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Noble-metal loading reverses the temperature dependent photocatalytic hydrogen generation in methanol-water solution

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Part 1: Materials Preparation and characterization

Materials Preparation

TiO_2: Nano-TiO_2 (P25, 70% in anatase phase and 30% in rutile, particle diameters: 30–50 nm) was bought from Degussa Co.

g-C_3N_4: 5 g of thiourea powder was put into an alumina crucible with a cover and heated at 500 °C for 3 h in a muffle furnace (5 °C min^{-1}). g-C_3N_4 was obtained after cooling down to room temperature.[1,2]

Pt loading photocatalysts: 0.2 g *photocatalyst* was dispersed into 40 mL distilled water under vigorous stirring, and then 10 mL of methanol and 0.13 mL of H_2PtCl_6(0.077 M) solution were added to the suspension in sequence. The mixture was irradiated by a 300 W high-pressure Xenon lamp for 3 h under continuous stirring. After centrifugation, the sample was washed with water and dried at 80 °C for 10 h to obtain 1 wt% Pt-loaded photocatalysts.[3]

MoS_2/TiO_2: 0.2 g of the TiO_2 was dispersed in 18 mL of aqueous solution consisting of 30 mg of sodium molybdate dehydrate and 60 mg of thioacetamide to form a transparent solution. The mixed solution was then transferred into a 50 mL Teflon-lined stainless steel autoclave and then heated at 200 °C for 24 h in an electric oven. The gray product was collected via centrifugation and washed thoroughly with ethanol before drying at 80 °C for 12 h to give a 1.00 wt% MoS_2/TiO_2 sample. All products were ground and heated to 400 °C for 2 h under a nitrogen atmosphere. [4]

$Ni(OH)_2/TiO_2$: 0.2 g of the TiO_2 P25 was dispersed in 50 mL of 1.0 M NaOH aqueous solution, and then a certain volume of 0.05M $Ni(NO_3)_2$ aqueous solution was added to obtain a 1.00 wt% $Ni(OH)_2/TiO_2$ sample. The mixed solutions were stirred for 24 h at room temperature. After that, the precipitates were collected by centrifuge and washed with distilled water and alcohol 10 times, respectively. The washed precipitates were dried at 80 °C for 24 h.[5]

Characterization

X-ray diffraction patterns (XRD) were recorded by Smart Lab X-ray diffractometer

(Rigaku, Tokyo, Japan) operating at 40 mA and 40 kV using Cu Kα radiation. The 2θ range of XRD patterns were taken over 10-60◦. Transmission electron microscopy (TEM) images were obtained by a JEOL JEM-2100F (RH) Field Emission Electron Microscope working at 200 kV. X-ray photoelectron spectroscopy (XPS) data were obtained by Thermo ESCALAB 250XI X-ray photoelectron spectrometer (Al Ka, 150 W, C 1s 284.8 eV). Brunauer-Emmett-Teller (BET) surface areas were measured by a quantachrome autosorb-1 automated gas adsorption systems at 77 K.

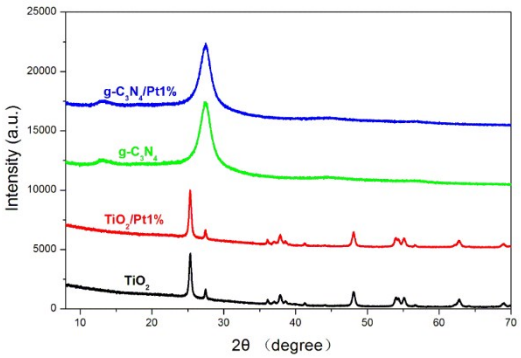

Figure S1 XRD patterns of TiO_2, TiO_2/Pt1%, g-C_3N_4, and g-C_3N_4/Pt1%.

