Controllable Synthesize Heterostructure Photocatalyst

Mo₂C@C/2D g-C₃N₄: Enhanced Catalytic Performance for Hydrogen Production and Organic Pollutants Degradation

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Synthesis of the samples

2D g-C$_3$N$_4$

2D g-C$_3$N$_4$ was synthesized in the muffle furnace using melamine as precursor at air atmosphere.\textsuperscript{S1} Briefly, 2 g melamine was calcined at 550 °C for 4 h with 2 °C/min heating rate. The obtained sample was grounded into powder and put into the combustion boat to perform second calcination. After these procedures, the obtained white sample was noted as 2D g-C$_3$N$_4$.

Mo$_2$C@C

To obtain Mo$_2$C@C nanoparticles, glucose (0.25 g) and (NH$_4$)$_6$Mo$_7$O$_{24}$•4H$_2$O (1 g) were dissolved in 25 ml DI water.\textsuperscript{S2} The mixture was sonicated for approximately 20 min and magnetic stirring 30 min at room temperature until a homogeneous solution was achieved. Then, the solution was transferred to a 50 ml Teflon-lined stainless steel autoclave and heated in an oven at 200 °C for 12 h with no intentional control of ramping or cooling rate. The black product was collected by centrifugation at 10000 rpm for 3 min and washed with DI water and ethanol for at least 3 times followed by freeze-drying. The dried sample was calcined in tube furnace at 750 °C for 5 h with 3 °C/min heating rate at 5% H$_2$/Ar mixture gas atmosphere. The resulting powder is Mo$_2$C@C and can be collected after the tube furnace cooling down to room temperature. It is worth noting that a certain time pretreatment to remove air before start warming up program is very important for the formation of Mo$_2$C@C.

15% MoO$_2$-C/2D g-C$_3$N$_4$

The MoO$_2$-C was synthesized by calcined self-sacrificial template precursor Mo$_3$O$_{10}$(C$_6$H$_8$N)$_2$•2H$_2$O. 2.48 g of ammonium heptamolybdate tetrahydrate and 3.28 mL aniline was dissolved in 40 mL distilled water. After stirred for few minutes, 1 M HCl aqueous was slowly added to adjust pH level to 4.5. And then, followed by a 50°C water bath reaction for 6 h, the product was washed with ethanol, and then dried at 50°C for 6 h. The dried sample was calcined in tube furnace at 750°C for 3 h with 5 °C/min heating rate at Ar gas atmosphere. A certain time pretreatment to remove air before start warming up program is very important. The obtained black sample is 1D
metallic carbon-doped MoO₂, noted as MoO₂-C in after article.  

15% MoO₂-C/2D g-C₃N₄ was synthesized by a simple assembly method. MoO₂-C was dispersed in hexane (2 mg/mL) and during 0.5 h ultrasonic. Then 30 mg of 2D g-C₃N₄ and 1.5 mL of MoO₂-C solution were added in an agate mortar and ground until dried. Later another 5 mL of ethanol was also added and ground. The obtained composite sample was washed with ethanol for at least 3 times and followed by freeze-dried.

10% MoN/2D g-C₃N₄

MoN was synthesized by calcining MoO₃ at reducing atmosphere. Generally speaking, MoO₃ sample was calcined in tube furnace at 750 ℃ for 6 h with a heating rate at 10 ℃/min in NH₃ atmosphere. A certain time of pretreatment to remove air before heating is very important. Finally, the obtained black sample is MoN.

10% MoN/2D g-C₃N₄ was synthesized by a simple self-assembly and high temperature annealing method. MoN dispersed in hexane (1 mg/mL) experienced a 30 min ultrasonic treatment. Then 50 mg of 2D g-C₃N₄ and 5 mL MoN solution were added in a beaker containing 10 mL of hexane under stirring until a dried sample formed. The obtained composite sample was washed with ethanol for at least 3 times followed by freeze-drying. Finally, the sample was calcined in tube furnace at 400 ℃ for 1 h with a heating rate at 10 ℃/min in NH₃ atmosphere.

