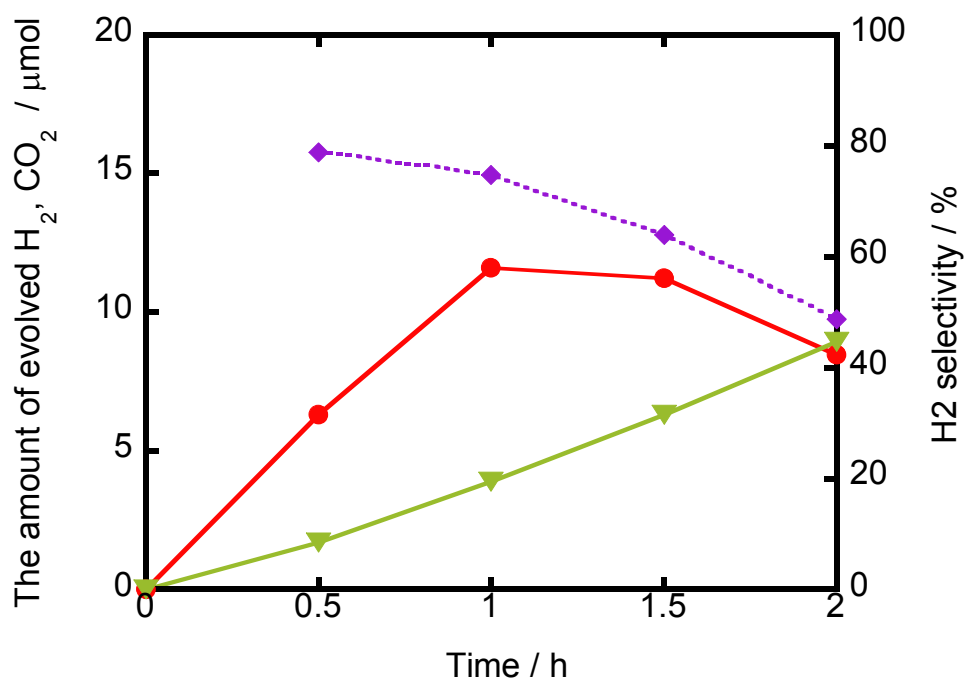


Fig. S5 Hydrogen evolution over Pt/TiO₂ (D) powder bed deposited at the bottom of the vial. Amount of H₂ (●) and CO₂ (▼) evolved during photo-irradiation and H₂ selectivity (◆). Pt/TiO₂ (D) 50 mg, V = 5.0 mL, T = 293 K, S = 3.6 cm², λ > 320 nm, I = 285 mW cm⁻².

