

Supplementary information

The 2D Van der Waals heterojunction MoC@NG@CN for enhanced photocatalytic hydrogen production

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1. Experiment

1.1 Synthesis

All the chemicals were used without further purification. Triethanolamine (TEOA), $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, ZnCl_2 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were purchased from Aladdin Reagent Co., Ltd. Thioacetamide (TAA), glycerol ($\text{C}_3\text{H}_8\text{O}_3$) and melamine ($\text{C}_3\text{H}_6\text{N}_6$) were supplied by Beijing J&K Scientific Co., Ltd.

1.1.1 Synthesis of MoC@NG

The samples of MoC@NG were synthesized by a simple solid-state reaction method. The 0.465 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 2.0 g $\text{C}_3\text{H}_6\text{N}_6$ were mechanically ground for 30 minutes. The obtained homogeneous mixture was calcined under N_2 atmosphere at 500 °C for 2 h with a heating rate of 5 °C min^{-1} , and finally sintered at 800 °C for 120 min.

1.1.2 Synthesis of g- C_3N_4

20 g urea was calcined at 550 °C for 3 h in a covered ceramic crucible with a heating rate of 2 °C min^{-1} . The yellow resultant bulk g- C_3N_4 was ground into fine powder. The g- C_3N_4 nanosheets were synthesized by thermal etching bulk g- C_3N_4 . The bulk g- C_3N_4 was placed in an open ceramic crucible and heated at 500 °C for 2 h with a heating rate of 5 °C min^{-1} . The obtained light-yellow samples were labeled as CN.

1.1.3 Synthesis of MoC@NG@CN hybrid photocatalyst

240 mg CN was uniformly dispersed in 30 mL deionized water and sonicated for 30 minutes. Subsequently, a certain amount of MoC@NG was added and sonicated for 30 minutes. Finally, the suspension was stirred for 24 h. The samples were obtained by centrifugation and dried overnight in a vacuum drying oven at 60 °C. The prepared samples were labeled as MoC@NG-x@CN (x = 0, 50, 60, 70, 80, 90), and x represents the mass of MoC@NG (mg).

1.2 Characterization

The crystal structure of photocatalysts was analyzed by X-ray diffraction (XRD, Rigaku Ultima IV, Japan) using Cu K α radiation (40 kV, 40 mA). The microscopic morphology was

observed by field-emission scanning electron microscope (FE-SEM, SUPRA 55, Zeiss) and transmission electron microscope (TEM, JEM-2200FS, JEOL). Energy-dispersive X-ray spectroscopy (EDS) mapping was also obtained by TEM. The X-ray photoelectron spectra (XPS) were determined by an AXIS ULTRA DLD spectrometer using a monochromatic Al K α radiation ($h\nu = 1486.6$ eV). The texture properties of samples were characterized by Brunauer-Emmett-Teller (BET, ASAP 2460). The Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were measured with Shimadzu UV-2550. The steady-state photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) decay plots were implemented on the spectrophotometer (FLS980) with an excitation wavelength of 314 nm. A typical three-electrode cell using the CHI660E electrochemical workstation was employed to determine the photoelectrochemical performance. The photocatalysts (5 mg) were dispersed in an ethanol solution containing 10 vol% Nafion reagents. The mixed solution was uniformly deposited on a 1 cm \times 1 cm FTO conductive glass as a working electrode, while the Pt sheets and Ag/AgCl electrodes were used as counter and reference electrodes, respectively, and 0.5 M Na₂SO₄ aqueous solution was used as the electrolyte. The electron paramagnetic resonance (EPR) characterization: Endor spectrometer (JES-FA300, JEOL) was used for the characterization of EPR with 300 W Xenon lamp and a 420 nm cutoff filter at room temperature. For the test of $\cdot\text{O}_2^-$, 5 mg sample was dispersed into methanol (1 mL). Then, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was added to the mixture. Under light irradiation, the signals at 0 and 10 min were collected. For the test of h^+ , 5 mg sample was dispersed into acetonitrile (1 mL), and then 2,2,6,6-tetramethylpiperidinoxy (TEMPO) was added into the mixture. Under light irradiation, the signals at 0 min and 10 min were collected.