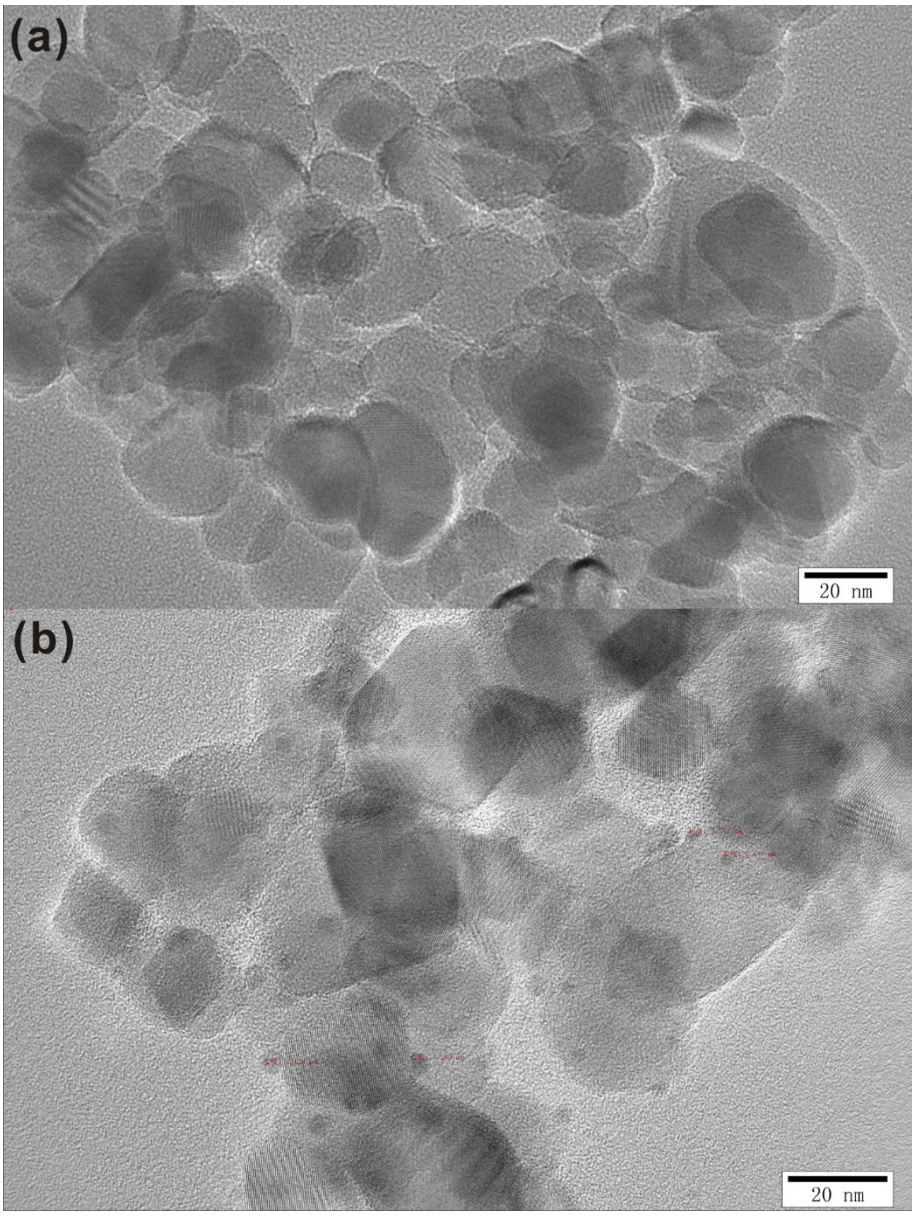

Figure S2 TEM images of TiO_2 (a) and TiO_2/Pt1% (b).