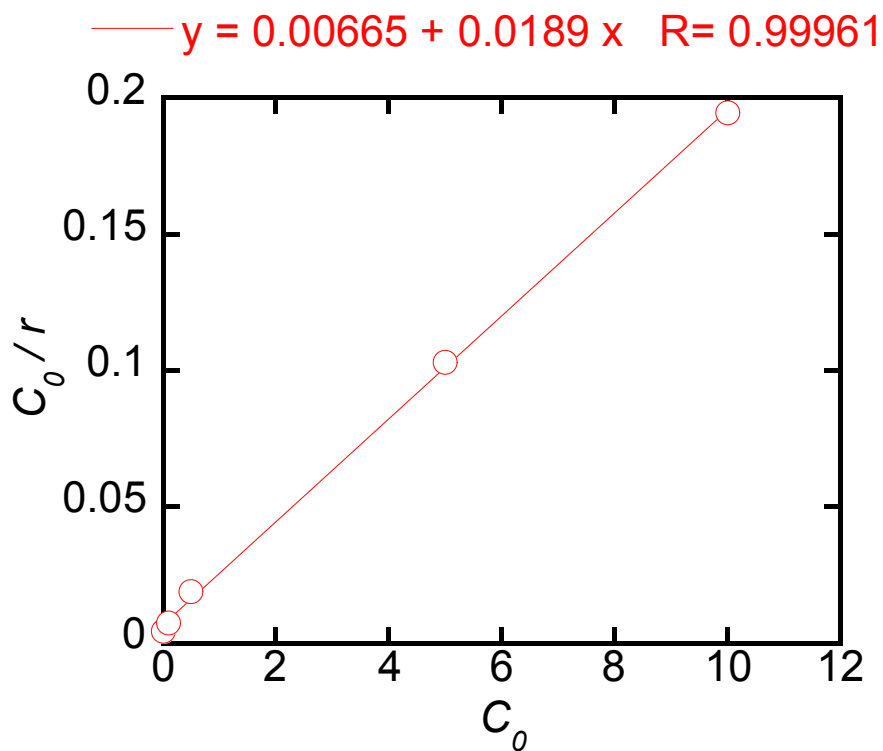


Fig. S6 Linear fitting of the Langmuir equation

$$r = dC(\text{H}_2)/dt = k_1 k_2 C_0 / (1 + k_2 C_0)$$

r : initial rate of the hydrogen evolution

k_1 : reaction rate constant

k_2 : adsorption constant of glycerol

C_0 : initial concentration of glycerol

$$C_0/r = 1/(k_1 k_2) + (1/k_1) C_0$$

y-axis

x-axis

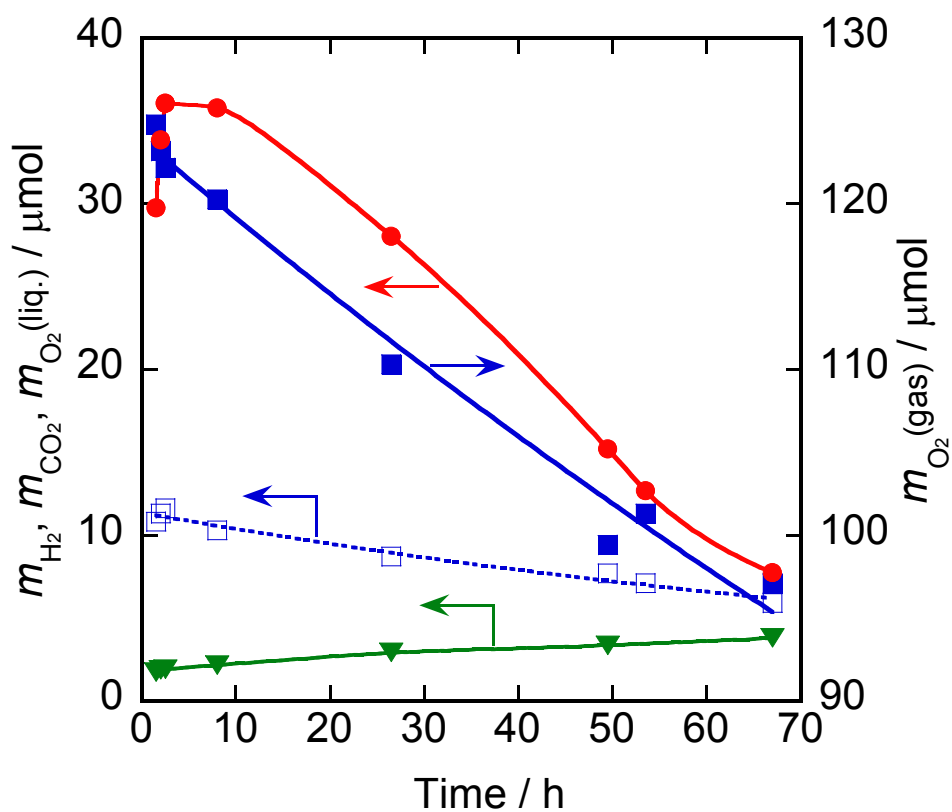


Fig. S7 Dark reaction over Pt/TiO₂ (A) after the photocatalytic reaction shown in Fig. 1. Time course of H₂ (●), CO₂ (▼), and O₂ (■) amount in gas phase and O₂ (□) amount in liquid phase after stopping light irradiation (time = 0). The hydrogen initially increased because the hydrogen bubbles (evolved during photo irradiation) adhering to the electrode rod of the DO meter migrated to the gas phase.