1.3 Photocatalytic test

The photocatalytic hydrogen evolution experiments were carried out in a sealed quartz flask (50 mL). In a typical test, the photocatalysts (5 mg) were added into 20 mL 20 vol% TEOA aqueous solution with ultrasonic dispersion for 5 min. Subsequently, the 26 μL H₂PtCl₆ \cdot 6H₂O

aqueous solution (5 mg/mL) was added to the reaction solution. Before irradiation, the reactor was evacuated and filled with N₂ to ensure that it remained in an anaerobic condition. A 300 W Xenon lamp equipped with a UV cut-off filter ($\lambda > 400$ nm) was adopted as a light source and was positioned about 10 cm away from the catalytic cell. After four hours of light exposure, the evolved H₂ was analyzed by a gas chromatograph (SHIMADZU GC-2014, TCD). The apparent quantum efficiency (AQE) was measured at monochromatic wavelengths (400 nm, 420 nm, 450 nm, 500 nm and 550 nm), and calculated according to the following equation:

$$\text{AQE} = \frac{N_e}{N_p} \times 100\% = \frac{2 \cdot N_{\text{H}_2} \cdot N_A \cdot h \cdot c}{W \cdot S \cdot t \cdot \lambda} \times 100\%$$

Where N_e represents the number of electrons participating in the reaction, N_p means the number of incident photons. N_{H₂}, N_A, h and c represent the number of evolved H₂ molecules, Avogadro constant, Planck constant and the speed of light. W, S, t and λ represent the irradiation intensity, the irradiation area, the reaction time and the wavelength of monochromatic light, respectively.

2. Figures

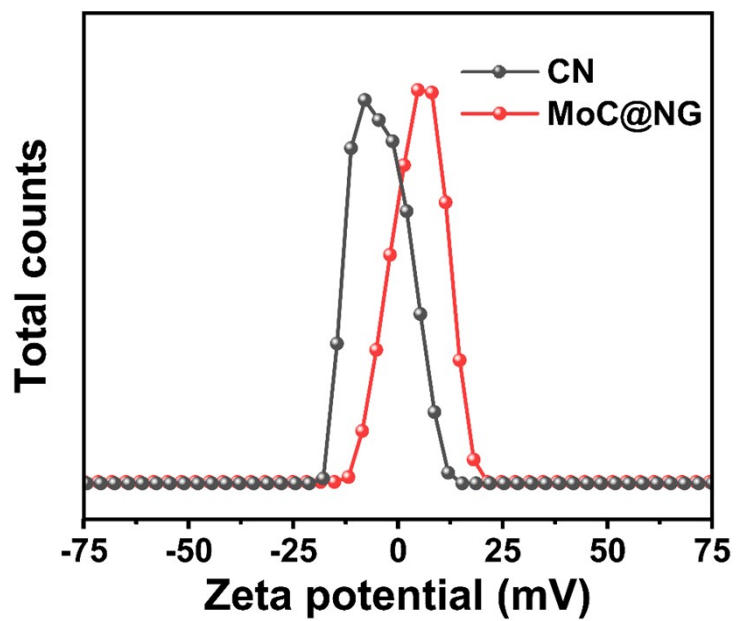


Fig. S1 Zeta potentials of CN and MoC@NG in deionized water at pH 7.