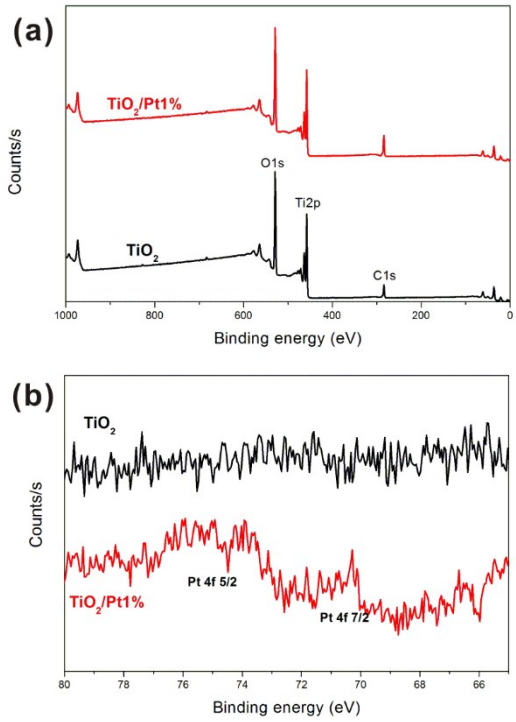

Figure S3 Survey (a) and Pt4f (b) XPS spectra of TiO_2 and TiO_2/Pt1%.

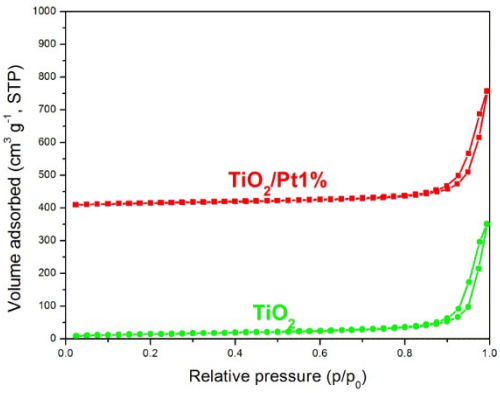

Figure S4 N_2 adsorption-desorption isotherms of TiO_2 and TiO_2/Pt1%.

Additional discussion:

XRD patterns (Figure S1) indicated that TiO_2 and g-C_3N_4 were the standard samples. After 1% Pt loading, the crystallographic information were not change. TEM image displayed the size of TiO_2 were about 25-50 nm (Figure S2a). The size of Pt nanoparticle were about 3-5 nm on the surface of TiO_2 (Figure S2b). And the existence of Pt also was proved by the XPS spectra as shown in Figure S3. BET surface area of TiO_2 and TiO_2/Pt1% were 53.0 and 53.8 $m^2\ g^{-1}$ (Figure S4). It indicated that Pt loading did not change the surface area.

Part 2: Photocatalytic H_2 generation

Experimental Procedure

The photocatalytic H_2 production experiments were performed in Labsolar-ⅢAG closed gas system (Beijing Perfect Light Technology Co., Ltd China) maintaining the photo-reaction temperature at 15 °C with a low-temperature thermostat bath (Poly Science, USA). In the photo-reaction system, 20 mg of samples was suspended in 50 mL of DI water containing methanol as an electron donor. To identify and quantify the gases produced, a volume of 1.5 mL of gas was hourly sampled and measured by a gas chromatography (GC 7806, Beijing Shiweipx analysis instrument co., LTD China) equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column, where N_2 was used as the carrier gas. At each time interval, 1 mL of gas was taken from the reaction cell for qualitative analysis using GC9790II gas chromatography (GC, Zhejiang Fuli Analytical Instrument Co., Ltd China) equipped with a flame ionization detector (FID, GDX-502 columns). The quantification of the CO and CO_2 yield were based on a calibration curve.

Apparent quantum efficiencies (AQE) calculations

The apparent quantum efficiency (AQE) was measured under the same photocatalytic reaction condition, except for the incident light wavelength. The H_2 yields of 1 h photoreaction under monochromatic light or LED light (365 nm) were measured. AQE was calculated by the following equation:

$$AQE = \frac{N_{H2}}{N_p} = \frac{2 \times the\ number\ of\ evolved\ H_2\ molecules}{the\ number\ of\ incident\ photons} \times 100\%$$

$$= \frac{2 \times N_a \times M_{H_2}}{\frac{PSt\lambda}{hc}} = \frac{2 \times 6.02 \times 10^{23} \times M_{H_2}}{\frac{PS \times 3600 \times 365 \times 10^{-9}}{6.6626 \times 10^{-34} \times 3 \times 10^{8}}}$$

Monochromatic light of 300 W Xenon lamp: λ = 365 ± 5 nm

Experimental conditions: TiO_2/Pt1% 30mg; 25 mL H_2O; 25 mL CH_3OH; 1h irradiation.

