Supporting information

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_3N_4

2D g-C_3N_4 was synthesized in the muffle furnace using melamine as precursor at air atmosphere.[S1] Briefly, 2 g melamine was calcined at 550 ºC for 4 h with 2 ºC/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_3N_4.

$Mo_2C@C$

To obtain $Mo_2C@C$ nanoparticles, glucose (0.25 g) and $(NH_4)_6Mo_7O_{24} \bullet 4H_2O$ (1 g) were dissolved in 25 ml DI water.[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 ºC 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 ºC for 5 h with 3 ºC/min heating rate at 5% H_2/Ar mixture gas atmosphere. The resulting powder is $Mo_2C@C$ 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 $Mo_2C@C$.

15% MoO_2-C/2D g-C_3N_4

The MoO_2-C was synthesized by calcined self-sacrificial template precursor $Mo_3O_{10}(C_6H_8N)_2 \cdot 2H_2O$. 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℃ water bath reaction for 6 h, the product was washed with ethanol, and then dried at 50℃ for 6 h. The dried sample was calcined in tube furnace at 750℃ for 3 h with 5 ℃/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 MoO_2, noted as MoO_2-C in after article.

15% MoO_2-C/2D g-C_3N_4 was synthesized by a simple assembly method. MoO_2-C was dispersed in hexane (2 mg/mL) and during 0.5 h ultrasonic. Then 30 mg of 2D g-C_3N_4 and 1.5 mL of MoO_2-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-C_3N_4

MoN was synthesized by calcining MoO_3 at reducing atmosphere. Generally speaking, MoO_3 sample was calcined in tube furnace at 750℃ for 6 h with a heating rate at 10℃/min in NH_3 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-C_3N_4 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-C_3N_4 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 NH_3 atmosphere.

Photodeposition noble-metal co-catalysts (3 wt %): 2D g-C_3N_4 (10 mg) was dispersed in 1:10 (v/v) water/TEOA solution (100 mL), and then the required amount of $HAuCl_4$ or H_2PtCl_6 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 ($\lambda > 400$ 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 spectraphotometer.

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 Ka 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 cm^2 (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 Na_2SO_4 solution was used as the electrolyte.
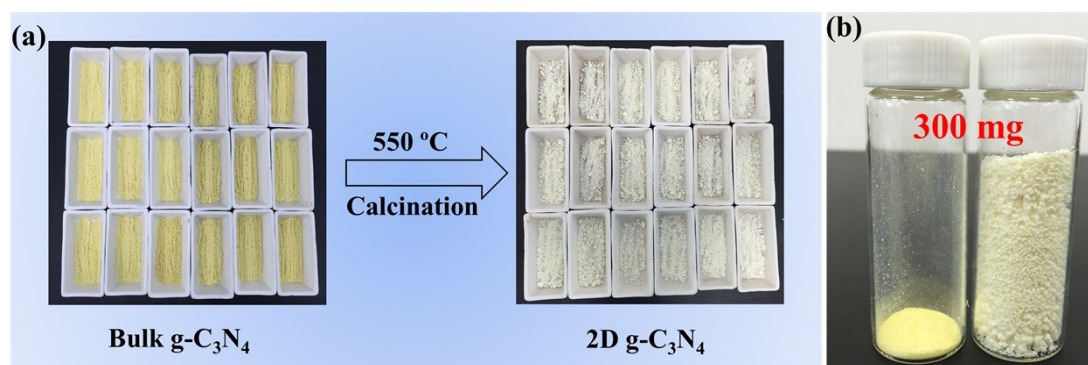
Fig. S1 (a) Digital photographs of the preparation process for bulk g-C_3N_4 and 2D g-C_3N_4, (b) Digital photograph of same weight of bulk g-C_3N_4 and 2D g-C_3N_4.
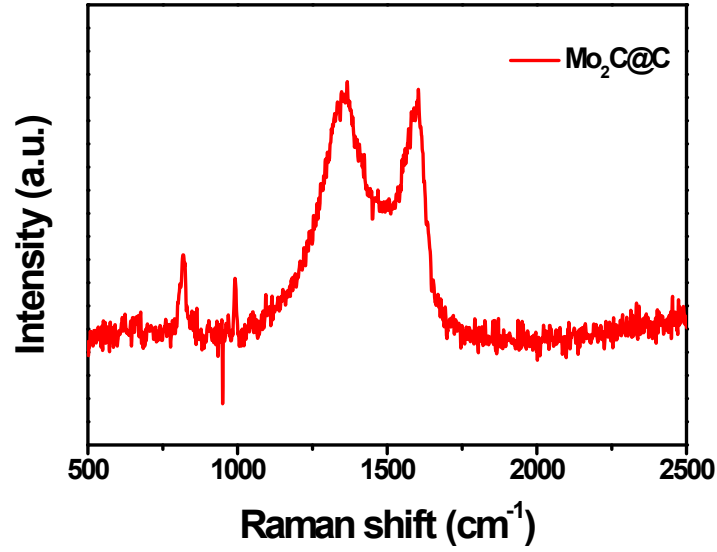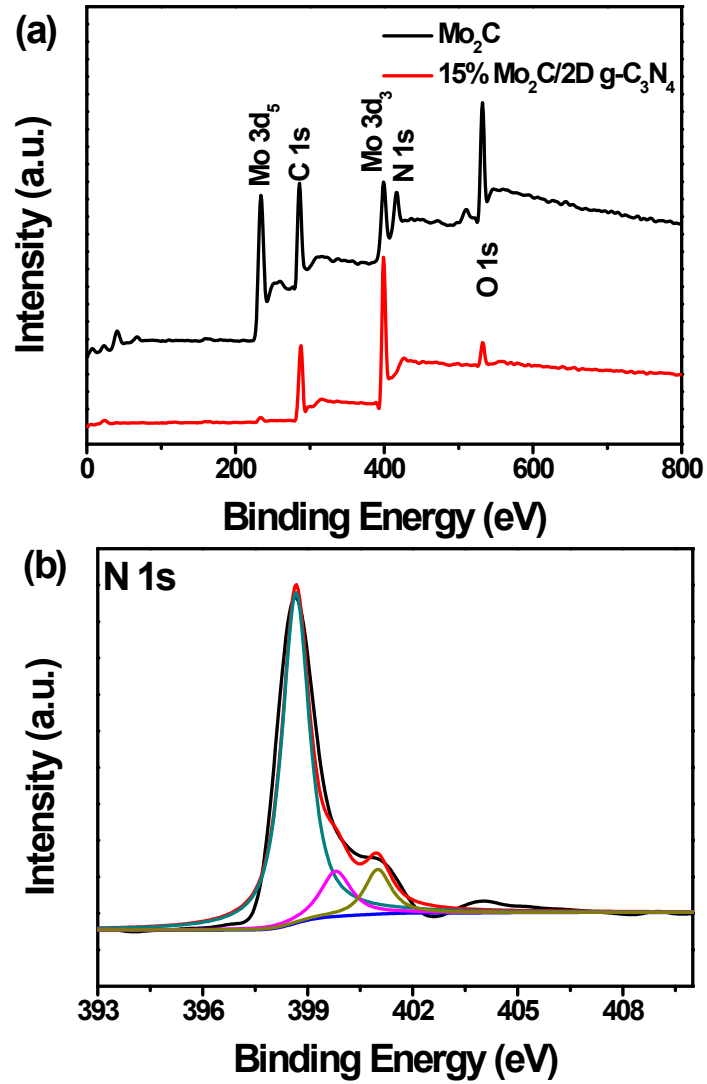
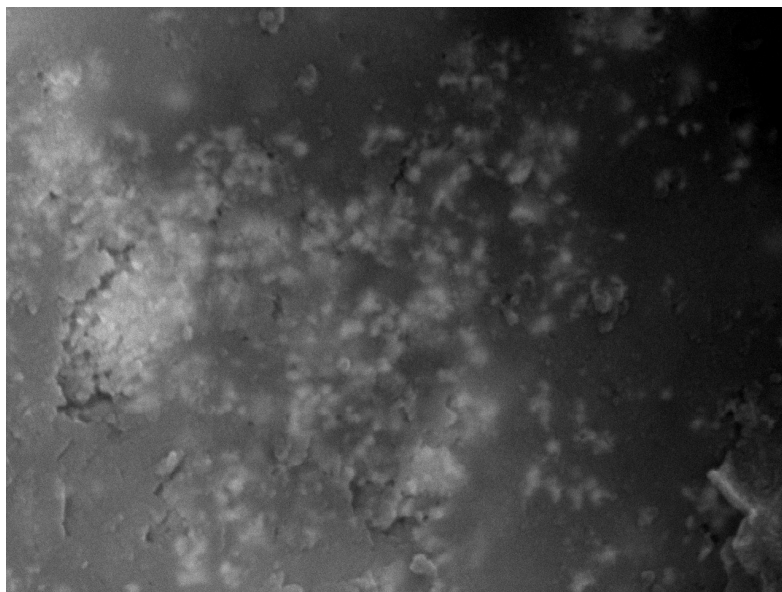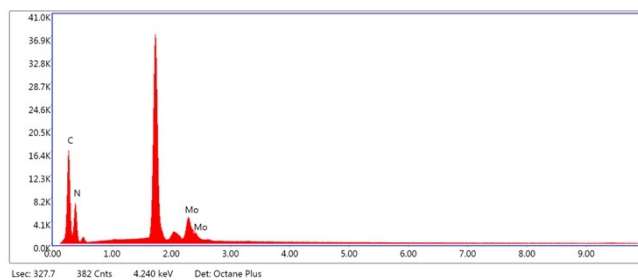**Fig. S2** Raman spectra of $Mo_2C@C$.

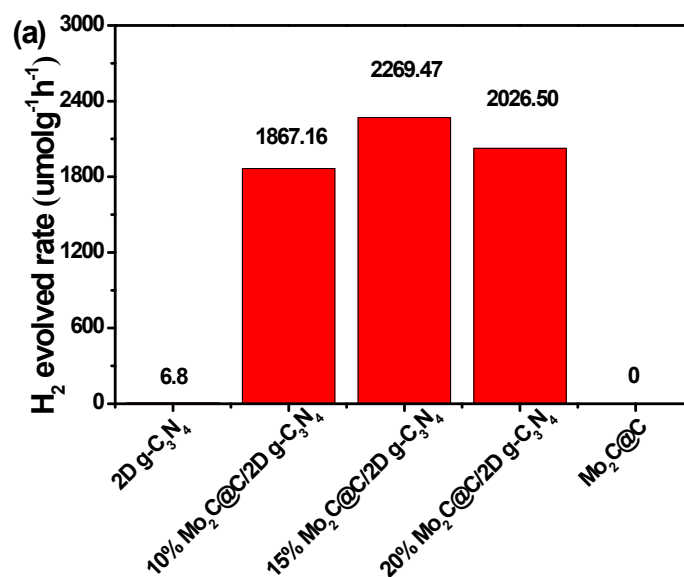**Fig. S3** (a) XPS survey spectra of $Mo_2C@C$ and 15% $Mo_2C@C/2D$ g-C_3N_4, (b) N 1s

spectrum of 15% $Mo_2C@C/2D$ g-C_3N_4.

Figure S4 SEM image of 15% $Mo_2C@C/2D$ g-C_3N_4.

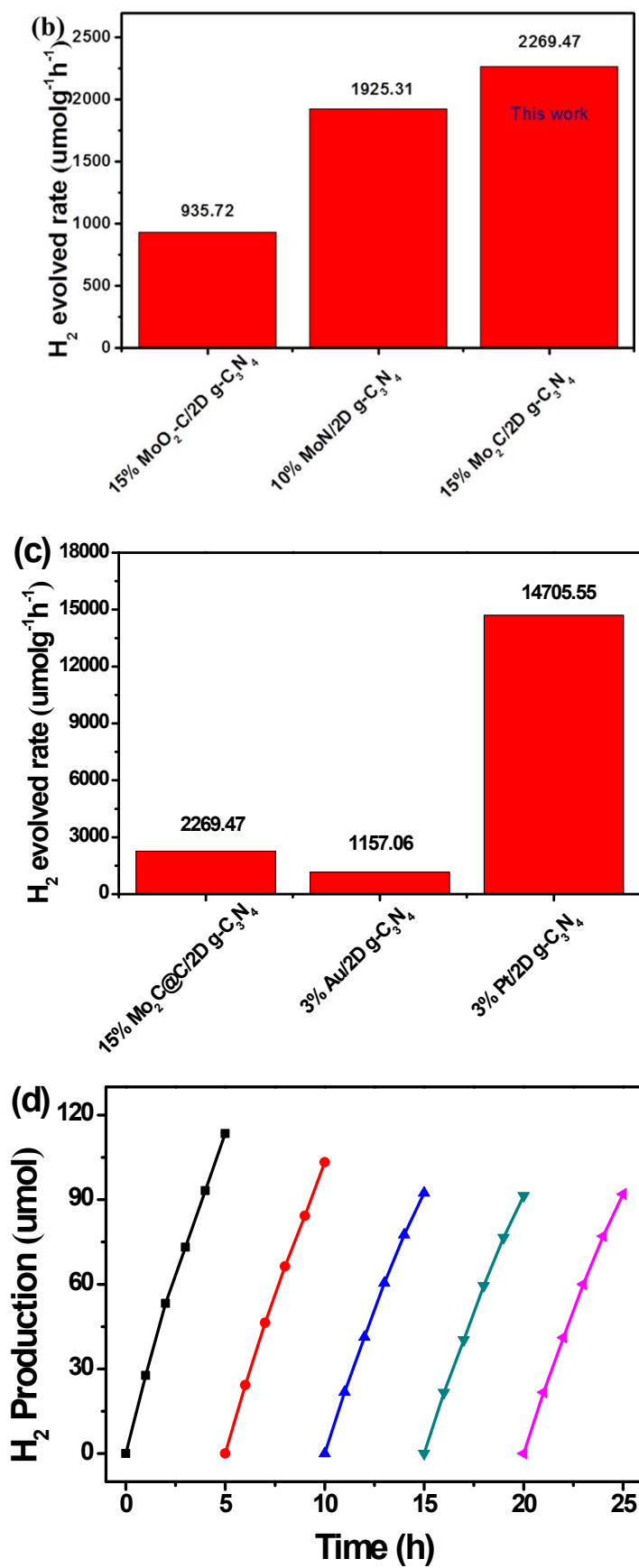**Fig. S5** EDX spectrum of 15% $Mo_2C@C/2D$ g-C_3N_4 composite.

(b)

(c)

(d)

Fig. S6 (a) Photocatalytic H_2 evolution in the presence of 2D g-C$_3$N$_4$, Mo$_2$C@C and

Mo$_2$C@C/2D g-C$_3$N$_4$ composites loaded with different amount 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.
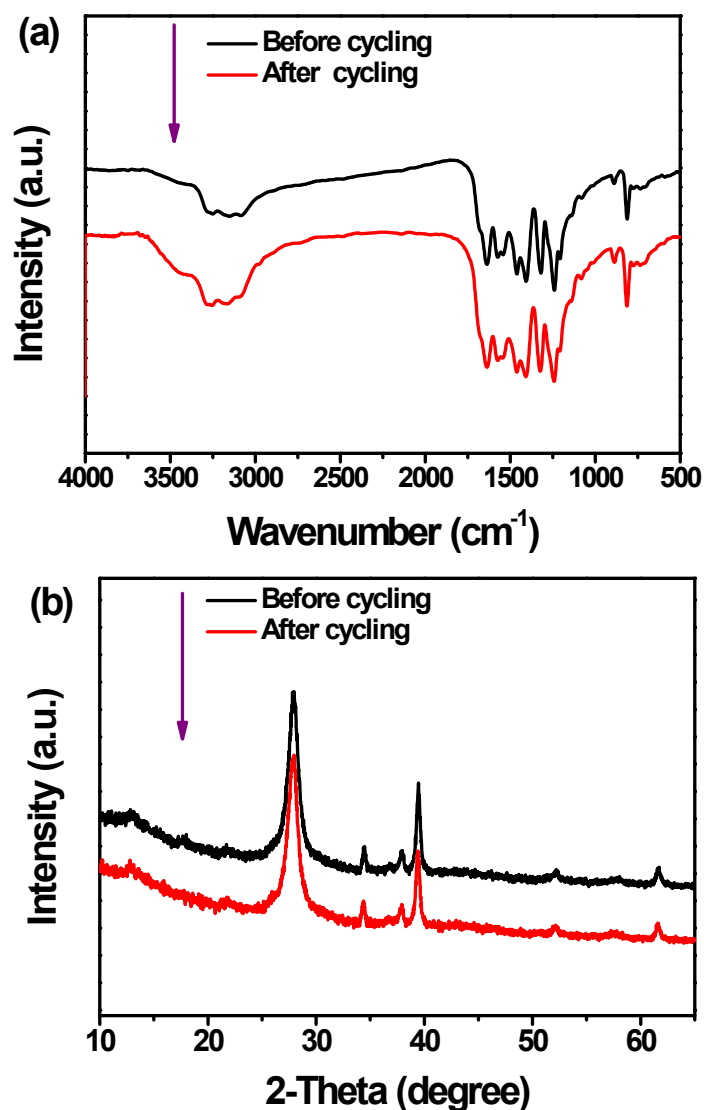
Fig. S7 (a) FT-IR spectra, (b) XRD patterns of before and after cycling samples.
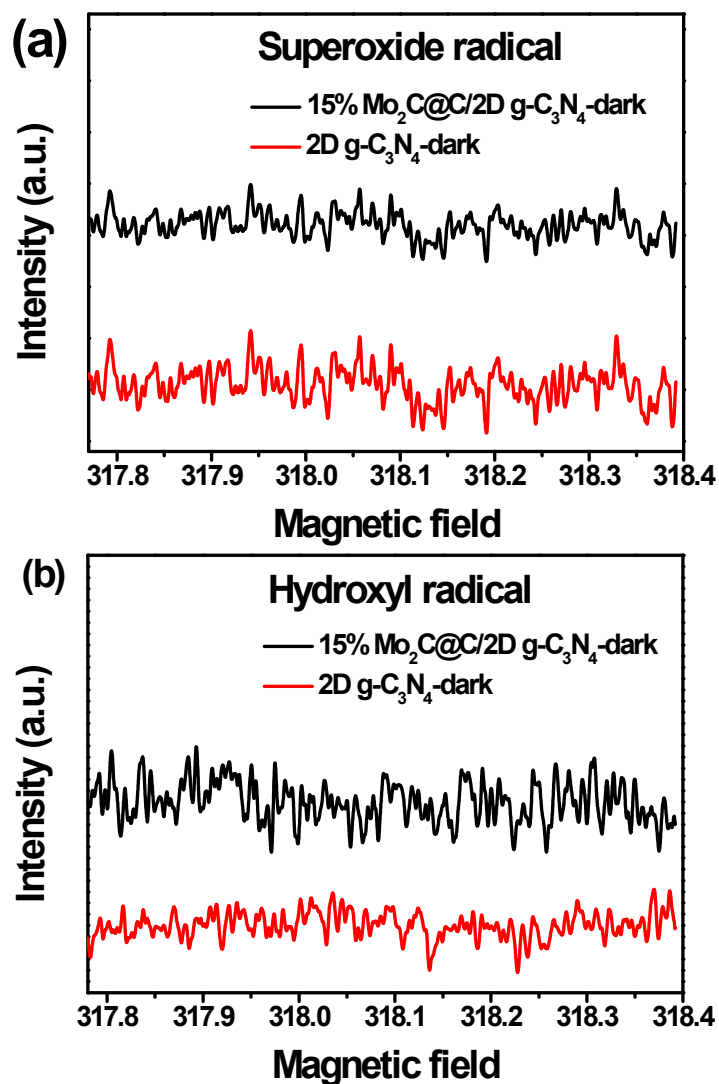
Fig. S8 ESR spectra of (a) DMPO-$O_2^{\bullet-}$ and (b) DMPO-$^{\bullet}OH$ in 2D g-C_3N_4 and 15% $Mo_2C@C$/2D g-C_3N_4 aqueous dispersion systems in dark.

Table S1 Time-resolved PL of 2D g-C_3N_4 and 15% $Mo_2C@C$/2D g-C_3N_4.

Samples	2D g-C_3N_4	15% $Mo_2C@C$/2D g-C_3N_4
τ_1 (ns)	2.53	2.54
τ_2 (ns)	8.70	9.07
A_1	1194.55	326.55
A_2	605.24	132.84
τ_{Ave} (ns)	6.44	6.41

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 4.79×10^{20} calculated by equation (1). The amount of H_2 molecules generated in 3 h are ~36.07 μmol. The EQE was then calculated in equation (2).

Table S2 The calculated External Quantum Efficiency (EQE) of 15% $Mo_2C@C/2D$ g-C_3N_4 at different wavelength.

Wavelength	H_2 Evolved (μmol)	Light Intensity (mW)	EQE
λ=405 nm	36.07	21.77	9.07%
λ=420 nm	24.31	25.26	5.08%
λ=435 nm	4.16	26.12	0.81%
λ=450 nm	0	27.02	0

15% $Mo_2C@C/2D$ g-C_3N_4, λ=405 nm:

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

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

$$= \frac{2 \times the\ number\ of\ evolved\ H2\ molecules}{N} \times 100\%$$

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

=9.07%

15% $Mo_2C@C/2D$ g-C_3N_4, λ=420 nm:

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

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

$$= \frac{2 \times the\ number\ of\ evolved\ H2\ molecules}{N} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 24.31 \times 10^{-6}}{5.76 \times 10^{20}} \times 100\%$$

=5.08%

15% Mo₂C@C/2D g-C₃N₄, λ=435 nm:

$$N = \frac{26.12 \times 10^{-3} \times 3 \times 3600 \times 435 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 6.17 \times 10^{20}$$

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

$$= \frac{2 \times the\ number\ of\ evolved\ H2\ molecules}{N} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 4.16 \times 10^{-6}}{6.17 \times 10^{20}} \times 100\%$$

=0.81%

Table S3 Comparison of the photocatalytic activity and Apparent Quantum Yield

reported all Pt-free g-C₃N₄ system.

Catalysts	Light Source	Reaction Conditions	H₂ Evolution Rate (μmol g⁻¹ h⁻¹)	[a]Apparent Quantum Yield	Reference
MoS₂/g-C₃N₄/Pt (0.5 *wt.*% MoS₂, 1% Pt)	300UV Xe arc lamp with a UV-cutoff filter ($\lambda >$ 400 nm)	120 ml of aqueous solution containing 25% methanol by volume	231	[d] 2.8%	S3
1T-MoS₂/O-g-C₃N₄ (0.2 *wt.*%)	300 W Xe lamp, $\lambda >$ 400 nm	Aqueous (100 mL) TEOA solution (10 *vol.* %)	1841.72	7.11% (420 nm) 2.03% (435 nm) 1.61% (450 nm)	S4

[b] a-MoS$_x$/g-C$_3$N$_4$ (3 wt.%)	four low-power LEDs (3 W, 420 nm)	80 mL aqueous solu-tion containing 10 vol. % of lactic acid	273.1	N/A	S5
[c] MoS$_2$/CN-Py (3% wt.%)	300 WXenon lamp with a UVcutoff filter (λ > 420 nm)	100 mL aqueous solution contain-ing TEOA (10 vol. %)	500	N/A	S6
[c] MoS$_2$/HCNS (0.5 wt.%)	Xenon 300 W lamp (λ > 400 nm)	Aqueous solution (100 mL) containing lactic acid (10 vol. %)	ca. 1300	N/A	S7
[c] MoS$_2$/g-C$_3$N$_4$ 2.89 wt.%	300 W Xe lamp equipped with UV cut off filter (λ > 400 nm).	9 mL water and 1 ml TEOA	320	N/A	S8
[c] MoS$_2$/mpg-CN (0.2 wt.%)	a Xenon 300 W lamp equipped with a 420 nm cut-off filter and a water IR filter	Aqueous solution (100 mL) containing lactic acid (10 vol. %)	ca. 1112.5	2.1% (420 nm)	S9
g-C$_3$N$_4$/5 wt% MSQD+ 2 wt% Pt	300 W Xe lamp, λ > 420 nm	Aqueous (120 mL) TEOA solution (25 vol. %)	576.6	N/A	S10
MoO$_2$-C/2D g-C$_3$N$_4$ (15 wt.%)	300 W Xe lamp, λ > 400 nm	Aqueous (100 mL) TEOA	1071.03	N/A	S11

		solution (10 *vol.* %)			
C₃N₄/Ni-Tu-TETN	300 W Xe lamp with a solar simulator filter	70 mL water and 10 mL TEOA	510	0.2% (420 nm)	S12
NiS₂/g-C₃N₄ (2 wt.%)	300 W Xe lamp with a 420 nm cutoff filter	10 mL of TEOA (15 vol. %)	406	N/A	S13
Au/g-C₃N₄	500 W HBO lamp with a water filter (λ > 420 nm)	100 mL of TEOA (10 vol. %)	107	N/A	S14
Ni(OH)₂/g-C₃N₄ (0.5 mol %)	350 W Xe lamp with a 400 nm cutoff filter	80 mL of TEOA (10 vol. %)	152	1.1 % (420 nm)	S15
WS₂/g-C₃N₄ (0.3 at.%)	300 W Xe lamp with a 420 nm cutoff filter	10 mL of lactic acid (10 vol. %)	ca. 240	N/A	S16
1T-WS₂/2D-C₃N₄ (15 *wt.*%)	300 W Xe lamp, λ > 400 nm	Aqueous (100 mL) TEOA solution (10 *vol.* %)	311.09	1.12% (420 nm)	S17
Mo₂C@C/2D-C₃N₄ (15 *wt.*%)	300 W Xe lamp, λ > 400 nm	Aqueous (100 mL) TEOA solution (10 *vol.* %)	2269.47	9.07% (405 nm) 5.08% (420 nm) 0.81% (435 nm)	This work

[a] Apparent quantum yield = (2 × amount of H_2 molecules evolved in unit time/ number of incident photons in unit time) × 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.

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