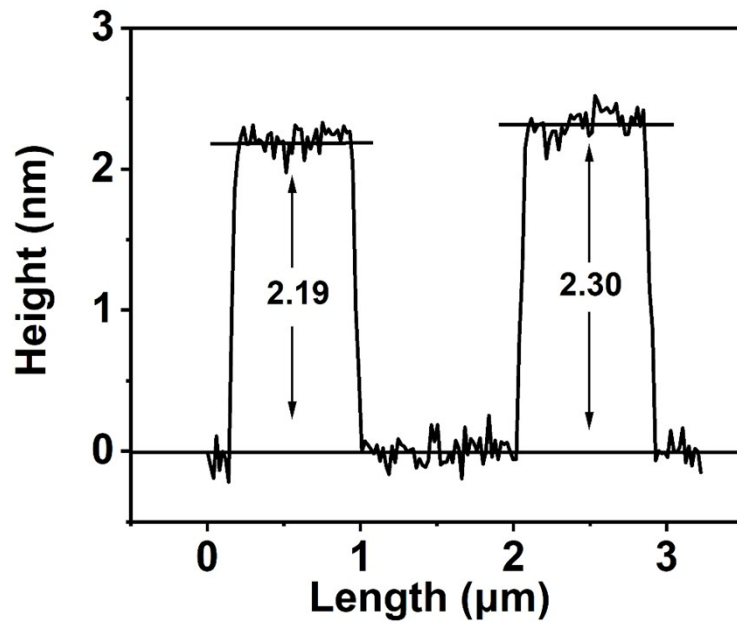


Fig. S2 The height spectra corresponding to the AFM image of MoC@NG-70@CN.

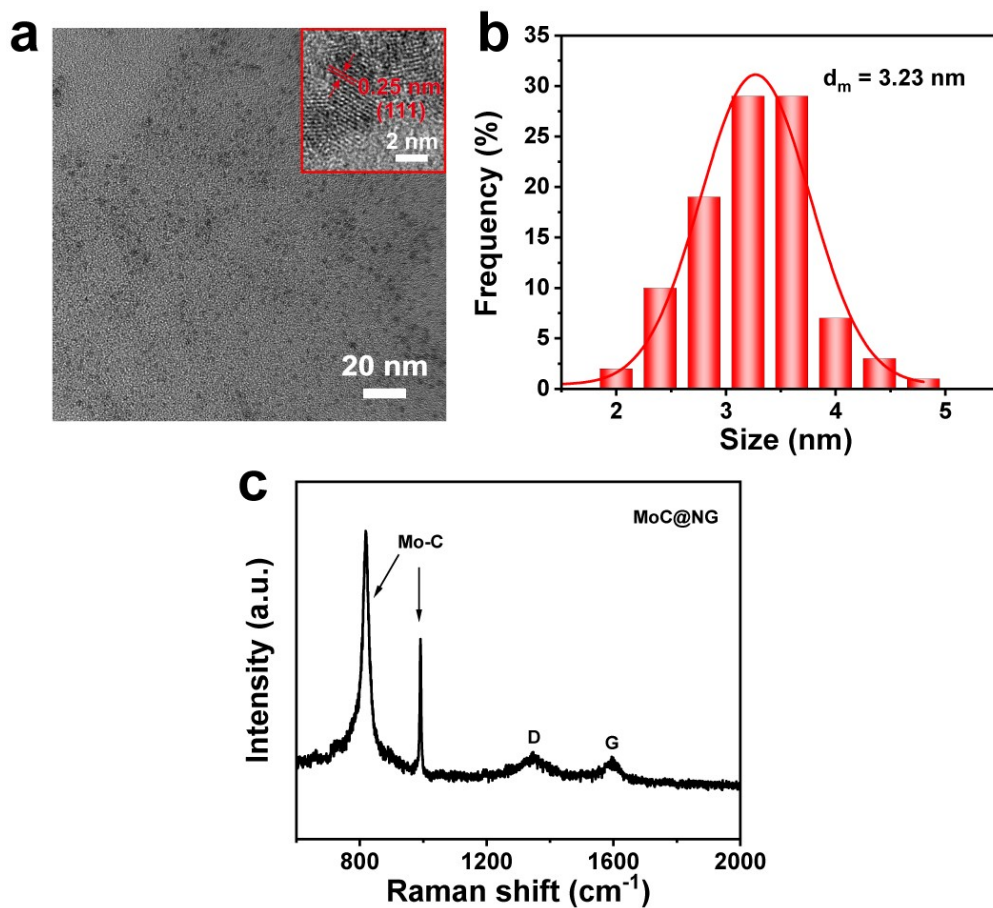


Fig. S3 (a) TEM image (the inset is the corresponding high-resolution TEM image); (b) the particle size distribution and (c) Raman spectrum of MoC@NG.

