Supporting Information

In situ synthesized rod-like MoS_2 as cocatalyst enhanced photocatalytic hydrogen evolution of graphitic carbon nitride (g-CN) without noble metal

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Material Characterizations

X-ray diffraction (XRD) patterns were measured with a Panalytical X'Pert PRO X-ray diffractometer with a Cu Kα radiation (λ = 1.5418 Å) as X-Ray source. The Fourier Transform infrared (FT-IR) absorption spectra of the samples was measured and recorded on a Perkin Elmer 100 spectrometer. The pictures of the micro-morphology were recorded by a field emission scanning electron microscope (SEM), ZEISS SUPRA55 FEGSEM and a transmission electron microscope (TEM), HITACHI JEM-2100, respectively. The X-ray photoelectron spectra (XPS) data of the sample were obtained using a PHI 5700 ESCA spectrometer working with an Al Kα radiation as the excitation source (hν =1486.6 eV) and the C 1s line was used as the calibration. The UV-Vis diffuse reflectance spectra (DRS) from 200 nm to 800 nm was recorded by a Perkin Elmer Lambda 750 spectrophotometer. The nitrogen adsorption–desorption isotherms and pore size distribution were recorded at 77 K with a Micromeritics ASAP2020.

Photocatalytic Activity Measurement

The photocatalytic activity was evaluated by splitting water to evolve hydrogen under visible light. Triethanolamine (TEOA) solution (10 vol%) was chosen as the sacrificial agent. The experiment was undergoing without co-catalyst. 0.1 g of as-prepared samples was added in 300 mL aqueous solution in a quartz reactor with TEOA under stirring. After fully dispersed by sonicating for 10 min, the solution was degassed under Nitrogen flowing. A 300W Xe Lamp working with a 420 nm cut off filter was used as the light source and the device was cooled with cold water circulation during the reaction. The evolved gas was measured by a gas chromatography equipped with a TCD detector.

Photo-electrochemical Measurement

The photo-electrochemical property of the samples was investigated on a CHI 660D electrochemical workstation with a three-electrode system and Na_2SO_4 (0.5 mol L^{-1}) solution was used as electrolyte. In this system, Ag/AgCl electrode (saturated KCl solution), Pt wire electrode and glassy carbon electrode with the ink of the samples were used as reference electrode, counter-electrode and working electrode, respectively. Appropriate amount of sample (0.2 mg·cm^{-2}) was fully dispersed in the solution of water, 5 wt% Nafion and alcohol under ultrasonic, and the mixture was dropped on the active area of working electrode (0.19625 cm^2). A 300W Xe lamp (HSX-F/UV300, Beijing NBeT) was used as the light source and the transient photocurrent responses analysis was measured in on-off cycles of visible light irradiation and the electrochemical impedance spectroscopy was measured without light irradiation.