Power of 365 nm of Xenon lamp (P): 1.95 mW/cm^2; Active area (S): 19.6 cm^2

M_{H2} at 10 °C: 86.2 µmol M_{H2} at 20 °C: 118 µmol

M_{H2} at 30 °C: 167 µmol M_{H2} at 40 °C: 399 µmol

$N_p = (1.95 \times 10^{-3} \times 19.6 \times 3600 \times 365 \times 10^{-9})/(6.626 \times 10^{-34} \times 3 \times 10^{8}) = 2.53 \times 10^{20}$

N_{H2} at 10 °C = $N_{10} = 2 \times 6.02 \times 10^{23} \times 86.2 \times 10^{-6} = 1.04 \times 10^{20}$

$N_{20} = 2 \times 6.02 \times 10^{23} \times 118 \times 10^{-6} = 1.42 \times 10^{20}$

$N_{30} = 2 \times 6.02 \times 10^{23} \times 167 \times 10^{-6} = 2.01 \times 10^{20}$

$N_{40} = 2 \times 6.02 \times 10^{23} \times 399 \times 10^{-6} = 4.80 \times 10^{20}$

AQE at 10 °C = $QE_{10} = N_{10}/ N_p = 1.04/2.53 = 41.1\%$

$QE_{20} = N_{20}/ N_p = 1.42/2.53 = 56.1\%$

$QE_{30} = N_{20}/ N_p = 2.01/2.53 = 79.4\%$

$QE_{40} = N_{20}/ N_p = 4.80/2.53 = 189.7\%$

Table S1 Quantum efficiencies (QE) calculation data.

Temperature (°C)	band pass filter λ = 365 ± 5 nm				LED λ = 365 nm			
	M_{H2} (µmol)	N_{H2} (X 10^{20})	N_p (X 10^{20})	AQE (%)	M_{H2} (µmol)	N_{H2} (X 10^{20})	N_p (X 10^{20})	AQE (%)
10	86.2	1.04	2.53	41.1	423	5.09	12.98	39.2
20	118	1.42		56.1	658	7.92		61.0
30	167	2.01		79.4	926	11.14		85.8
40	399	4.80		189.7	2195	26.41		203.5

365 LED lamp: λ = 365 nm

Experimental conditions: TiO_2/Pt1% 30mg; 25 mL H_2O; 25 mL CH_3OH; 1h irradiation.

Power of 365 nm of Xenon lamp (P): 6.04 mW/cm^2; Active area (S): 32.5 cm^2

M_{H2} at 10 °C: 423 µmol M_{H2} at 20 °C: 658 µmol

M_{H2} at 30 °C: 926 μmol M_{H2} at 40 °C: 2195 μmol

$N_p = (6.04 \times 10^{-3} \times 32.5 \times 3600 \times 365 \times 10^{-9})/(6.626 \times 10^{-34} \times 3 \times 10^{8}) = 12.98 \times 10^{20}$

N_{H2} at 10 °C = $N_{10} = 2 \times 6.02 \times 10^{23} \times 423 \times 10^{-6} = 5.09 \times 10^{20}$

$N_{20} = 2 \times 6.02 \times 10^{23} \times 658 \times 10^{-6} = 7.92 \times 10^{20}$

$N_{30} = 2 \times 6.02 \times 10^{23} \times 926 \times 10^{-6} = 11.14 \times 10^{20}$

$N_{40} = 2 \times 6.02 \times 10^{23} \times 2195 \times 10^{-6} = 26.41 \times 10^{20}$

AQE at 10 °C = $QE_{10} = N_{10}/ N_p = 5.09/12.98 = 39.2\%$

$QE_{20} = N_{20}/ N_p = 7.92/12.98 = 61.0\%$

$QE_{30} = N_{20}/ N_p = 11.14/12.98 = 85.8\%$

$QE_{40} = N_{20}/ N_p = 26.41/12.98 = 203.5\%$

Light to hydrogen (LTH) conversion efficiency calculations

The light energy conversion was evaluated by using 300 W Xenon lamp as the light source 1 h of illumination, the total incident power over the 19.6 cm^2 irradiation area was 24.6 W.

