Electronic Supplementary Information for

# Self-Anchored Nickel Co-catalyst on Nitrogen-Doped Carbon Dots for Enhanced Photocatalytic Hydrogen Evolution

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#### **Catalyst preparation**

### Synthesis of carbon nitride nanosheets (CN)

The graphite-phase carbon nitride nanosheets were prepared using a simple two-step calcination method. First, 10 g of melamine was placed in an alumina crucible and transferred to a muffle furnace, where the temperature was increased to 600°C at a heating rate of 2°C/min and maintained for 2 hours. After natural cooling to room temperature, bulk carbon nitride was obtained. Next, 0.4 g of the bulk carbon nitride was evenly spread in a ceramic boat and transferred to a tube furnace. The temperature was raised to 550°C at a heating rate of 5°C/min and maintained for 6 hours. After natural cooling to room temperature, milky-white carbon nitride nanosheets were obtained, which were simply named CN.

#### Synthesis of Nitrogen doped carbon dots (NCQDs)

Nitrogen-doped carbon quantum dots (NCQDs) were synthesized via a hydrothermal method using citric acid and urea as the carbon and nitrogen sources. The specific procedure was as follows: 2.1 g of citric acid and 1.8 g of urea were dissolved in 50 mL of deionized water and then transferred into a 100 mL stainless steel autoclave lined with polytetrafluoroethylene (PTFE). The mixture was subjected to hydrothermal treatment at 160°C for 4 hours. After cooling to room temperature, the obtained NCQDs were collected and stored in the dark for further use.

## Synthesis of carbon nitride supported Nickel doped carbon dots (CNNiC)

200 mg of the synthesized CN was added to a mixture containing different volumes (0.5, 1, 2 mL) of NCQDs and 0.02 g of hexahydrate nickel nitrate solution (V<sub>ethanol</sub> : V<sub>water</sub> = 1:1). After ultrasonic treatment for 30 min, the mixture was stirred for 1 h, then transferred to a high-pressure reactor and subjected to hydrothermal reaction at 160°C for 4 h. The precipitate was collected by centrifugation, washed several times with water and ethanol, and vacuum-dried (60°C) overnight.

## Characterization

The morphology of the catalyst was analyzed using a high-resolution transmission electron microscope (HRTEM, FEI Tecnai G2 F20 S-TWIN). The crystalline structure of the catalyst was investigated using an X-ray diffractometer (XRD, Bruker D8 ADVANCE) and a Fourier transform infrared spectrometer (FTIR, Thermo Scientific Nicolet iS50, USA). The surface composition of the catalyst was determined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, USA). The photoabsorption properties of the catalyst were recorded using a UV-Vis-NIR spectrophotometer (Agilent Cary5000, USA). The fluorescence characteristics of the catalyst were studied using a steady-state fluorescence spectrometer (PL, Hitachi F7000). The PL lifetime was measured with a transient fluorescence spectrometer (Edinburgh Instruments, FLS980).

#### Photocatalytic performance evaluation

The photocatalytic hydrogen evolution performance was tested in an online photoreaction system (CEL-SPH2N, Beijing China Education Au-light Co., Ltd., China). Specifically, 10 mg of the prepared photocatalyst was uniformly distributed in a topirradiation two-necked photoreactor (containing 45 mL of deionized water and 5 mL of triethanolamine). Prior to light exposure, the system was evacuated. The reaction temperature was controlled at 6°C using a circulating cooling water system. A 300W xenon lamp (CEL-NP2000) equipped with an AM1.5 filter served as the light source. The produced H<sub>2</sub> were analyzed using a gas chromatograph (GC7920, N<sub>2</sub> carrier) equipped with a thermal conductivity detector (TCD).

## **Photoelectrochemical tests**

Photoelectrochemical tests were carried out on a CHI760E electrochemical workstation (ChenHua Instruments, China) using a three-electrode cell. The working electrode consisted of FTO conductive glass loaded with 2 mg of photocatalyst, while Ag/AgCl and Pt served as the reference and counter electrodes, respectively. A 300W xenon lamp was employed as the light source. A 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution was chosen as the electrolyte.



Fig. S1 (a) EDX line-scan and (b) corresponding elemental signal profiles of CNNiC-1 catalyst.



Fig. S2 XRD patterns of prepared catalysts.



Fig. S3 FTIR spectra of prepared catalysts.



Fig. S4 VSM measurement curve for the CNNiC-1 catalyst.



Fig. S5 XPS survey spectra of prepared catalysts.



Fig. S6 High-resolution XPS spectra: (a) C 1s, (b) N 1s, (c) O 1s, and (d) Ni 2p.



 $\label{eq:Fig.S7} \textbf{Fig. S7} (a) \, UV \text{-} Vis \, DRS \ spectra \ of \ as-prepared \ catalysts. (b) \ Tauc \ plot \ and \ (c) \ Mott-Schottky \ curves$ 

of CN. (d) Band alignment diagram of CNNiC catalyst.



Fig. S8 (a) PL, (b) TRPL, (c) EIS spectra, and (d) transient photocurrent response of CN, CN-Ni, and CNNiC-1 catalysts.



Fig. S9 Water contact angle tests of prepared catalysts.



Fig. S10 CV curves of the CNNiC-1 catalyst at various scan rates (10–50 mV s<sup>-1</sup>).



Fig. S11 Tafel polarization curves of prepared samples.

Photocatalyst	Reaction solution	Light source	H2 yields (μmol g <sup>-1</sup> h <sup>-</sup> <sup>1</sup> )	Ref.
400-4	15 vol.% TEOA	150 W Xe lamp, AM1.5G	4.55	1
CN(T)-7-NP	pure water	150 W Xe lamp, AM1.5	76.8	2
NiS/g-C <sub>3</sub> N <sub>4</sub> (0.3 wt%)	10 vol.% TEOA	3 W LED (420 nm)	244	3
CNN-Pt (0.5 wt%)	pure water /methanol	300 W Xe lamp (>420nm)	68.844	4
$NiS_2/g-C_3N_4$ (3 wt%)	10 vol.% lactic acid	3 W LED (> 420 nm)	116.343	5
NiS-LaFeO <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	10 vol.% TEOA	300 W Xe lamp (> 400 nm)	121	6
HCN	10 vol.% TEOA	300 W Xe lamp (> 420nm)	392	7
PtSAs-Au <sub>2.5</sub> /PCN	20 vol.% TEOA	300 W Xe lamp (550 nm)	264	8
Zn-PCN (4.79%)	pure water	300 W Xe lamp (> 420nm)	35.2	9
CNNiC-1	10 vol.% TEOA	300 W Xe lamp, AM1.5	378.87	this work

Table S1 Comparison for  $\mathrm{H}_2$  evolution with reported photocatalysts.

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