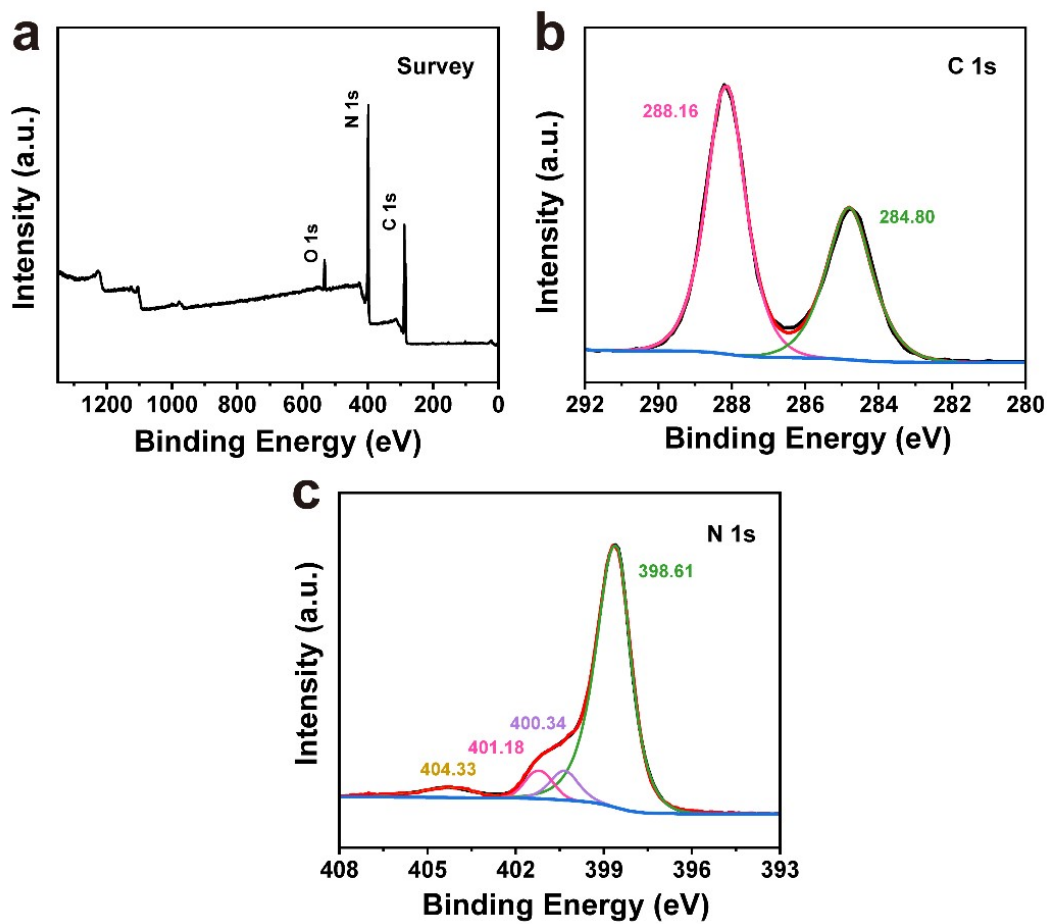


Fig. S4 The XPS spectra of (a) survey, (b) C 1s, (c) N 1s for CN.