Photodeposition noble-metal co-catalysts (3 wt %): 2D g-C₃N₄ (10 mg) was dispersed in 1:10 (v/v) water/TEOA solution (100 mL), and then the required amount of HAuCl₄ or H₂PtCl₆ solution was added in. The mixture was evacuated several times with magnetic stirring to remove air completely prior to irradiation with a 300 W Xenon lamp for several minutes at room temperature.

It is worth noting that we only prepared the best proportion of composites.

**Photocatalytic activity**

The photocatalytic performance of the samples was evaluated by hydrogen evolution from water under visible irradiation in an online photocatalytic hydrogen
production system (LabSolar-3AG, PerfectLight, Beijing). 10 mg of photocatalytic powder was well dispersed in 90 mL distilled water with 10 mL of triethanolamine (TEOA) added as hole sacrificial. Then, the suspension was under ultrasonic treatment for 0.5 h to the homogenized state of the suspension. The vacuum pump and cooling water were needed throughout the hydrogen evolution process. A 300 W Xe lamp (PLS-SXE 300C (BF), PerfectLight, Beijing) with an optical filter (λ> 400 nm) was chosen as a visible-light source, the current of the lamp source used in the photocatalytic reaction is 15 A. The photocatalytic hydrogen formation was measured using an online gas chromatograph (GC D7900P, TCD detector).

In order to investigate the photocatalytic degradation activity of the as-prepared samples, Rhodamine B (Rh B) was chosen as the model pollutant, using the same lamp used in the photocatalytic hydrogen generation process. In each photodegradation process, 0.01 g photocatalyst were dissolved into 50 mL Rh B (10 mg/L) and reacted in a Pyrex photocatalytic reactor, which was connected to a circulating water system to keep the reaction temperature at 30°C during the whole degradation process. Prior to irradiation, to ensure the Rh B reaching the absorption-desorption equilibrium, the suspensions were stirring in the dark for 0.5 h magnetically. 5 mL of the suspension was collected after a certain time of irradiation. The resulting solution was then centrifuged for 3 min at a speed of 12000 rpm to separate the catalyst particles. The final concentration of Rh B was analyzed at a wavelength of 553 nm on an UV-2450 spectrophotometer.

Characterizations

The samples were characterized by X-ray diffraction (XRD) using a Shimadzu XRD-6100 diffractometer with Cu Kα radiation. Raman spectra were recorded at room temperature using a micro-Raman spectrometer (Renishaw Invia) in the backscattering geometry with a 532 nm laser as an excitation source. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet FT-IR spectrophotometer (Nexus 470, Thermo Electron Corporation) using KBr as a reference. The X-ray photoelectron (XPS) spectra were determined using a VG Multi Lab 2000 system with a Monochromatic Mg Kα source operating at 20 kV. Scanning
electron microscopy (SEM) (JEOL JSM-7001F) and transmission electron microscopy (TEM) (JEOL-JEM-2010) were employed to study the morphology of the samples. The light absorption properties of the samples were analysed by UV-vis diffuse reflectance spectra (DRS) using a UV-vis spectrophotometer (Shimadzu UV-3600 plus, Japan). The photoluminescence (PL) spectra of the samples were obtained by a QuantaMaster & TimeMaster Spectrofluorometer.

**Photoelectrochemical measurement**

The samples were dispersed in ethylene glycol (EG) and ethanol dispersion (1:1) and the concentration of the sample was 1 mg/ml. After ultrasonic treatment, 50 μL of the suspension was drop-casted onto an indiumtin oxide (ITO)-coated glass with an exposed area of 0.5 cm² (1 cm × 0.5 cm) and then dried under infrared lamp irradiation. The photocurrents of the samples were measured by using the CHI660 B electrochemical analyzer (Shanghai Chenhua, China) under a 500 W Xe lamp irradiation. Ag/AgCl (saturated KCl solution), photocatalyst coated indium tin oxide (ITO) glass and platinum (Pt) wire were used as the reference electrode, working electrode and the counter electrode, respectively. In the experiments, the bias potential of -0.2 V (vs. Ag/AgCl) was used. 0.1 M Na₂SO₄ solution was used as the electrolyte.

![Fig. S1](image)

**Fig. S1** (a) Digital photographs of the preparation process for bulk g-C₃N₄ and 2D g-C₃N₄, (b) Digital photograph of same weight of bulk g-C₃N₄ and 2D g-C₃N₄.
Fig. S2 Raman spectra of Mo$_2$C@C.