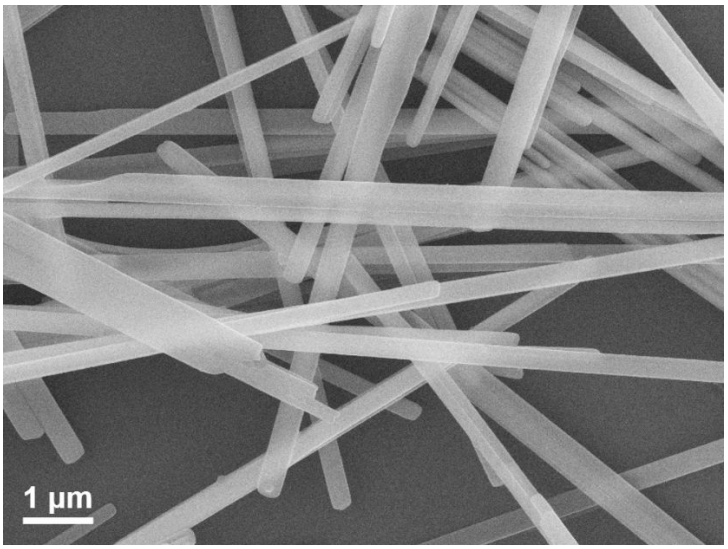


Figure S1. The morphology of rod-like MoO_3 by SEM

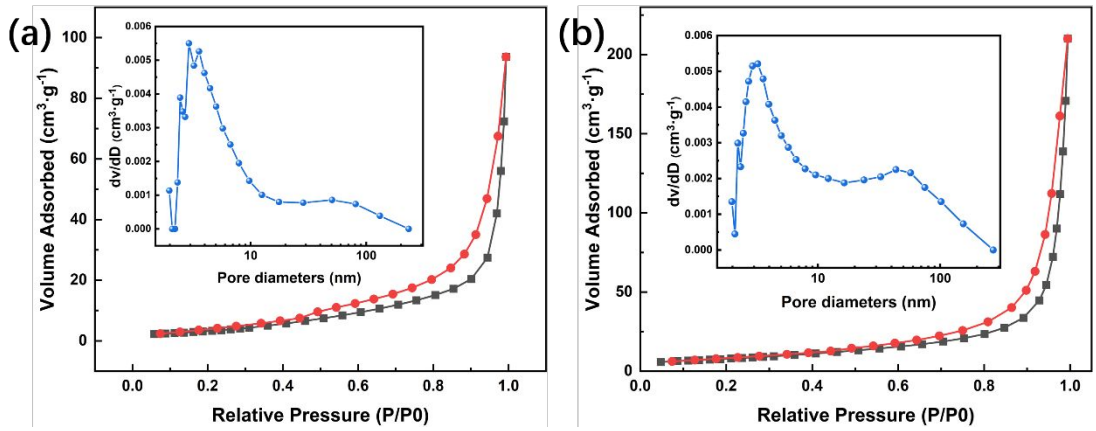


Figure S2 N_2 adsorption-desorption isotherms and corresponding Barret-Joyer-Halenda (BJH) pore-size distribution curves (inset) of the sample. a g-CN and b g-CN/MoS_2-0.2

Table S1 physical properties of g-CN and g-CN/MoS2-0.2

Sample	S_{BET} (m^2g^{-1})	Center pore size (nm)	Pore Volume (cm^3g^{-1})
g-CN	13.75	3.85	0.160
g-CN/MoS_2-0.2	29.01	3.84	0.341