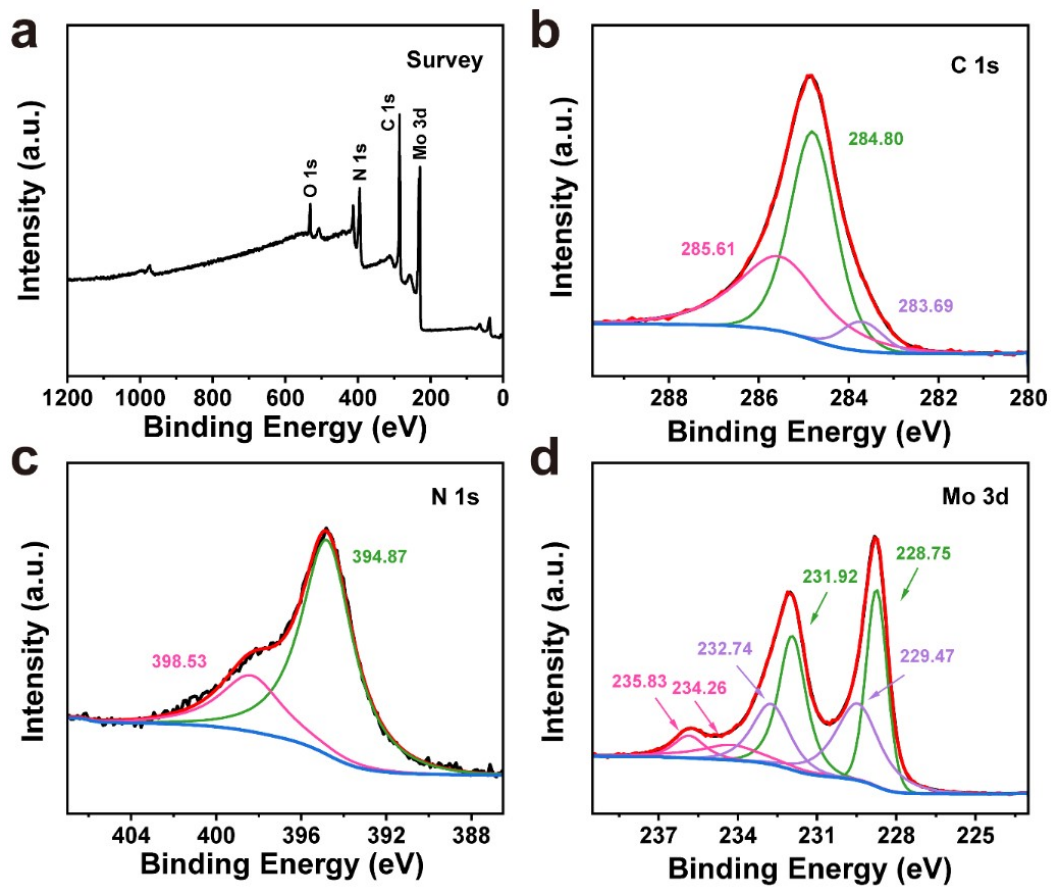


Fig. S5 The XPS spectra of (a) survey, (b) C 1s, (c) N 1s, (d) Mo 3d for MoC@NG.

