

## Supplementary Information

### **Metallic plasmons significantly boosted visible-light photocatalytic hydrogen evolution from water splitting**

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## 1. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer (MXPAHF, Japan) with Cu  $k\alpha$  radiation ( $\lambda = 1.541 \text{ \AA}$ ), 20 mA current, and 40 kV operating voltage. XRD data were collected at a diffraction angle of  $10\text{-}80^\circ$  with a scanning rate of  $10^\circ \text{ min}^{-1}$ . Fourier-transformed infrared (FTIR) spectroscopy of samples with KBR pellets were characterized by a Nicolet Nexus spectrometer. UV-vis diffuse reflectance spectra (DRS) of the synthesized photocatalysts were collected in a Shimadzu UV-2501 PC spectrophotometer. Electron paramagnetic resonance (EPR) tests of the samples were carried out on a Bruker model A300 spectrometer. Transmission electron microscopy (TEM) and elemental mapping images of the photocatalysts were taken on HITACHI H-7650 TEM operated at 100 kV. Scanning electron microscopy (SEM) images were obtained on a JEOL SM-6601F. X-ray photoelectron spectroscopy (XPS) measurements were conducted on Perkin-Elmer RBD upgraded PHI-5000C ESCA technique. Photoluminescence (PL) measurements were recorded on JY Fluorolog-3-Tau apparatus. Time-resolved photoluminescence (TRPL) spectra were obtained on a Laser strobe time-resolved spectrometer with an  $\text{N}_2$  laser and a USHIO xenon light source. The specific surface areas were measured via Brunauer-Emmett-Teller (BET) method.

## 2. Photoelectrochemical tests

The photoelectrochemical measurement of the photocatalysts were conducted at the CHI 760E electrochemical workstation integrated with a reference (Ag/AgCl), counter (Pt), and the working electrode, respectively. The electrolyte solution was formed by adding 7.1 g of  $\text{Na}_2\text{SO}_4$  in deionized water (100 mL) and xenon lamp (300 W) was used as a light-source in the experiments. For the working electrode, the samples were prepared by sonicating 2 mg of samples in 1 mL

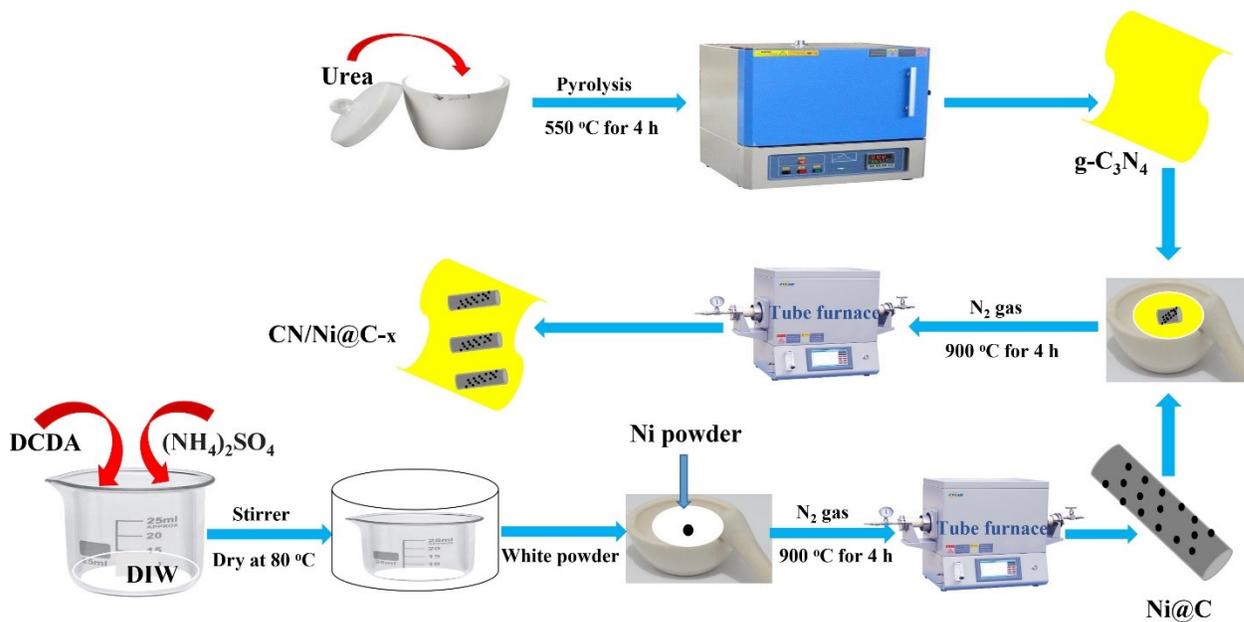
ethanol and 15  $\mu\text{L}$  Nafion solution (5%). After that, the well-mixed solution was dropped on glass with an exact area of  $1\text{ cm}^2$ , respectively. The transient photocurrent response was carried out with a 0.5 V bias voltage applied by an on/off switch. The EIS Nyquist patterns were measured under visible-light irradiation with -1 V bias and frequency ranging from 10 MHz to 100.