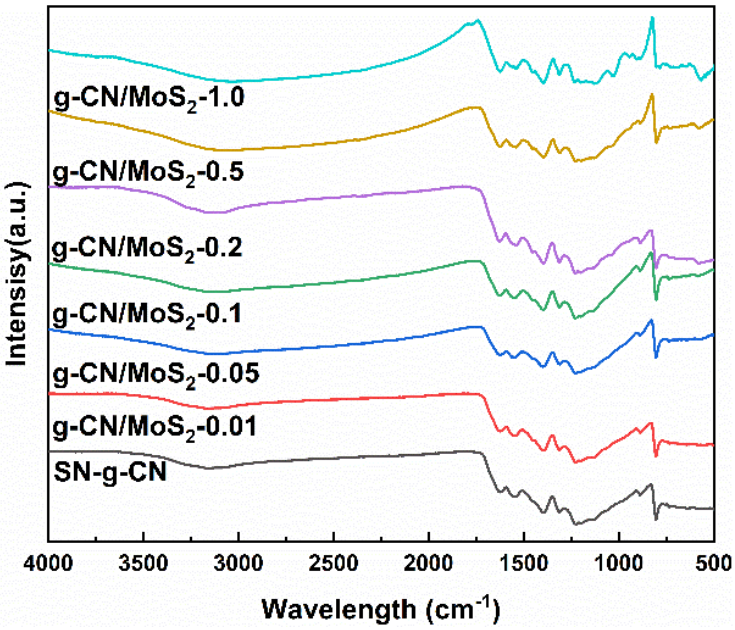


Figure S3 FT-IR spectrum of the prepared samples

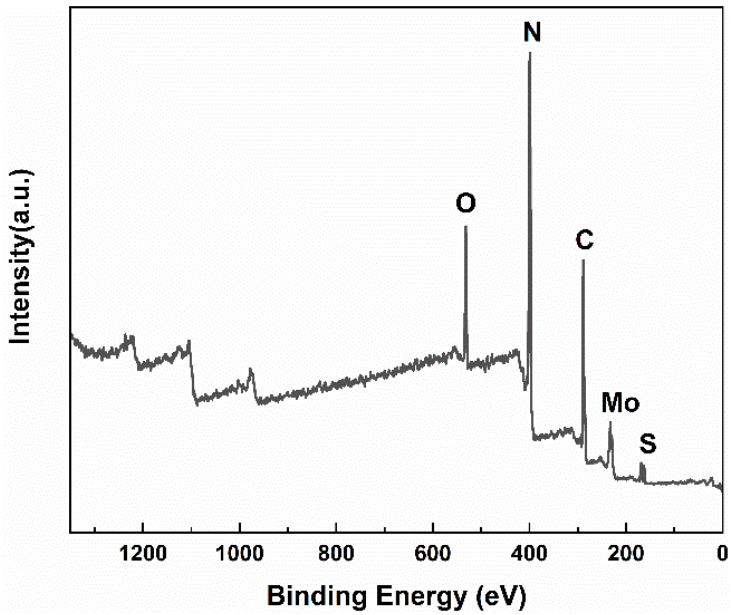


Figure S4 the survey XPS spectra of g-CN/MoS_2

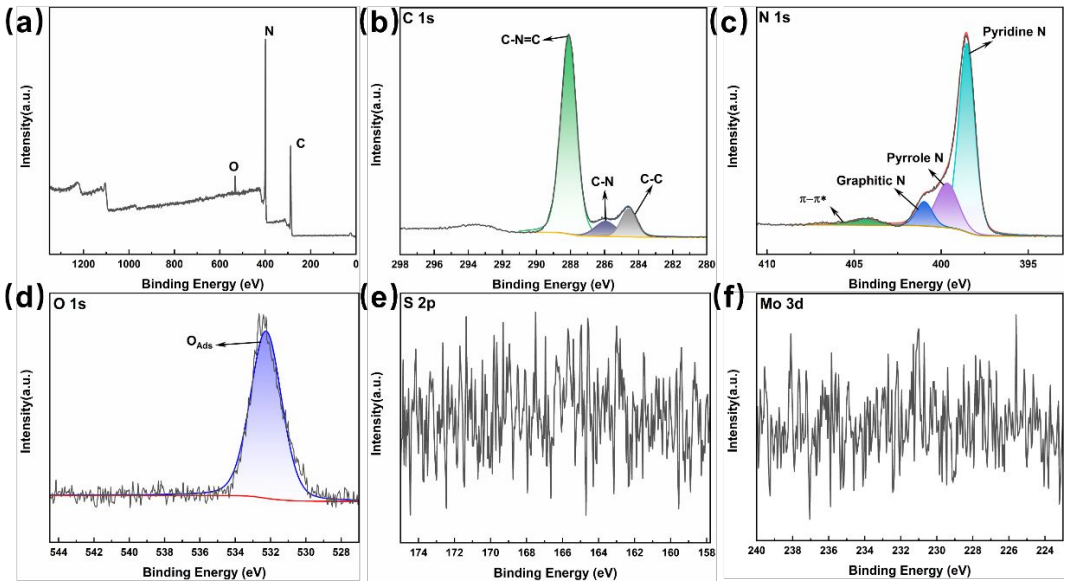
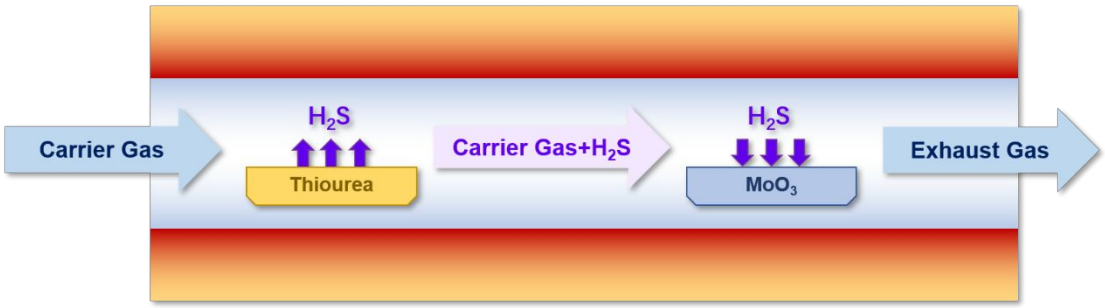