So, $E_{light} = T*W = 3600 \times 24.6 = 8.856X10^4$ J.

E_F was the energy generated by water splitting

$E_F = N_a * E_{water} * E_e * M_{H2} = 6.02 \times 10^{23} \times 2.46 \times 1.609 \times 10^{-19} \times M_{H2}$

The "light -to-hydrogen" conversion efficiency (LTH) was determined to be:

LTH = (Energy of generation of hydrogen by water splitting) / (light energy irradiating the reaction cell).

$LTH = E_F/E_{light}$

Table S2 Light to hydrogen (LTH) conversion efficiency calculation data.

Temperature (°C)	M_{H2} (μmol)	E_F (J)	E_{light} (J)	LTH (%)
10	379	90.31	$8.856X10^4$	0.10
20	593	141.30		0.16
30	1032	245.91		0.28

40	1850	440.82		0.50

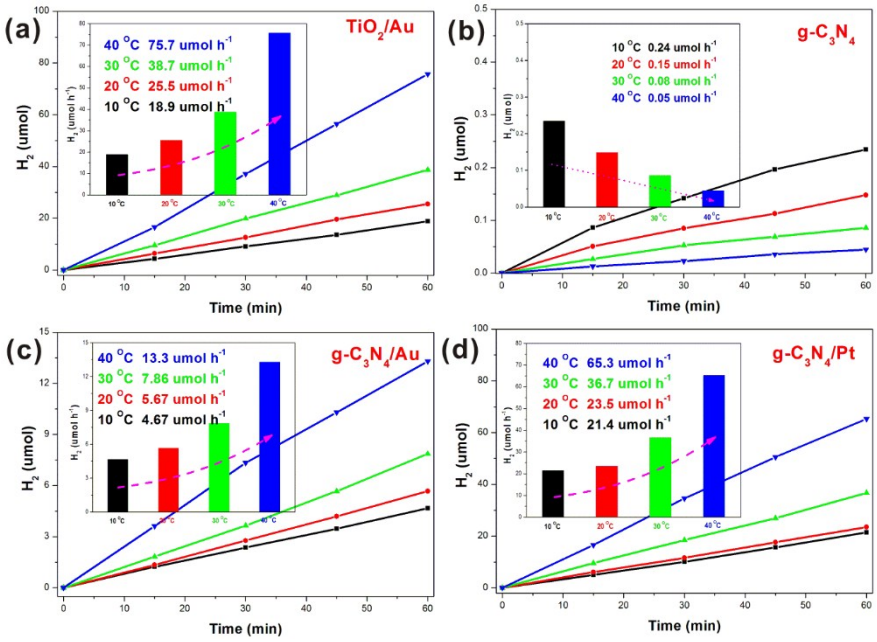

Figure S5 The photocatalytic activity for H_2 generation at different temperature (10 °C, 20 °C, 30 °C, 40°C) over 20 mg TiO_2/Au1% (a), g-C_3N_4(b), g-C_3N_4/Pt1% (c) and g-C_3N_4/Au1% (d) in CH_3OH-H_2O (10% V/V) solution under UV-visible light (320-800 nm).

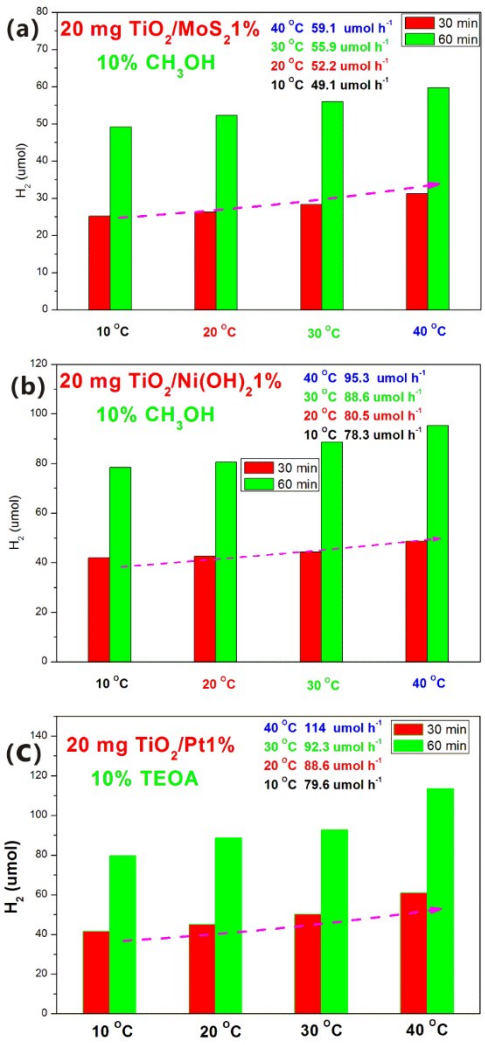

Figure S6 The control experiments: (a) MoS_2; (b) $Ni(OH)_2$; (c) TEOA solution.

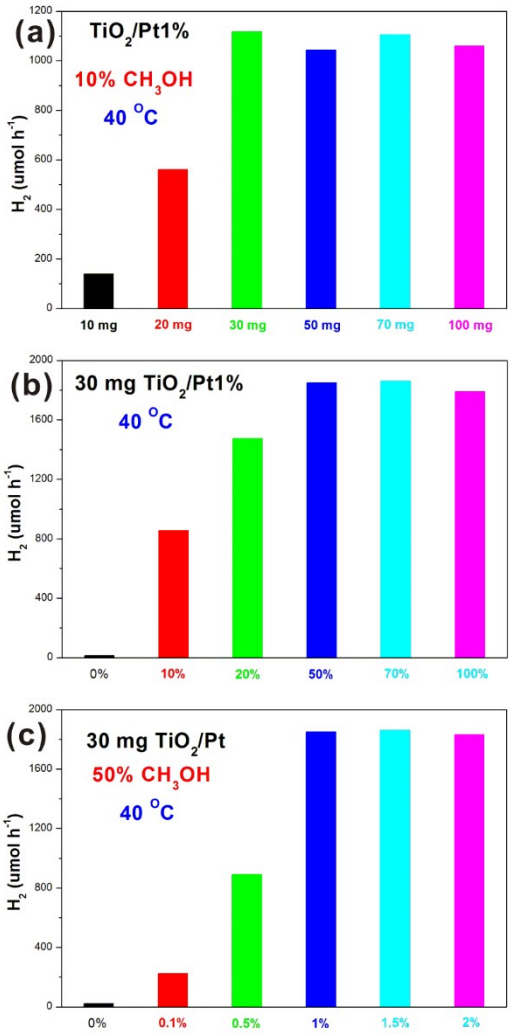

Figure S7 The effects of dosage (a), concentration of CH_3OH (b), and amount of Pt-loading amount (c) at 40°C under UV-visible light (320-800 nm).

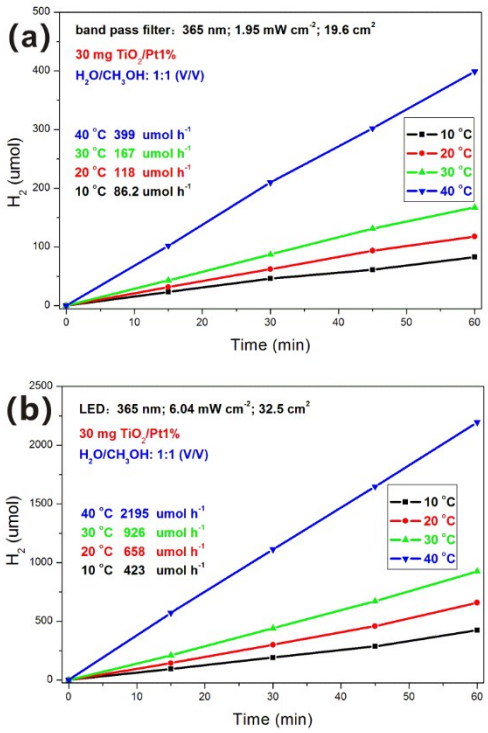

Figure S8 The photocatalytic activity for H_2 generation at different temperature (10, 20, 30, and 40°C) over TiO_2/Pt1% (30 mg) in CH_3OH-H_2O (50% V/V) solution under 365 nm irradiation (a for a Xenon lamp with a band pass filter and b for LED light).