### 3. Photocatalytic hydrogen evolution measurements

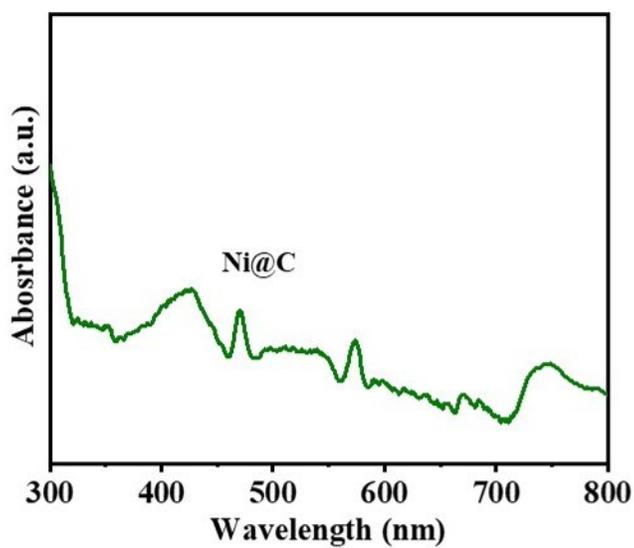
The hydrogen evolution tests were conducted on an irradiated Pyrex reaction vessel (500 mL) in a connected photocatalytic water splitting system (Labsolar 6A, Beijing Perfect Light Co. Ltd, China). Xenon lamp (300 W) was employed as a light-source with 420 nm cutoff filter during experiments. In a conventional procedure, 100 mL solution comprising 0.05 g photocatalyst was dissolved in 100 mL solution containing 10 vol% TEAO with 1 wt% Pt ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  precursor). The resultant suspension was sonicated for 40 min before the photocatalytic reaction. Then, the well-mixed solution was expunged by  $\text{N}_2$  gas for 45 min to eliminate the inside air before being exposed to light. Afterward, irradiated by Xe lamp for 30 min without cutoff filter for photo-deposition of Pt over the surface of the catalyst. To maintain uniform irradiation, the suspension was agitated during the photocatalytic experiment. Gas chromatograph (GC 1120, Shanghai Sunny Hengping Limited, HTCD,  $\text{N}_2$  carrier gas) was used to measure the evolved  $\text{H}_2$ . The photocatalytic reaction time for each test was set as 4 h.

The apparent quantum yield (AQY) was calculated to assess the consistency between optical absorption and the AQY of CN/Ni@C-1 by using various wavelength monochromatic light illumination ( $\lambda = 420, 450, 500, 550, \text{ and } 600\text{ nm} \pm 5\text{ nm}$ ). The AQY was estimated based on the following equation:

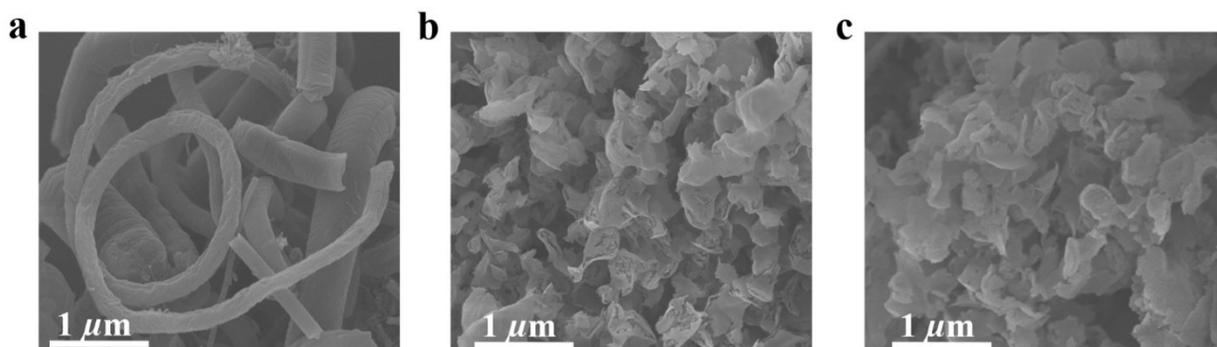
$$\text{AQY} = \frac{2 \times \text{number of evolved } \text{H}_2 \text{ molecules}}{\text{number of incident photons}} \times 100\%$$