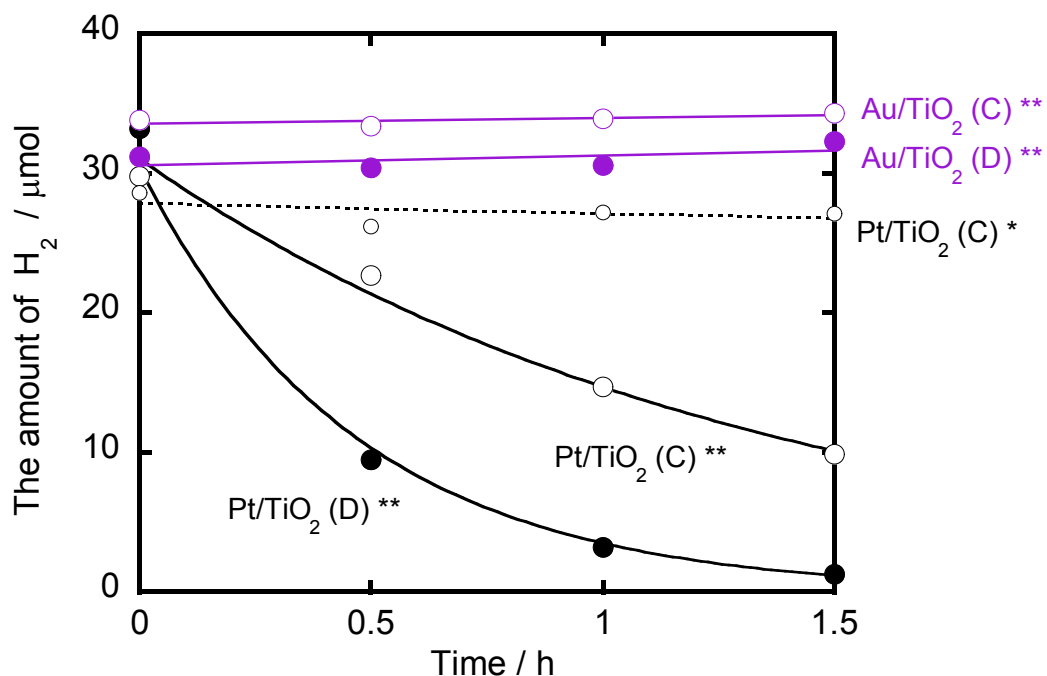


Fig. S8 Backward reaction in pure water over Pt/TiO₂ and Au/TiO₂ after injection of H₂ gas into the headspace, without light irradiation and mixing by shaker at 298 K. Granular Pt/TiO₂ (C), Au/TiO₂ (C) and powder Pt/TiO₂ (D), Au/TiO₂ (D) catalysts (20 mg) were added to 5 mL H₂O. The catalysts were homogeneously dispersed in water with vigorous shaking (**) at 180 rpm or not dispersed (mainly water mixing) with slower shaking (*) at 70 rpm.

Table S1. Example of STH comparison with the literature data

Photocatalyst	Cr ₂ O ₃ /Ru-modified SrTiO ₃ :La,Rh/Au/BiVO ₄ :Mo	Pt/TiO ₂
Reactant	Pure water	Glycerol (10 wt%) aqueous solution
Initial gas phase	Argon (10 kPa)	Air (100 kPa)
Light source	Solar simulator (AM 1.5G)	Solar simulator (AM 1.5G)
STH defined by eq. S1	1.1 (331 K) 0.56 (293 K from Arrhenius plot)	Cannot be calculated (ΔG of the hydrogen evolution reaction is unknown at this stage)
STH defined by eq. S2	1.4 (331 K) 0.71 (293 K)	1.0 (293 K)
Ref.	[1]	This work

<STH definition 1 in Ref. [1]>

$$\text{STH (\%)} = (R(\text{H}_2) \times \Delta G_r) / (P \times S) \times 100 \quad (\text{eq. S1})$$

<STH definition 2 in Ref. [2]>

$$\text{STH (\%)} = (m_p \times \Delta H_{\text{liq.}}) / I_s \times 100 = (R(\text{H}_2) \times \Delta H_{\text{liq.}}) / (P \times S) \times 100 \quad (\text{eq. S2})$$

R(H₂), m_p Rate of hydrogen evolution

ΔG_r Reaction Gibbs energy of the water splitting reaction (H₂O(l) → H₂(g) + 1/2 O₂(g))

ΔH_{liq.} Higher hydrogen heating value (286 kJ mol⁻¹). m_p × ΔH_{liq.} is the theoretical maximum energy that can be recovered from the produced hydrogen

I_s, P × S Total incident solar irradiance

P Energy intensity of the AM 1.5G solar irradiation (100 mW cm⁻²)

S Irradiated sample area

[1] Q. Wang, T. Hisatomi, Q. Jia, H. Tokudome, M. Zhong, C. Wang, Z. Pan, T. Takata, M. Nakabayashi, N. Shibata, Y. Li, I. D. Sharp, A. Kudo, T. Yamada and K. Domen, *Nat. Mater.*, 2016, **15**, 1–3.

[2] Z. Wang, R. R. Roberts, G. F. Naterer and K. S. Gabriel, *Int. J. Hydrogen Energy*, 2012, **37**, 16287–16301.