Supporting Information

of

Identifying and eliminating false positives in thermal-assisted photocatalysis

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Experimental section

Materials and chemicals

TiO_2 (anatase-80%, rutile-20%,) was purchased from Deggussa Corporation, Germany. $H_2PtCl_6 \cdot xH_2O$ was purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD.

Preparation of Pt/TiO_2 catalyst

Pt was induced on TiO_2 by an in situ photodeposition method. Typically, 100 mg TiO_2 and 0.1 wt.% $H_2PtCl_6 \cdot xH_2O$ were dispersed into 40 ml 10 vol.% methanol aqueous solution. Then, the solution was purged with argon for 20 min to remove oxygen and sealed for postdeposition induced by a 300 W Xe lamp for 1 hours. Finally, the Pt/TiO_2 was obtained by centrifugation, washed with deionized water for three times, and dried in the oven for 6 h at 60 °C.

Thermal-assisted photocatalytic hydrogen evolution

The thermal-assisted photocatalytic hydrogen evolution experiment was performed in a Pyrex vessel connected to a closed glass circulation and evacuation system (Beijing Perfectlight, Labsolar-6A), and the temperature of the system was controlled by circulating condensed water system. A 300 W Xe lamp was used as a light source. A 20 mg of catalysts dispersed in 100 ml of methanol aqueous solution was prepared. Firstly, the slurry in the reactor was vacuumed for 30 minutes in order to remove the dissolved gas molecular and to assure that the reactor can be operated in an anaerobic condition. During the hydrogen production test, the catalyst was kept in suspension by continuous magnetic stirring. The reaction temperatures are kept at about 15, 35, 55 and 75°C. The amount of hydrogen gas was calculated by the peak area of the product signal, which is recorded by an on-line gas chromatograph (Techcomp, GC7900, MS-5A column, thermal conductivity detectors, Ar carrier). An amount of ~0.45 mmol Ar gas was injected into the system every time before testing the yield to

promote the gas diffusion. The evolved H_2 for Fig. S3-S6 were measured by chromatograph (GC2014, Shimadzu) with a TCD detector using Ar as the carrier gas.

Material characterizations

To characterize the crystal structures of catalysts, powder X-ray diffraction (XRD) was conducted using a PANalytical X'Pert Power apparatus (Netherlands) operated at Cu $K\alpha$ radiation was collected on a LabRAM HR Evolution imaging microscope system. A scanning electron microscopy (Thermo Fisher Scientific Quattro S, USA) was conducted to investigate the morphology. Transmission electron microscopy (TEM, Thermo Fisher Scientific Talos F200S) was utilized to investigate the morphology of the samples. HAADF-STEM images and STEM-EDS mapping images of samples were collected on a FEI Titan Themis.