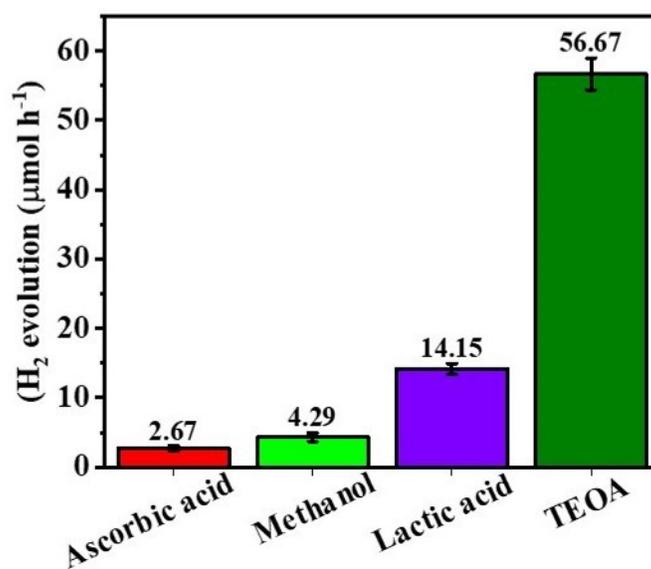
**Figure S1.** The schematic synthesis path of  $g\text{-C}_3\text{N}_4$ ,  $\text{Ni@C}$ , and  $\text{CN/Ni@C-x}$  samples.



**Figure S2.** UV-vis diffuse reflectance spectra (UV-DRS) of  $\text{Ni@C}$  nanoparticles.



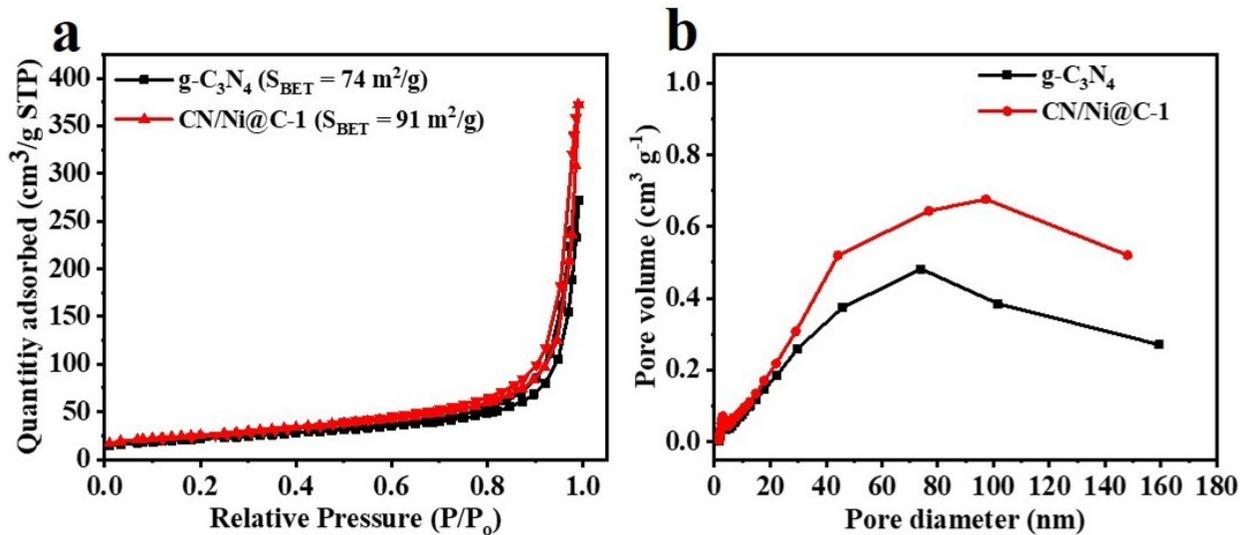
**Figure S3.** SEM Images of Ni@C NPs, g-C<sub>3</sub>N<sub>4</sub> nanosheets, and CN/Ni@C-1 photocatalysts.



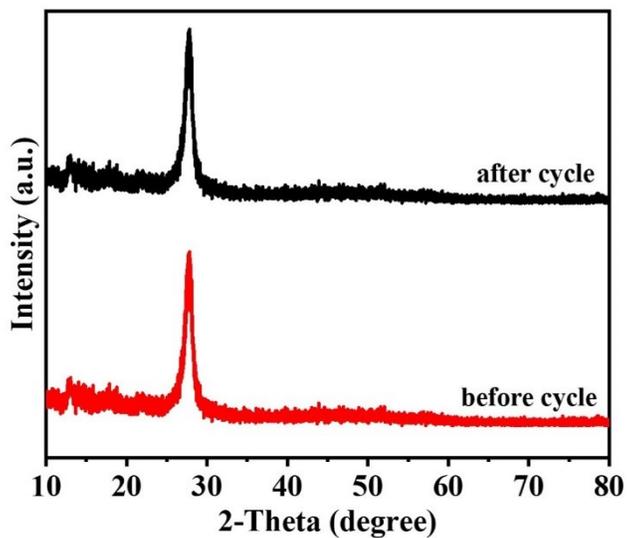
**Figure S4.** Visible-light irradiated H<sub>2</sub> evolution from water splitting over CN/Ni@C-1 nanocomposite photocatalyst in the presence of different sacrificial agents.