Figure S5. XPS spectra of g-CN. (a) Survey XPS spectra (b-f) High resolution spectra of C 1s, N 1s, O 1s, S 2p and Mo 3d.

Control Experiment

In order to investigate the synthesis mechanism, a control experiment was designed, and the calcination illustration was shown as **Scheme S1**. To be specific, thiourea and MoO_3 nanorod were placed upstream and downstream of the carrier gas flow, respectively, and the two crucibles were placed without directly contact. The calcination condition was consistent with the synthesis method in manuscript, and the sample downstream was denoted as MoS_2-S1.



Scheme S1. Schematic illustration of the confirmatory experiment

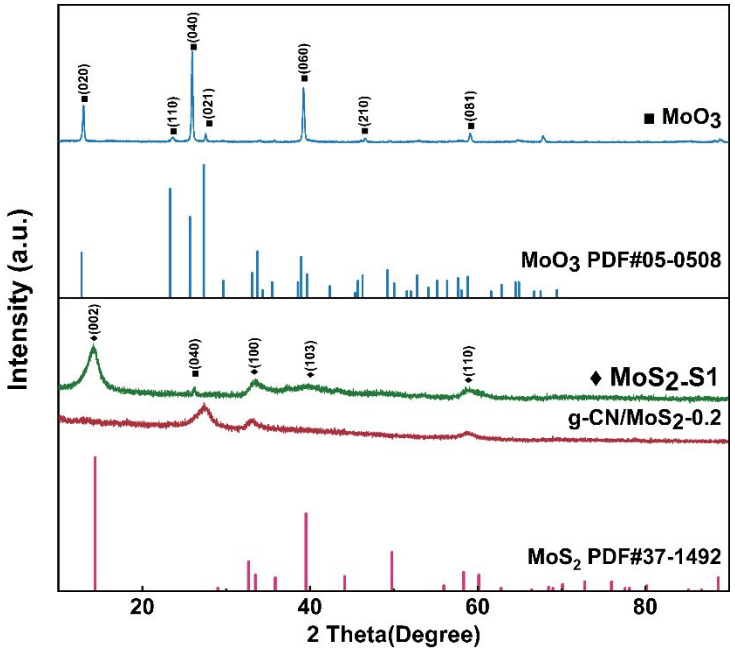


Figure S6 the XRD pattern of MoS_2-S1, MoO_3 and g-CN/MoS_2-0.2

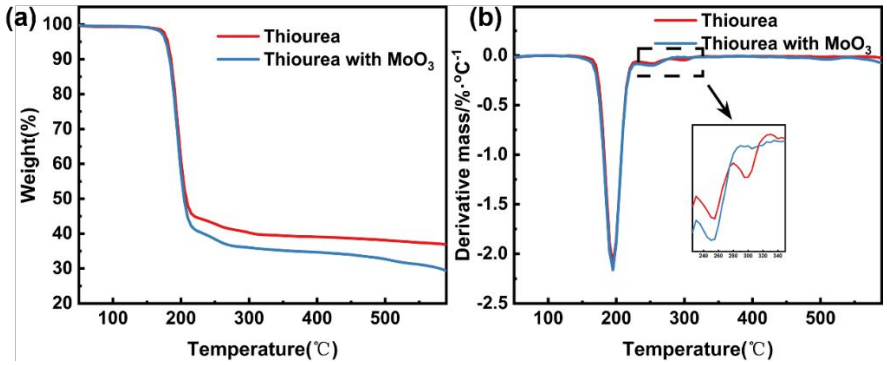


Figure S7 Thermogravimetric test of the precursor. (a) TG (b) DTA

The synthesis of g-CN/MoO_3 for control experiment: 10 g of melamine was fully mixed with the dispersion of 0.2 g MoO_3 and was dried over night at 60°C. The mixture was completely grinded and calcinated at 550°C for 90 min with a heat rate of 5°C·min^{-1}. The sample was collected, fully washed by deionized water and alcohol and denoted as g-CN/MoO_3-0.2

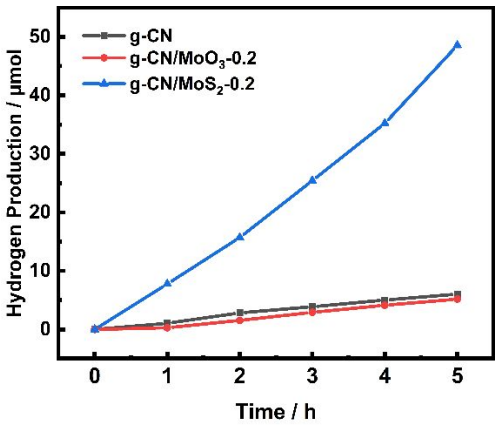


Figure S8 The comparison spectra of photocatalytic hydrogen evolution between g-CN, g-CN/MoO_3-0.2 and g-CN/MoS_2-0.2

Table S2 the amount of loading MoS_2 measured by ICP

Sample	Amount of MoS_2 (wt%)
g-CN	0
g-CN/MoS_2-0.01	0.10
g-CN/MoS_2-0.05	1.13
g-CN/MoS_2-0.1	2.56
g-CN/MoS_2-0.2	8.54
g-CN/MoS_2-0.5	27.92
g-CN/MoS_2-1.0	96.56

Table S3 Comparison of photocatalytic hydrogen evolution efficiency by composite of MoS_2 and graphitic carbon nitride

Photocatalyst	Synthesis method			Increased multiple*	Ref.
	g-CN	MoS_2	composite		
0D(MoS_2)/2D(g-C_3N_4)	Calcination	Hydrothermal method	Sonicated & thermal treatment	8.1 times	[1]
crystalline MoS_2/g-C_3N_4	Calcination-hydrothermal method	Hydrothermal method	Sonicated treatment	16.8 times	[2]
2D-2D MoS_2/g-C_3N_4	Calcination & sonicated treatment	Solvent-thermal method	Thermal treatment	15.8 times	[3]
MoS_2-g-C_3N_4	Calcination	Hydrothermal method	Thermal treatment	11.3 times	[4]
3D porous MoS_2/g-C_3N_4	Calcination	Freeze drying & calcination	In situ Thermal treatment	6.14 times	[5]
MoS_2/CO-C_3N_4	Calcination in CO_2	Hydrothermal method	Ultrasonic treatment	1.85 times	[6]
Nanoflower MoS_2/g-C_3N_4	Calcination	Hydrothermal method	Ultrasonic treatment	5 times	[7]
Rod-like g-CN/MoS_2	Calcination	Gas-solid reaction	In situ sulfurization	13.4 times	This work

***Obtained by comparing the photocatalytic hydrogen evolution rate of modified**

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