Fig. S3 (a) XPS survey spectra of Mo$_2$C@C and 15% Mo$_2$C@C/2D g-C$_3$N$_4$, (b) N 1s
spectrum of 15% Mo$_2$C@C/2D g-C$_3$N$_4$.

Figure S4 SEM image of 15% Mo$_2$C@C/2D g-C$_3$N$_4$.

Fig. S5 EDX spectrum of 15% Mo$_2$C@C/2D g-C$_3$N$_4$ composite.
Fig. S6 (a) Photocatalytic H₂ evolution in the presence of 2D g-C₃N₄, Mo₂C@C and
Mo$_2$C@C/2D g-C$_3$N$_4$ composites loaded with different amounts of Mo$_2$C@C, (b) The performance comparison of the photocatalytic H$_2$ evolution activity for loaded with MoO$_2$-C, MoN and Mo$_2$C@C as co-catalyst (all the samples are optimal proportion), (c) Photocatalytic hydrogen evolution of 15% Mo$_2$C@C/2D g-C$_3$N$_4$, 3% Au/2D g-C$_3$N$_4$ and 3% Pt/2D g-C$_3$N$_4$, (d) The photocatalytic stability of the 15% Mo$_2$C@C/2D g-C$_3$N$_4$ sample.

![Fig. S7](a) FT-IR spectra, (b) XRD patterns of before and after cycling samples.
Fig. S8 ESR spectra of (a) DMPO-O$_2^•$ and (b) DMPO-•OH in 2D g-C$_3$N$_4$ and 15% Mo$_2$C@C/2D g-C$_3$N$_4$ aqueous dispersion systems in dark.

<table>
<thead>
<tr>
<th>Samples</th>
<th>2D g-C$_3$N$_4$</th>
<th>15% Mo$_2$C@C/2D g-C$_3$N$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$ (ns)</td>
<td>2.53</td>
<td>2.54</td>
</tr>
<tr>
<td>$\tau_2$ (ns)</td>
<td>8.70</td>
<td>9.07</td>
</tr>
<tr>
<td>$A_1$</td>
<td>1194.55</td>
<td>326.55</td>
</tr>
<tr>
<td>$A_2$</td>
<td>605.24</td>
<td>132.84</td>
</tr>
<tr>
<td>$\tau_{ave}$ (ns)</td>
<td>6.44</td>
<td>6.41</td>
</tr>
</tbody>
</table>

Table S1 Time-resolved PL of 2D g-C$_3$N$_4$ and 15% Mo$_2$C@C/2D g-C$_3$N$_4$.

The External Quantum Efficiency (EQE) were analyzed at different wavelength
(405, 420, 435 and 450 nm, $\lambda \pm 10$ nm) in the 300 W Xenon lamp (PLS-SXE 300C (BF), PerfectLight, Beijing). The other experimental condition is similar to the photocatalytic hydrogen evolution measurement as described before. The light intensity was obtained with an optical power meter (CEL-NP2000, CEAULIGHT, Beijing). For example, if 405 nm was used, the average light intensity is 21.77 mW. The number of incident photons ($N$) is $4.79 \times 10^{20}$ calculated by equation (1). The amount of H$_2$ molecules generated in 3 h are $\sim 36.07 \mu$mol. The EQE was then calculated in equation (2).

Table S2 The calculated External Quantum Efficiency (EQE) of 15% Mo$_2$C@C/2D g-C$_3$N$_4$ at different wavelength.

<table>
<thead>
<tr>
<th>Wavelength ($\lambda$)</th>
<th>H$_2$ Evolved ($\mu$mol)</th>
<th>Light Intensity (mW)</th>
<th>EQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$=405 nm</td>
<td>36.07</td>
<td>21.77</td>
<td>9.07%</td>
</tr>
<tr>
<td>$\lambda$=420 nm</td>
<td>24.31</td>
<td>25.26</td>
<td>5.08%</td>
</tr>
<tr>
<td>$\lambda$=435 nm</td>
<td>4.16</td>
<td>26.12</td>
<td>0.81%</td>
</tr>
<tr>
<td>$\lambda$=450 nm</td>
<td>0</td>
<td>27.02</td>
<td>0</td>
</tr>
</tbody>
</table>

