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\(_3\)N\(_4\):** 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\(_3\)N\(_4\) 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\(_2\)PtCl\(_6\)(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$_3$N$_4$, and g-C$_3$N$_4$/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$_3$N$_4$ 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 H₂ generation

Experimental Procedure
The photocatalytic H₂ 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 N₂ 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 CO₂ 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 H₂ yields of 1 h photoreaction under monochromatic light or LED light (365 nm) were measured. AQE was calculated by the following equation:

$$\text{AQE} = \frac{N_{H_2}}{N_p} = \frac{2 \times \text{the number of evolved H}_2\text{molecules}}{\text{the number of incident photons}} \times 100\%$$

$$= \frac{2 \times N_a \times M_{H_2}}{PS \frac{\lambda}{hc}} = \frac{2 \times 6.02 \times 10^{23} \times M_{H_2}}{PS \times 3600 \times 365 \times 10^{-9}} = \frac{6.6626 \times 10^{-34} \times 3 \times 10^8}{PS \times 3600 \times 365 \times 10^{-9}}$$
**Monochromatic light of 300 W Xenon lamp: λ = 365 ± 5 nm**

Experimental conditions: TiO$_2$/Pt1% 30mg; 25 mL H$_2$O; 25 mL CH$_3$OH; 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 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 = $QE_{10} = N_{10}/N_p = 1.04/2.53 = 41.1\%$

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

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

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

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**Table S1 Quantum efficiencies (QE) calculation data.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>band pass filter λ = 365 ± 5 nm</th>
<th>LED λ = 365 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_{H2}$ (µmol)</td>
<td>$N_{H2}$ (X $10^{20}$)</td>
</tr>
<tr>
<td>10</td>
<td>86.2</td>
<td>1.04</td>
</tr>
<tr>
<td>20</td>
<td>118</td>
<td>1.42</td>
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<tr>
<td>30</td>
<td>167</td>
<td>2.01</td>
</tr>
<tr>
<td>40</td>
<td>399</td>
<td>4.80</td>
</tr>
</tbody>
</table>

**365 LED lamp: λ = 365 nm**

Experimental conditions: TiO$_2$/Pt1% 30mg; 25 mL H$_2$O; 25 mL CH$_3$OH; 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
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, $E_{\text{light}} = T \times W = 3600 \times 24.6 = 8.856 \times 10^4$ J.

$E_{\text{F}}$ was the energy generated by water splitting

$E_{\text{F}} = N_{\text{a}} \times E_{\text{water}} \times E_{\text{e}} \times M_{\text{H2}} = 6.02 \times 10^{23} \times 2.46 \times 1.609 \times 10^{-19} \times M_{\text{H2}}$

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

$LTH = \frac{\text{Energy of generation of hydrogen by water splitting}}{\text{light energy irradiating the reaction cell}}$.

$LTH = \frac{E_{\text{F}}}{E_{\text{light}}}$

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$M_{\text{H2}}$ (µmol)</th>
<th>$E_{\text{F}}$ (J)</th>
<th>$E_{\text{light}}$ (J)</th>
<th>LTH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>379</td>
<td>90.31</td>
<td>8.856x10^4</td>
<td>0.10</td>
</tr>
<tr>
<td>20</td>
<td>593</td>
<td>141.30</td>
<td>8.856x10^4</td>
<td>0.16</td>
</tr>
<tr>
<td>30</td>
<td>1032</td>
<td>245.91</td>
<td>8.856x10^4</td>
<td>0.28</td>
</tr>
</tbody>
</table>
**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\(_3\)N\(_4\) (b), g-C\(_3\)N\(_4\)/Pt1% (c) and g-C\(_3\)N\(_4\)/Au1% (d) in CH\(_3\)OH-H\(_2\)O (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 CH₃OH (b), and amount of Pt-loading amount (c) at 40°C under UV-visible light (320-800 nm).
Figure S8 The photocatalytic activity for \( \text{H}_2 \) generation at different temperature (10, 20, 30, and 40°C) over TiO\(_2\)/Pt1% (30 mg) in CH\(_3\)OH-H\(_2\)O (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, BaSO₄ 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](image)

**Figure S9** UV-vis diffuse reflectance spectroscopy and PL spectra of TiO₂ 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$_2$SO$_4$ (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](image)

**Figure S10** Photocurrent of TiO$_2$ film (a) and TiO$_2$/Pt1% film (b) at 10 and 40 °C Na$_2$SO$_4$ solution (0.1 mol L$^{-1}$) under UV-visible light (320-800 nm).
Part 5: Thermodynamic analysis

Table S3 Thermodynamic data of H₂O (l), HCOOH (l), CO (g), CO₂ (g) and H₂ (g) at 298.15K.

<table>
<thead>
<tr>
<th></th>
<th>H₂O (l)</th>
<th>HCOOH (l)</th>
<th>CO (g)</th>
<th>CO₂ (g)</th>
<th>H₂ (g)</th>
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</thead>
<tbody>
<tr>
<td>(\Delta H_m^0) (kJ mol(^{-1}))</td>
<td>-285.83</td>
<td>-424.72</td>
<td>-110.53</td>
<td>-393.51</td>
<td>0</td>
</tr>
<tr>
<td>(\Delta G_m^0) (kJ mol(^{-1}))</td>
<td>-237.13</td>
<td>-361.35</td>
<td>-137.17</td>
<td>-394.36</td>
<td>0</td>
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<tr>
<td>(S_m^0) (J mol(^{-1}) K(^{-1}))</td>
<td>69.91</td>
<td>128.95</td>
<td>197.67</td>
<td>213.74</td>
<td>130.68</td>
</tr>
</tbody>
</table>

HCOOH (l) = CO (g) + H₂O (l) \hspace{1cm} (1)

HCOOH (l) = CO₂ (g) + H₂ (g) \hspace{1cm} (2)

\(\Delta G = \Delta H_m^0 - T \Delta S_m^0\)

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

\(\Delta G1 = 28.36-0.13863T\)

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

\(= 31.21-0.21547T\)

Figure S12 \(K^0\) of pathway-1 and pathway-2 at 10-40 °C

\(\Delta G_m^0 = -RT \ln K^0\)

Table S4 \(\Delta G_m^0\) and the corresponding \(K^0\) of pathway-1 at different temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>283.15K</th>
<th>293.15K</th>
<th>303.15K</th>
<th>313.15K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta G_m^0) (kJ mol(^{-1}))</td>
<td>-10.89</td>
<td>-12.28</td>
<td>-13.67</td>
<td>-15.05</td>
</tr>
<tr>
<td>(K^0)</td>
<td>102</td>
<td>154</td>
<td>227</td>
<td>324</td>
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</table>
Table S5 \( \Delta G_m^\theta \) and the corresponding \( K^0 \) of pathway-2 at different temperature

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \Delta G_m^\theta ) (kJ mol(^{-1}))</th>
<th>( K^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>283.15K</td>
<td>-29.8</td>
<td>314 488</td>
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<tr>
<td>293.15K</td>
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<td>489 351</td>
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<td>313.15K</td>
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Part 6: References