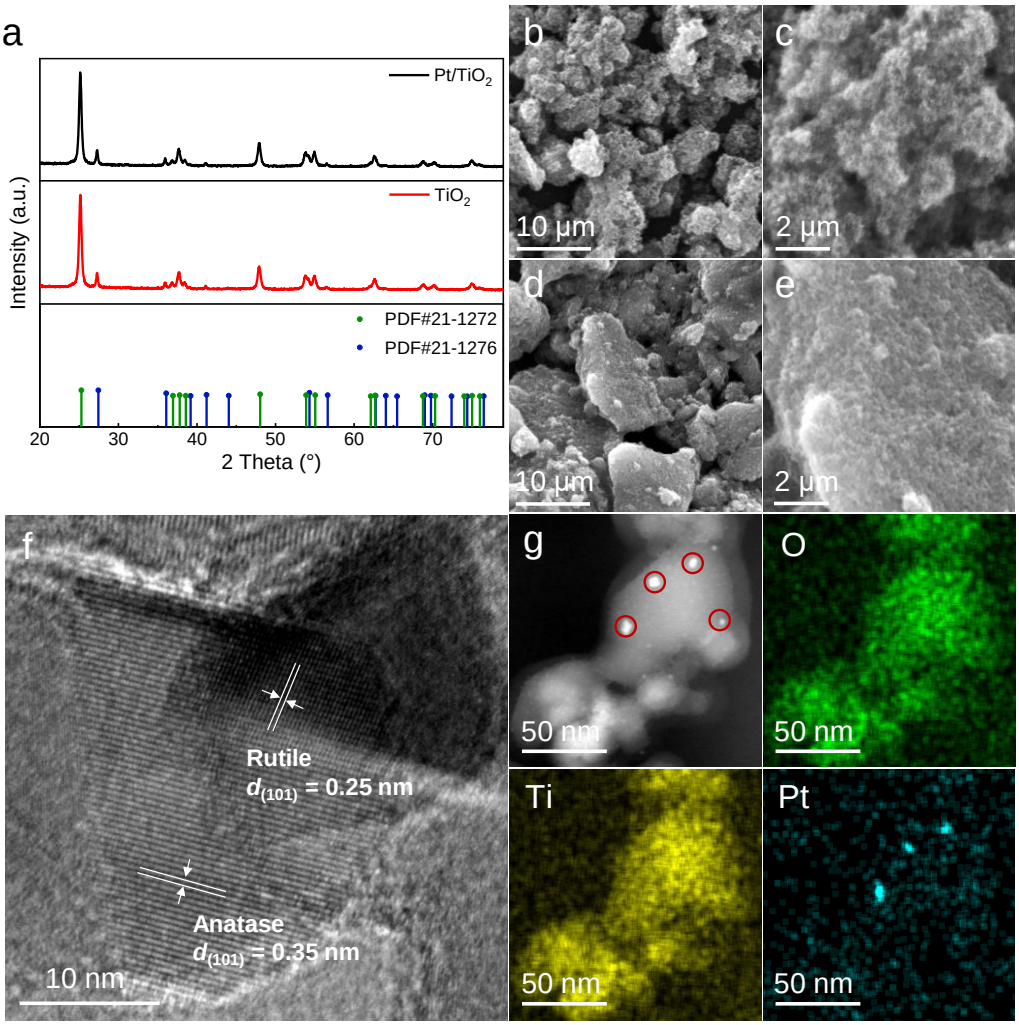

Figure S1. Characterization of TiO_2 and Pt/TiO_2 particles. (a) XRD pattern. (b), (c) SEM image of TiO_2. (d), (e) SEM image of Pt/TiO_2. (f) HRTEM image of TiO_2. (g) EDS mapping of Pt/TiO_2.

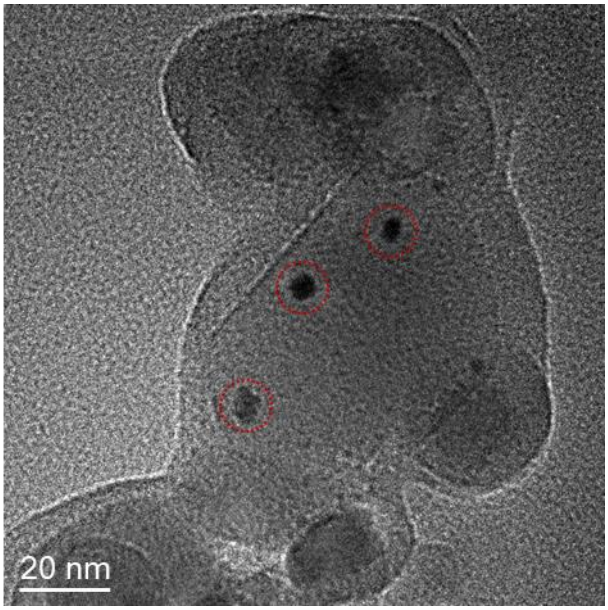

Figure S2. The TEM of Pt/TiO_2 catalyst.