15% Mo$_2$C@C/2D g-C$_3$N$_4$, $\lambda$=405 nm:

$$N = \frac{21.77 \times 10^{-3} \times 3 \times 3600 \times 405 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^8} = 4.79 \times 10^{20}$$

$$EQE = \frac{the \ number \ of \ reacted \ electrons}{the \ number \ of \ incident \ photons} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 36.07 \times 10^{-6}}{4.79 \times 10^{20}} \times 100\%$$

$$=9.07\%$$

15% Mo$_2$C@C/2D g-C$_3$N$_4$, $\lambda$=420 nm:

$$N = \frac{25.26 \times 10^{-3} \times 3 \times 3600 \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^8} = 5.76 \times 10^{20}$$

$$EQE = \frac{the \ number \ of \ reacted \ electrons}{the \ number \ of \ incident \ photons} \times 100\%$$
\[
\frac{2 \times \text{the number of evolved } H2 \text{ molecules}}{N} \times 100% = \frac{2 \times 6.02 \times 10^{23} \times 24.31 \times 10^{-6}}{5.76 \times 10^{20}} \times 100% = 5.08%
\]

15% Mo\textsubscript{2}C@C/2D g-C\textsubscript{3}N\textsubscript{4}, \( \lambda = 435 \text{ nm} \):
\[
N = \frac{26.12 \times 10^{-3} \times 3 \times 3600 \times 435 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^8} = 6.17 \times 10^{20}
\]

\[
EQE = \frac{\text{the number of reacted electrons}}{\text{the number of incident photons}} \times 100%
\]
\[
= \frac{2 \times \text{the number of evolved } H2 \text{ molecules}}{N} \times 100% = \frac{2 \times 6.02 \times 10^{23} \times 4.16 \times 10^{-6}}{6.17 \times 10^{20}} \times 100% = 0.81%
\]