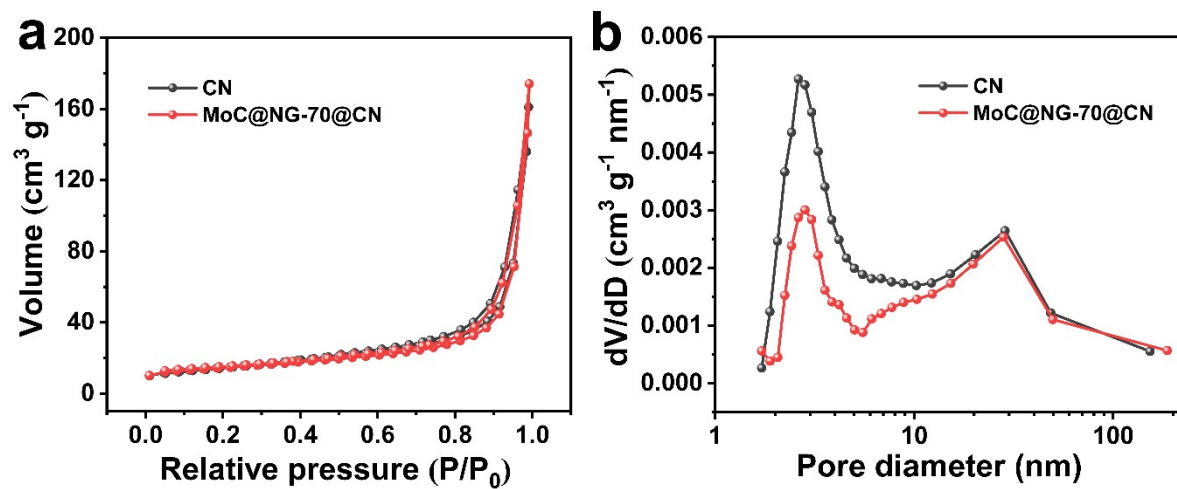


Fig. S6 Textural properties of photocatalysts. (a) N₂ adsorption-desorption isotherms and (b) the pore size distribution curves of CN and MoC@NG-70@CN.

3. Tables

Table S1 Textural properties of samples.

Samples	S_{BET} (m² g⁻¹)	Pore volume (cm³ g⁻¹)	Average pore size (nm)
CN	50.90	29.76	0.2615
MoC@NG-70@CN	51.58	23.04	0.2438

Table S2 List of the photocatalytic hydrogen production performance of photocatalysts in related systems.

Photocatalyst	Sacrificial agent	Cocatalyst/sensitizer	Activity ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	Light source	Ref
CN/CBV ²⁺	10 vol% TEOA	Pt	831.4	300 W Xe lamp ($\lambda > 420$ nm)	R ¹
Ni(OH) ₂ /CN	10 vol% TEOA	—	921.4	300 W Xe lamp ($\lambda > 400$ nm)	R ²
KPCN	10 vol% TEOA	Pt	1188	300 W Xe lamp ($\lambda > 420$ nm)	R ³
PFNBtBr Pdots/CN	10 vol% TEOA	—	1200.9	300 W Xe lamp ($\lambda > 400$ nm)	R ⁴
CNCNT/CN	10 vol% TEOA	—	1208	300 W Xe lamp	R ⁵
MoNi@MoO ₂ /CN	15 vol% TEOA	—	1359	300 W Xe lamp ($\lambda > 400$ nm)	R ⁶
CN@HG	10 vol% TEOA	—	1430	350 W Xe lamp ($\lambda > 420$ nm)	R ⁷
B-TiO ₂ /CN/MoS ₂ QDs	10 vol% TEOA	—	1524.37	300 W Xe lamp simulated solar light	R ⁸
FeSe ₂ /CN	0.15/0.35 M Na ₂ S/Na ₂ S O ₃	—	1655.6	300 W Xe lamp (Microsolar 300UV)	R ⁹
MoC@NC@CN	15 vol% TEOA	—	1709	300 W Xe lamp ($\lambda > 400$ nm)	R ¹⁰
CdS/CN	14 vol% lactic acid	Pt	1809.07	300 W Xe lamp ($\lambda > 420$ nm)	R ¹¹

1T-MoS₂ QDs/CN	20 vol% TEOA	—	1857	300 W Xe lamp (AM 1.5 G filter)	R ¹²
Ag-N₂C₂/CN	10 vol% TEOA	—	1866	300 W Xe lamp (λ > 400 nm)	R ¹³
In₂O₃/PUCN	10 vol% TEOA	Pt	1917	300 W Xe lamp (λ > 400 nm)	R ¹⁴
WX_y/CN	10 vol% TEOA	—	1960	AM 1.5 solar simulator	R ¹⁵
MoC@NG@CN	20 vol% TEOA	Pt	2109	300 W Xe lamp (λ > 400 nm)	This work

Table S3 The AQEs of MoC@NG-70@CN at different wavelengths.

Wavelength (nm)	400	420	450	500	550
AQE (%)	0.256	0.089	0.013	0.002	0.0009

Table S4 Exponential decay-fitted parameters of fluorescence lifetimes for CN and MoC@NG-70@CN.

Samples	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_A (ns)
CN	2.46	50.26	14.00	49.74	12.26
MoC@NG-70@CN	2.44	50.85	15.07	49.15	13.26

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