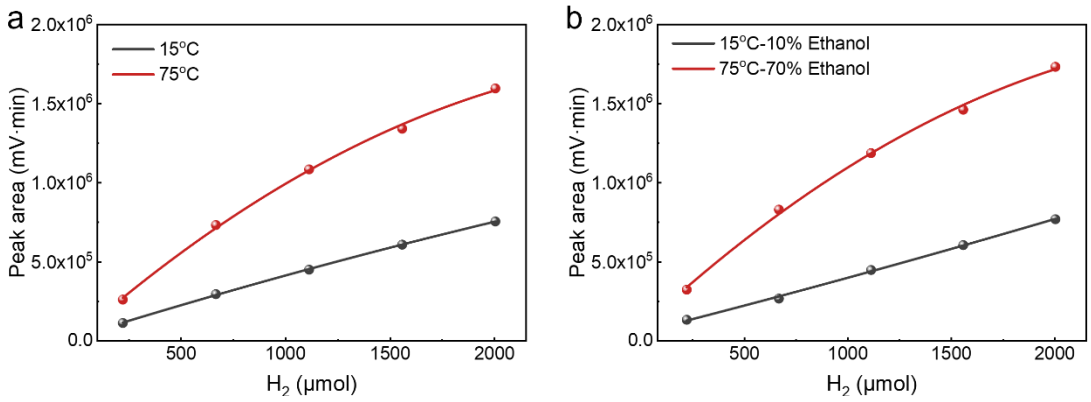

Figure S3. (a) Calibration curves of hydrogen at T = 15°C, 75°C with pure water. (b) Calibration curves of hydrogen at 15°C with 10 vol.% ethanol and at 75°C with 70 vol.% ethanol. The H_2 were measured by chromatograph (GC2014, Shimadzu) with a TCD detector using Ar as the carrier gas.

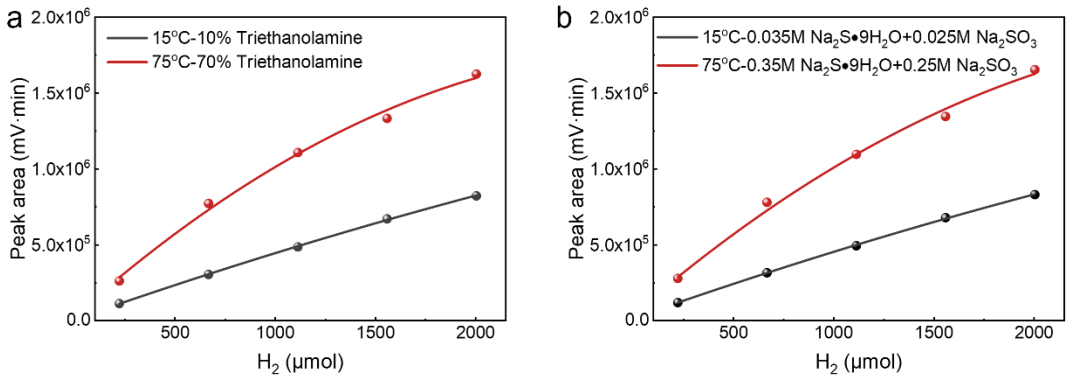

Figure S4. (a) Calibration curves of hydrogen at 15°C with 10 vol.% triethanolamine, and at 75°C with 70 vol.% triethanolamine. (b) Calibration curves of hydrogen at 15°C with 0.035 M $Na_2S•9H_2O$ and 0.025 M Na_2SO_3, and at 75°C with 0.35 M $Na_2S•9H_2O$ and 0.25 M Na_2SO_3. The H_2 were measured by chromatograph (GC2014, Shimadzu) with a TCD detector using Ar as the carrier gas.