**Table S1.** Comparison of our study H<sub>2</sub> evolution rate results with the previous reported photocatalysts.

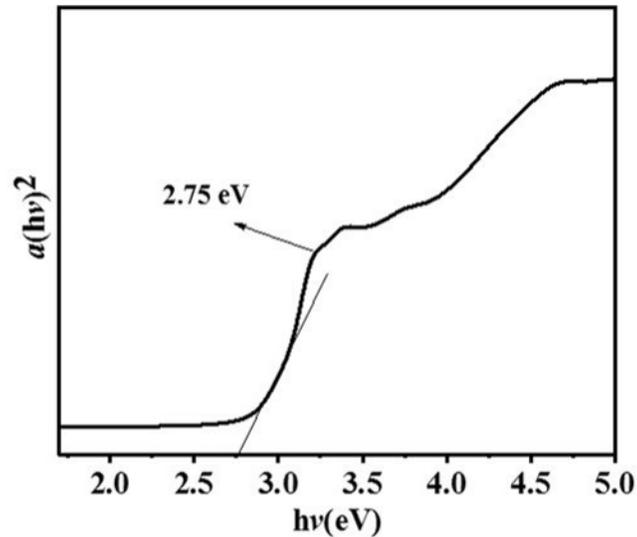
S.#	Photocatalysts	Cocatalyst	Light source	H <sub>2</sub> evolution ( $\mu\text{mol h}^{-1}$ )	AQY (%)	References
1	Co/g-C <sub>3</sub> N <sub>4</sub>	3% Pt	300 Xe- lamp (420 nm)	28.0	-	1
2	g-C <sub>3</sub> N <sub>4</sub> /CoTPP	1% Pt	300 Xe-lamp (420 nm)	46.93	4.2	2
3	g-C <sub>3</sub> N <sub>4</sub> /NiFe <sub>2</sub> O <sub>4</sub>	1% Pt	300 Xe- lamp (420 nm)	161.3	2.46	3
4	C/g-C <sub>3</sub> N <sub>4</sub>	1% Pt	300 Xe-lamp (420 nm)	21.88	0.90	4
5	P-TCN	1% Pt	300 Xe-lamp (420 nm)	67.0	5.68%	5
6	CoP/g-C <sub>3</sub> N <sub>4</sub>	2% Pt	300 Xe-lamp (420 nm)	51.90	1.1%	6
7	MoS <sub>2</sub> /g-C <sub>3</sub> N <sub>4</sub>	2% Pt	300 Xe-lamp (420 nm)	43.38	-	7
8	g-C <sub>3</sub> N <sub>4</sub> /Ni@C-1	1% Pt	300 Xe-lamp (420 nm)	56.67	5.20	This work



**Figure S5.** (a) Nitrogen adsorption-desorption isotherms. (b) Pore size distribution curves of g-C<sub>3</sub>N<sub>4</sub> and CN/Ni@C-1 samples.



**Figure S6.** XRD patterns of CN/Ni@C-1 sample before and after recycle photocatalytic test.



**Figure S7.** Plot of Kubelka-Munk calculated energy band gap of g-C<sub>3</sub>N<sub>4</sub>.

## REFERENCES

1. P.-W. Chen, K. Li, Y.-X. Yu and W.-D. Zhang, *Appl. Surf. Sci.*, 2017, **392**, 608-615.
2. M. Kombo, L.-B. Ma, Y.-N. Liu, X.-X. Fang, N. Ullah, A. H. Odda and A-W. Xu, *Catal. Sci. Technol.*, 2019, **9**, 2196-2202.
3. J. Chen, D. Zhao, Z. Diao, M. Wang and S. Shen, *Sci. Bull.*, 2016, **61**, 292-301.
4. Q. Xu, B. Cheng, J. Yu and G. Liu, *Carbon*, 2017, **118**, 241-249.
5. S. Guo, Z. Deng, M. Li, B. Jiang, C. Tian, Q. Pan and H. Fu, *Angew. Chem. Int. Ed.*, 2016, **128**, 1862-1866.

6. Y. Liu, J. Zhang, X. Li, Z. Yao, L. Zhou, H. Sun and S. Wang, *Energ. Fuel.*, 2019, **33**, 11663-11676.
7. Y. Liu, X. Xu, J. Zhang, H. Zhang, W. Tian, X. Li, M. O. Tade, H. Sun and S. Wang, *Appl. Catal. B: Environ.*, 2018, **239**, 334-344.