**Table S3** Comparison of the photocatalytic activity and Apparent Quantum Yield reported all Pt-free g-C\textsubscript{3}N\textsubscript{4} system.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Light Source</th>
<th>Reaction Conditions</th>
<th>( H_2 ) Evolution Rate (( \mu \text{mol g}^{-1} \text{ h}^{-1} ))</th>
<th>(^{a})Apparent Quantum Yield</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo\textsubscript{2}S\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}/Pt (0.5 wt.% MoS\textsubscript{2}, 1% Pt)</td>
<td>300UV Xe arc lamp with a UV-cutoff filter (( \lambda = 400 \text{ nm} ))</td>
<td>120 ml of aqueous solution containing 25% methanol by volume</td>
<td>231</td>
<td>(^d) 2.8%</td>
<td>S3</td>
</tr>
<tr>
<td>1T-MoS\textsubscript{2}/O-g-C\textsubscript{3}N\textsubscript{4} (0.2 wt.%)</td>
<td>300 W Xe lamp, ( \lambda = 400 \text{ nm} )</td>
<td>Aqueous (100 mL) TEOA solution (10 vol. %)</td>
<td>1841.72</td>
<td>7.11% (420 nm)</td>
<td>S4</td>
</tr>
<tr>
<td>Material</td>
<td>Description</td>
<td>Solution Details</td>
<td>Yield</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------</td>
<td>-------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>a-MoS₂/g-C₃N₄ (3 wt.%)</td>
<td>four low-power LEDs (3 W, 420 nm)</td>
<td>80 mL aqueous solution containing 10 vol. % of lactic acid</td>
<td>273.1</td>
<td>S5</td>
<td></td>
</tr>
<tr>
<td>MoS₂/CN-Py (3% wt.%)</td>
<td>300 W Xenon lamp with a UV cutoff filter (λ &gt; 420 nm)</td>
<td>100 mL aqueous solution containing TEOA (10 vol. %)</td>
<td>500</td>
<td>S6</td>
<td></td>
</tr>
<tr>
<td>MoS₂/HCNS (0.5 wt.%)</td>
<td>Xenon 300 W lamp (λ &gt; 400 nm)</td>
<td>Aqueous solution (100 mL) containing lactic acid (10 vol. %)</td>
<td>ca. 1300</td>
<td>S7</td>
<td></td>
</tr>
<tr>
<td>MoS₂/g-C₃N₄ 2.89 wt.%</td>
<td>300 W Xe lamp equipped with UV cut off filter (λ &gt; 400 nm).</td>
<td>9 mL water and 1 ml TEOA</td>
<td>320</td>
<td>S8</td>
<td></td>
</tr>
<tr>
<td>MoS₂/mpg-CN (0.2 wt.%)</td>
<td>a Xenon 300 W lamp equipped with a 420 nm cut-off filter and a water IR filter</td>
<td>Aqueous solution (100 mL) containing lactic acid (10 vol. %)</td>
<td>ca. 1112.5</td>
<td>2.1% (420 nm)</td>
<td>S9</td>
</tr>
<tr>
<td>g-C₃N₄/5 wt% MSQD+ 2 wt% Pt</td>
<td>300 W Xe lamp, λ &gt; 420 nm</td>
<td>Aqueous solution (120 mL) TEOA (25 vol. %)</td>
<td>576.6</td>
<td>N/A</td>
<td>S10</td>
</tr>
<tr>
<td>MoO₂-C/2D g-C₃N₄ (15 wt.%)</td>
<td>300 W Xe lamp, λ &gt; 400 nm</td>
<td>Aqueous solution (100 mL) TEOA</td>
<td>1071.03</td>
<td>N/A</td>
<td>S11</td>
</tr>
<tr>
<td>System</td>
<td>Solution (10 vol. %)</td>
<td>Power Source</td>
<td>λ cut-off Filter</td>
<td>Apparent Quantum Yield</td>
<td>Notes</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------------</td>
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<td>-------</td>
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<tr>
<td>C$_3$N$_4$/Ni-Tu-TETN</td>
<td>300 W Xe lamp with a solar simulator filter, 70 mL water and 10 mL TEOA</td>
<td>510</td>
<td>0.2% (420 nm)</td>
<td>S12</td>
<td></td>
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<tr>
<td>NiS$_2$/g-C$_3$N$_4$</td>
<td>300 W Xe lamp with a 420 nm cutoff filter, 10 mL of TEOA (15 vol. %)</td>
<td>406</td>
<td>N/A</td>
<td>S13</td>
<td></td>
</tr>
<tr>
<td>Au/g-C$_3$N$_4$</td>
<td>500 W HBO lamp with a water filter (λ &gt; 420 nm), 100 mL of TEOA (10 vol. %)</td>
<td>107</td>
<td>N/A</td>
<td>S14</td>
<td></td>
</tr>
<tr>
<td>Ni(OH)$_2$/g-C$_3$N$_4$</td>
<td>350 W Xe lamp with a 400 nm cutoff filter, 80 mL of TEOA (10 vol. %)</td>
<td>152</td>
<td>1.1% (420 nm)</td>
<td>S15</td>
<td></td>
</tr>
<tr>
<td>WS$_2$/g-C$_3$N$_4$</td>
<td>300 W Xe lamp with a 420 nm cutoff filter, 10 mL of lactic acid (10 vol. %)</td>
<td>ca. 240</td>
<td>N/A</td>
<td>S16</td>
<td></td>
</tr>
<tr>
<td>1T-WS$_2$/2D-C$_3$N$_4$</td>
<td>300 W Xe lamp, λ &gt; 400 nm, Aqueous (100 mL) TEOA solution (10 vol. %)</td>
<td>311.09</td>
<td>1.12% (420 nm)</td>
<td>S17</td>
<td></td>
</tr>
<tr>
<td>Mo$_2$C@C/2D-C$_3$N$_4$</td>
<td>300 W Xe lamp, λ &gt; 400 nm, Aqueous (100 mL) TEOA solution (10 vol. %)</td>
<td>2269.47</td>
<td>9.07% (405 nm), 5.08% (420 nm), 0.81% (435 nm)</td>
<td>This work</td>
<td></td>
</tr>
</tbody>
</table>

a Apparent quantum yield = \((2 \times \text{amount of } \text{H}_2 \text{ molecules evolved in unit time/number of incident photons in unit time}) \times 100\%\).
b a-MoS$_x$ is amorphous MoS$_x$.

c In the article, the structure of MoS$_2$ was not studied.

d In the article, the wavelength was not stated.

References: