

Supporting Information

Improved H-adsorption ability and conductivity of Co-doped Mo₂N cocatalyst for efficient photocatalytic H₂ generation of g-C₃N₄

Zhongxi Lu ^{a1}, Xudong He ^{a1}, Cheng Jin ^a, Haopeng Jiang ^a, Xiaohui Yu ^{a,*}, Lijuan Sun ^a, Weikang Wang ^a, Lele Wang ^a, Qinqin Liu ^{a,*}

^a School of Materials Science & Engineering, Jiangsu University, Zhenjiang 212013, China

*Corresponding Authors

E-mail address: yutoukiki@163.com (X. Yu)

qqliu@ujs.edu.cn

(Q.

Liu)

S1 Experimental

S1.1 Preparation of g-C₃N₄ nanosheets

Mesoporous g-C₃N₄ nanosheets were synthesized by a calcination method. Usually, 5 g of urea is placed in an aluminum oxide boat with a lid and tightly wrapped around the boat with aluminum foil to achieve a seal. Mesoporous g-C₃N₄ nanosheets were prepared by calcining the porcelain boat in a tube furnace at 550 °C for 4 h with a heating rate of 10 °C/min in argon atmosphere.

S1.2 Preparation of MoO_{3-x} olive-like nanosheets

MoO_{3-x} olive-like nanosheets were synthesized by a hydrothermal method. First, 2 mmol of commercial molybdenum powder was dissolved in 24 mL of n-butanol, to which 3 mL of H₂O₂ (30 wt%) was added dropwise and stirred at room temperature for 30 min to form a transparent yellow solution. The yellow solution was then added to a 50 mL autoclave and heated to 140 °C for 12 h. The precipitate was washed with deionized water and ethanol, and then dried in vacuum at 60 °C for 12 h to obtain MoO_{3-x} olive-like nanosheets.

S2 Characterization

The structure, composition and light absorption were investigated by the X-ray diffraction (XRD, XRD-6100, Shimadzu), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Nexsa) and ultraviolet-visible diffuse reflectance spectrum (UV-vis DRS, UV-2600 spectrophotometer), respectively. The morphology was studied by the scanning electron microscope (SEM, JSM-7001F) and transmission electron microscope (TEM, JEM-2100). The photoluminescence (PL) spectrum was obtained by fluorescence spectrophotometer (Hitachi, F-7000).

S3 Photocatalytic experiments

10 mg catalysts were dispersed in an 80 ml three-necked reactor containing 10 % triethanolamine solution and then purged with N₂ to eliminate air. The reaction system was placed under the irradiation of a LED lamp equipped with a cutoff filter ($\lambda = 420$ nm) as the source for testing H₂ evolution. The H₂ production was checked by a gas chromatograph (GC-2014, Japan). The apparent quantum yield (AQY) was investigated. 10 mg catalysts were dispersed in an 80 ml three-necked reactor containing 10 % triethanolamine solution and then purged with N₂ to eliminate air. The reaction system was placed under the irradiation of a Xe lamp equipped with a band-pass filter cutoff filter ($\lambda = 420$ and 550 nm) as the source. The light intensity was 47251.6 and 39553.6 uW, respectively. The illumination area was 6 cm².

The AQY calculated by the following equation

$$AQY (\%) = \frac{2 \times \text{amount of } H_2 \text{ molecules evolved in unit time}}{\text{number of incident photons in unit time}} \times 100\%$$

$\lambda = 420$ nm:

$$E = \frac{hc}{\lambda}, E_{total} = ISt, N = \frac{E_{total}}{E},$$
$$N_{total} = \sum_{k=N_{\lambda 1}}^{N_{\lambda x}} (N_{\lambda 1} + N_{\lambda 2} + \dots + N_{\lambda x}) = (N_{405} + N_{406} + \dots + N_{435}) =$$

$$N_{produce/s} = N_{total} \times S_{light\ source} = 7.802 \times 10^{16} \times 6 = 4.681 \times 10^{17}$$

$$N_{consume/s} = \frac{H_{H_2} \times M \times N_A \times 2}{T} = \frac{367.8 \times 10^{-6} \times 10 \times 10^{-3} \times 6.02 \times 10^{23}}{3600} = 1.23 \times 10^{15}$$

$$AQY = \frac{N_{consume/s}}{N_{produce/s}} \times 100\% = \frac{1.23 \times 10^{15}}{4.681 \times 10^{17}} \times 100\% = 0.26\%$$

$\lambda = 550\text{ nm}$:

$$E = \frac{hc}{\lambda}, E_{total} = ISt, N = \frac{E_{total}}{E},$$

$$N_{total} = \sum_{k=N_{\lambda 1}}^{N_{\lambda x}} (N_{\lambda 1} + N_{\lambda 2} + \dots + N_{\lambda x}) = (N_{535} + N_{536} + \dots + N_{565}) = 4.93391$$

$\times 10^{16}$

$$N_{produce/s} = N_{total} \times S_{light\ source} = 4.93391 \times 10^{16} \times 6 = 2.96 \times 10^{17}$$

$$N_{consume/s} = \frac{H_{H_2} \times M \times N_A \times 2}{T} = \frac{9.068 \times 10^{-6} \times 10 \times 10^{-3} \times 6.02 \times 10^{23}}{3600} = 3.23 \times 10^{13}$$

$$AQY = \frac{N_{consume/s}}{N_{produce/s}} \times 100\% = \frac{3.32 \times 10^{13}}{4.681 \times 10^{17}} \times 100\% = 0.007\%$$

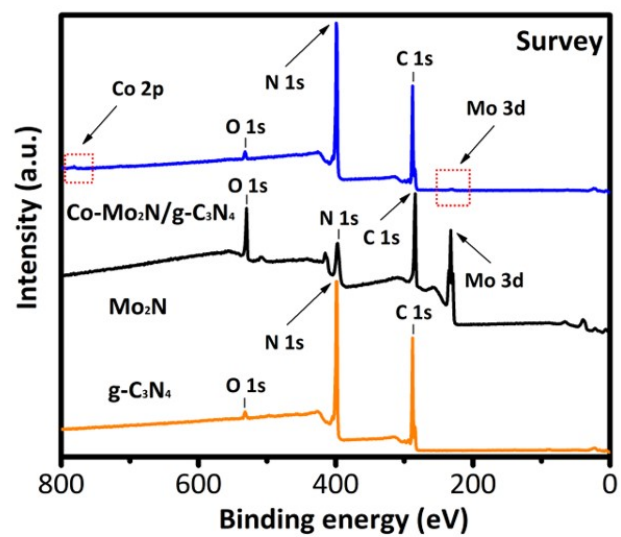


Fig. S1 Survey XPS spectra of the $g\text{-C}_3\text{N}_4$ and $\text{Co-Mo}_2\text{N/g-C}_3\text{N}_4$.

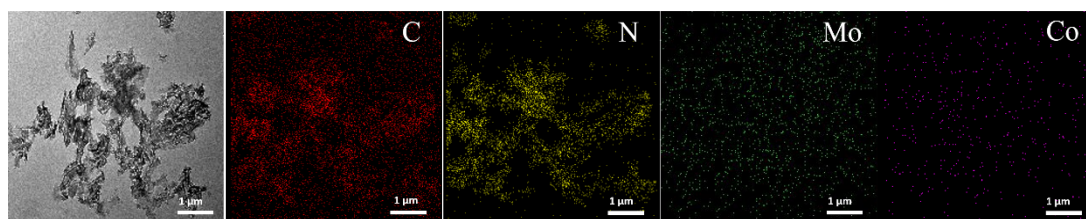


Fig. S2 TEM elemental mapping of the $\text{Co-Mo}_2\text{N/g-C}_3\text{N}_4$.

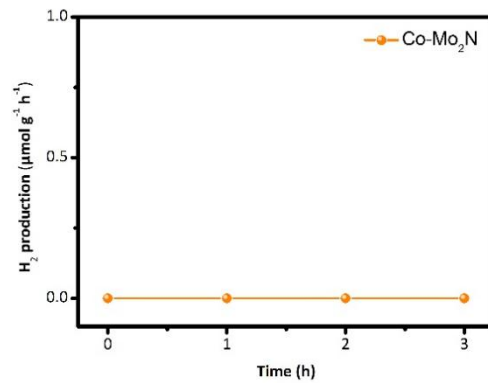


Fig. S3 H₂ generation of the Co-Mo₂N under visible light.

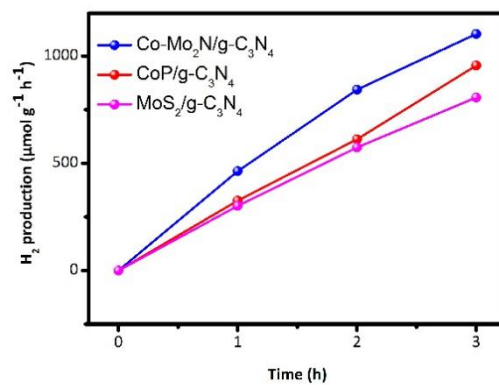


Fig. S4 H₂ generation of the MoP/g-C₃N₄ and Mo₂S/g-C₃N₄ under visible light.

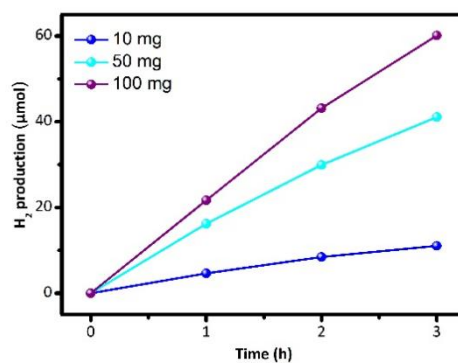


Fig. S5 H₂ generation by using different amount of Co-Mo₂N/g-C₃N₄ under visible light.

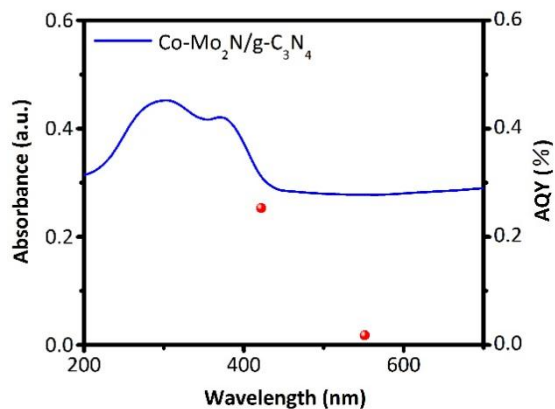


Fig. S6 AQY of the Co-Mo₂N/g-C₃N₄ under visible light.

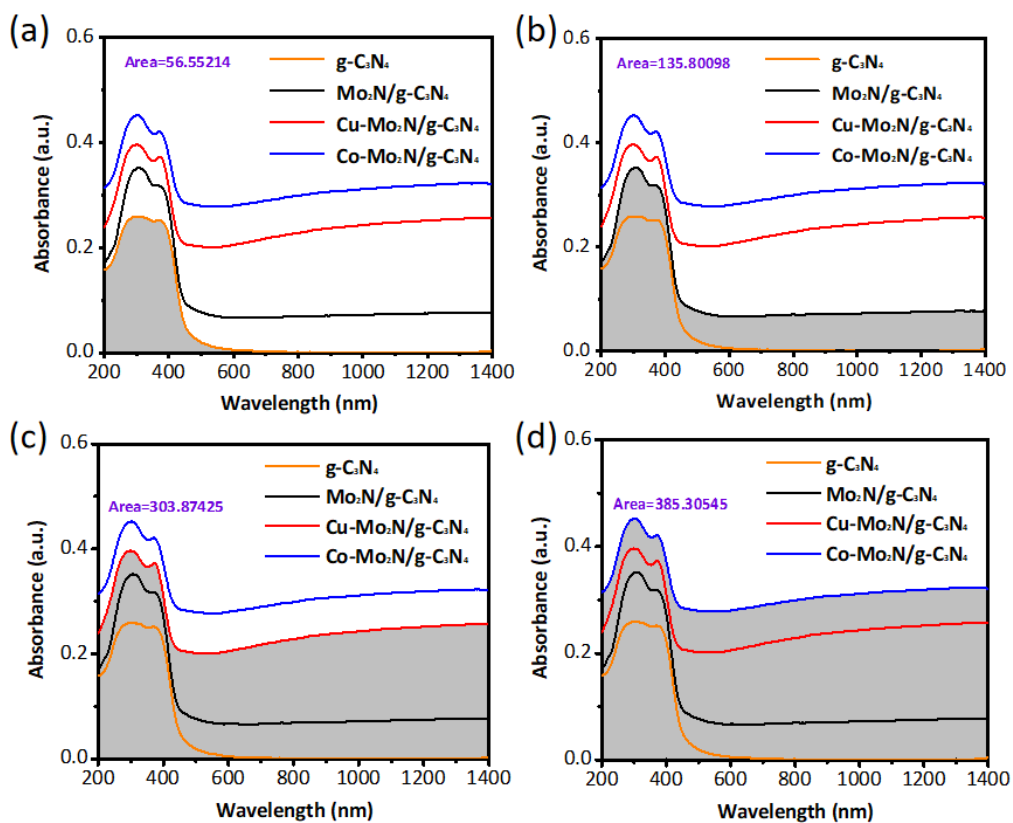


Fig. S7 UV-vis spectra of area: (a) g-C₃N₄, (b) Mo₂N/g-C₃N₄, (c) Cu-Mo₂N/g-C₃N₄, (d) Co-Mo₂N/g-C₃N₄.

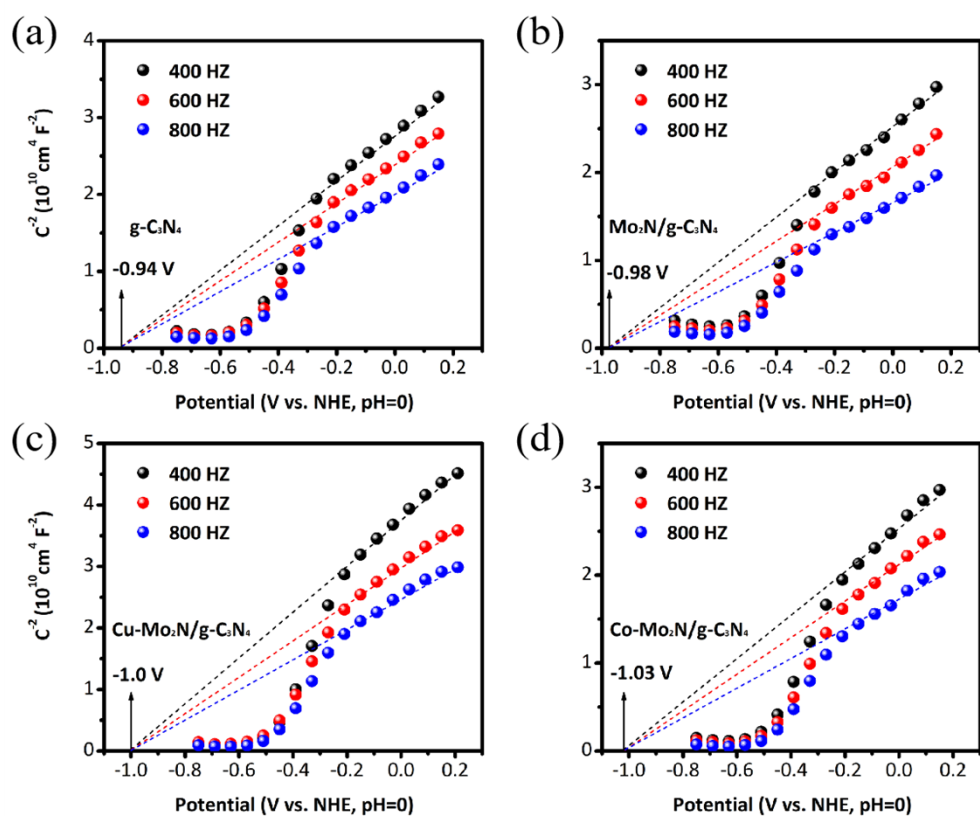


Fig. S8 M-S plots of $g\text{-C}_3\text{N}_4$ (a), $\text{Mo}_2\text{N}/g\text{-C}_3\text{N}_4$ (b), $\text{Cu-Mo}_2\text{N}/g\text{-C}_3\text{N}_4$ (c) and $\text{Co-Mo}_2\text{N}/g\text{-C}_3\text{N}_4$.

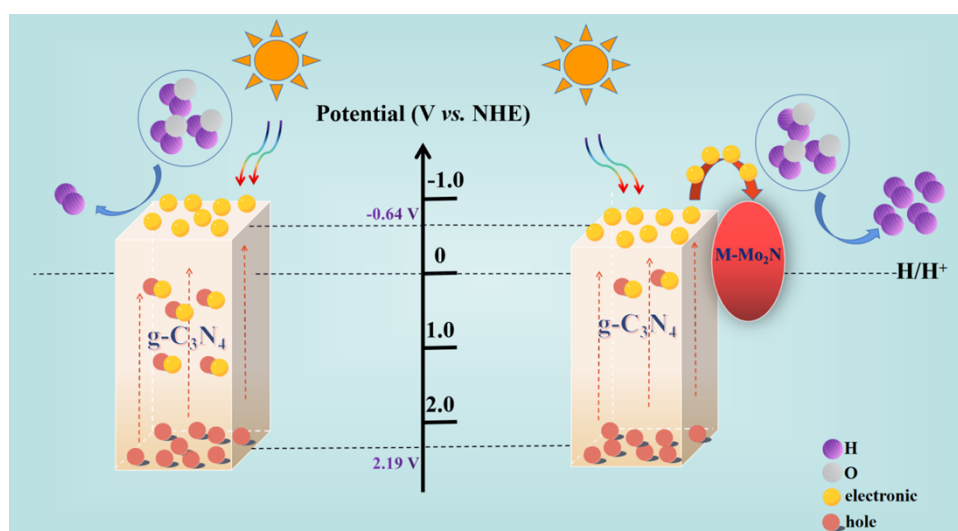


Fig. S9 Mechanism of higher H_2 generation of the $\text{Co-Mo}_2\text{N}/g\text{-C}_3\text{N}_4$.

Table. S1 The information of the AQY measurements

Wavelength (nm)	light area (cm ²)	Substrate (uW)
420	6	47251.6
550	6	39553.6

Table. S2 Area and integral fraction for UV-vis spectra.

Samples	g-C ₃ N ₄	Mo ₂ N/g-C ₃ N ₄	Cu-Mo ₂ N/g-C ₃ N ₄	Co-Mo ₂ N/g-C ₃ N ₄
Area	56.6	135.8	303.9	385.3
Fraction	1	2.4	5.37	6.81

Table. S3 Comparison of the photocatalytic H₂ generation over different catalysts.

Catalysis	light source	substrate	H ₂ production ($\mu\text{mol g}^{-1}\cdot\text{h}^{-1}$)	Ref.
MoP/g-C ₃ N ₄	80W LED $\lambda=400$ nm	10% TEOA	327.5	1
CoP/g-C ₃ N ₄	300 W Xe lamp $\lambda>320$ nm	20% TEOA	201.5	2
MoO ₃ /g-C ₃ N ₄	300 W Xe lamp $\lambda\geq 420$ nm	20% TEOA	328.75	3
Mo ₂ N/g-C ₃ N ₄	300 W Xe lamp $\lambda\geq 420$ nm	20% TEOA	0.89	4
Ni ₃ N/g-C ₃ N ₄	300 W Xe lamp $\lambda\geq 420$ nm	20% TEOA	305.4	5
MoS ₂ /g-C ₃ N ₄ /TiO ₂	300 W Xe lamp $\lambda>400$ nm	25% methanol	125	6
Co(Mo-Mo ₂ C)/g-C ₃ N ₄	300W Xe lamp $\lambda\geq 420$ nm	20% TEOA	11291	7
Co-Mo ₂ N/g-C ₃ N ₄	80W LED $\lambda=420$ nm	10% TEOA	367.8	This Work

References

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