Part 3: DRS and PL spectrum analysis

UV-vis diffuse reflectance spectroscopy (DRS) was carried out using UV-Vis spectrometer (Perkin Elmer, Lambda 650s, $BaSO_4$ as a reference). Photoluminescence (PL) spectra were recorded by a Multifunction Steady State and Transient State Fluorescence Spectrometer (FES920, Edinburgh Instruments) at 381 nm with excitation at 252 nm.

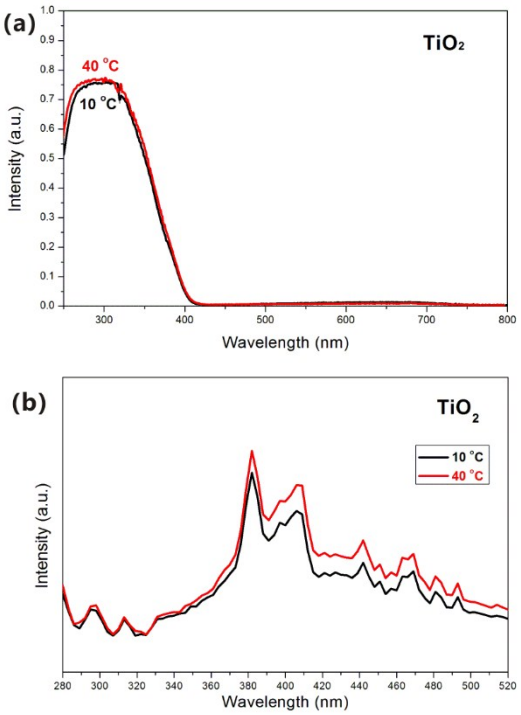

Figure S9 UV-vis diffuse reflectance spectroscopy and PL spectra of TiO_2 at 10 and 40 °C.

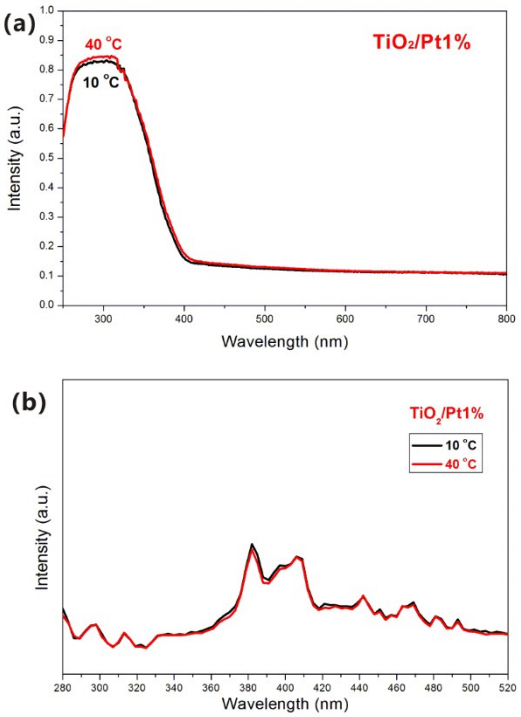

Figure S11 UV-vis diffuse reflectance spectroscopy and PL spectra of TiO_2/Pt1% at 10 and 40 °C.

Part 4: Photoelectrochemical measurement

The transient photocurrent responses and electrochemical impedance spectra (EIS) of the samples were determined using a CHI630E electrochemical working station (CHI Instruments, Shanghai, China) in a three-electrode quartz cell with Na_2SO_4 (0.1 M) electrolyte solution. Samples were deposited on a fluorinated-tin-oxide (FTO) conducting glass as the working electrode. Ag/AgCl and Pt were used as the reference and the counter electrodes, respectively.