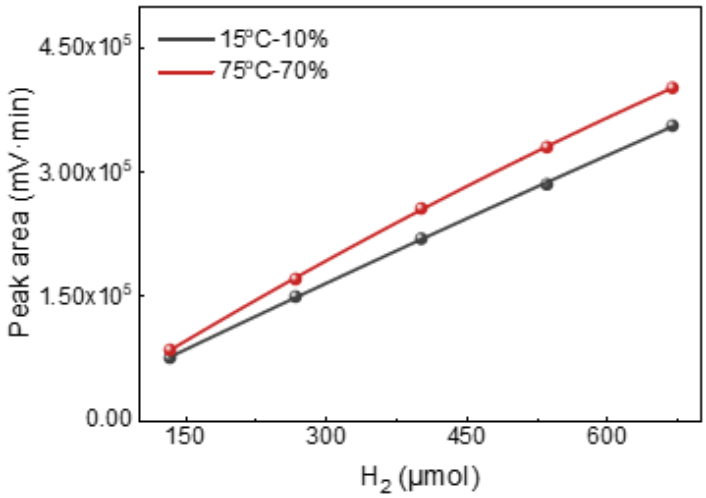

Figure S5. Calibration curves of hydrogen at T = 15℃, 75℃ and C(methanol) = 10% and 70%. The experiments were performed with 1ml of H_2O solution containing 10 vol.% and 70 vol.% methanol at 15℃ and 75℃. The H_2 were measured by chromatograph (GC2014, Shimadzu) with a TCD detector using Ar as the carrier gas.

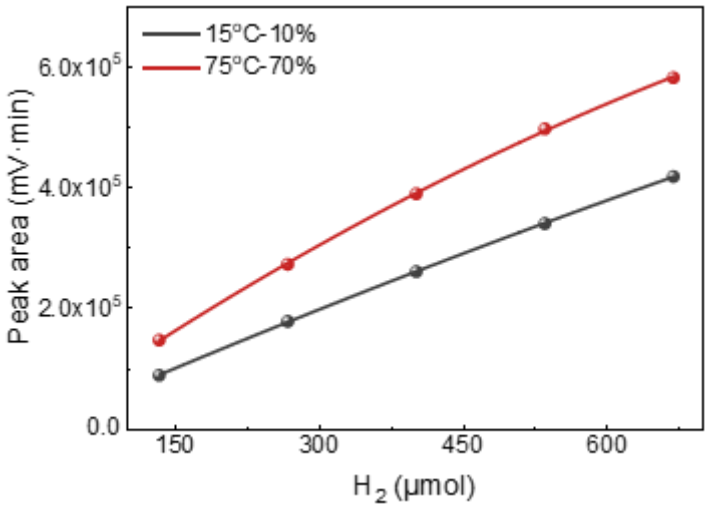

Figure S6. Calibration curves of hydrogen at T = 15℃, 75℃ and $C_{(methanol)}$ = 10% and 70%. The experiments were performed with 20 ml of H_2O solution containing 10 vol.% and 70 vol.% methanol. The H_2 were measured by chromatograph (GC2014, Shimadzu) with a TCD detector using Ar as the carrier gas.

Table S1. Fitting parameters of the calibration curves.

Equation	$y = ax + bx^2$		
Reaction condition	a	b	R^2
15℃-10 vol.%	2177.40439	-0.12734	0.99989
15℃-30 vol.%	2422.3322	-0.13532	0.99987
15℃-50 vol.%	3282.26996	-0.51194	0.99692
15℃-70 vol.%	3758.97446	-0.67975	0.99815
35℃-10 vol.%	3220.00883	-0.3987	0.99944
35℃-30 vol.%	3426.3584	-0.45473	0.99854
35℃-50 vol.%	4123.19048	-0.66009	0.99883
35℃-70 vol.%	5632.86803	-1.20042	0.99786
55℃-10 vol.%	4935.00418	-0.8746	0.99981
55℃-30 vol.%	5693.5552	-1.05628	0.99997
55℃-50 vol.%	6842.05768	-1.06145	0.99939
55℃-70 vol.%	7736.70662	-1.36244	0.99989
75℃-10 vol.%	5473.58139	-0.41836	0.99997
75℃-30 vol.%	5737.32296	-0.38392	0.99994
75℃-50 vol.%	7109.57474	-1.1356	0.99927
75℃-70 vol.%	7267.93908	-1.10728	0.99893