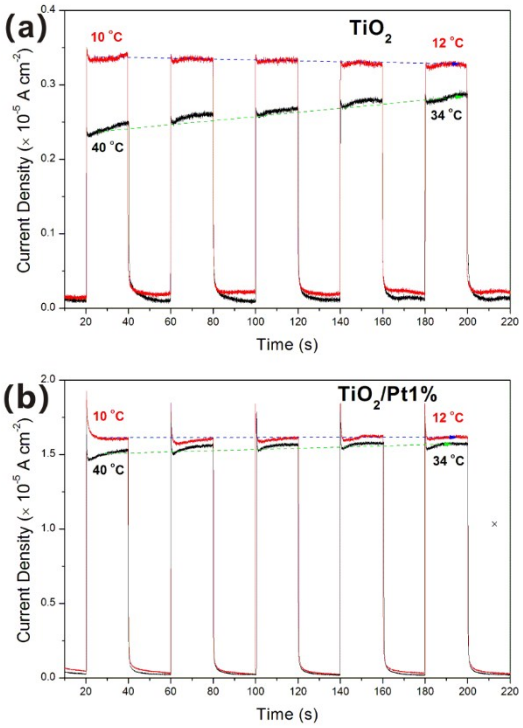

Figure S10 Photocurrent of TiO_2 film (a) and TiO_2/Pt1% film (b) at 10 and 40 °C Na_2SO_4 solution (0.1 mol L^{-1}) under UV-visible light (320-800 nm).

Part 5: Thermodynamic analysis

Table S3 Thermodynamic data of H_2O (l), HCOOH (l), CO (g), CO_2 (g) and H_2 (g) at 298.15K.

	H_2O (l)	HCOOH (l)	CO (g)	CO_2 (g)	H_2 (g)
$\Delta_f H_m^\theta$ (kJ mol^{-1})	-285.83	-424.72	-110.53	-393.51	0
$\Delta_f G_m^\theta$ (kJ mol^{-1})	-237.13	-361.35	-137.17	-394.36	0
S_m^θ (J mol^{-1} K^{-1})	69.91	128.95	197.67	213.74	130.68

HCOOH (l) = CO (g) + H_2O (l) (1)

HCOOH (l) = CO_2 (g) + H_2 (g) (2)

$\Delta G = \Delta_f H_m^\theta - T\,\Delta S_m^\theta$

$\Delta G1 = \Delta H - T\Delta S = (-110.53-285.83+424.72) - T\,(69.91+197.67-128.95)\,10^{-3}$

$\Delta G1 = 28.36-0.13863T$

$\Delta G2 = \Delta H - T\Delta S = (-393.51+0+424.72) - T\,(213.74+130.68-128.95)\,10^{-3}$

$= 31.21-0.21547T$

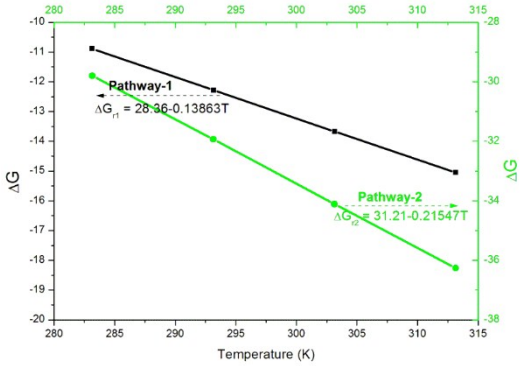

Figure S12 K^θ of pathway-1 and pathway-2 at 10-40 °C

$\Delta_r G_m^\theta = -RT\ln K^\theta$

Table S4 $\Delta_r G_m^\theta$ and the corresponding K^θ of pathway-1 at different.

Temperature	283.15K	293.15K	303.15K	313.15K
$\Delta_r G_m^\theta$ (kJ mol^{-1})	-10.89	-12.28	-13.67	-15.05
K^θ	102	154	227	324

Table S5 $\Delta_r G_m^{\theta}$ and the corresponding K^{θ} of pathway-2 at different

temperature	283.15K	293.15K	303.15K	313.15K
$\Delta_r G_m^{\theta}$ (kJ mol^{-1})	-29.8	-31.93	-34.11	-36.26
K^{θ}	314 488	489 351	753 878	1 118 221

Part 6: References

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