

Highly dispersed Ag nanoparticles in situ creating rich cyano defects in carbon nitride for efficient photocatalytic H₂ production

Siqie Qin,^a Hui Zhang,^{*a} Yuqi Cao,^a Fukai Zheng,^a Zhigang Mou,^a Jianhua Sun,^a and Mingshan Zhu^b

^a *School of Chemistry and Environmental Engineering, Institute of Advanced Functional Materials for Energy, Jiangsu University of Technology, Changzhou 213001, Jiangsu Province, China.*

^b *School of Environment, Jinan University, Guangzhou 510632, China.*

*Corresponding Author

E-mail addresses: zhanghui@jsut.edu.cn

Experimental section

Synthesis of the photocatalysts

Ag-C-CN photocatalyst was prepared by a one-step condensation method: 15 g urea, 100 mg silver acetate, and 10 mg ascorbic acid were thoroughly ground. The resulting mixture was put into a 50 mL crucible and then heated in a muffle furnace at 550 °C for 4 h. The ramp rate was 2.2 °C·min⁻¹. The obtained light brown powder was collected as the product.

The preparation procedures of Ag-CN and C-CN were the same as that of Ag-C-CN, except for not adding ascorbic acid and silver acetate, respectively.

Pure CN was synthesized by direct calcining 15 g urea in the same conditions.

Characterization

Field mission scanning electron microscopy (FESEM) and energy-dispersive spectroscopy (EDS) mapping images were recorded on a ZEISS Sigma 500 microscope equipped with an Oxford Instruments X-Max^N 50 energy-dispersive spectrometer. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) characterization was carried out on a JEM-2100 instrument. X-ray diffraction (XRD) patterns were collected on a PANalytical PW3040/60 X'pert PRO diffractometer. Fourier transform infrared (FT-IR) spectra were measured on a Thermo Nicolet iS10 spectrometer. Elemental analysis (EA) was performed on a Vario EL cube element analyzer. N₂ adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2020 instrument. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a VG Multilab 2000 X-ray photoelectron spectrometer. UV-vis diffuse reflection spectra (DRS) were recorded on a Shimadzu UV-2600 Spectrophotometer. Time-resolved photoluminescence (PL) decay spectra were measured on a FluoroMax+ spectrophotometer (HORIBA).

Photocatalytic activity test

The photocatalytic hydrogen evolution reactions were carried out in a top-irradiation reaction vessel connected to a glass closed system. Typically, 50 mg photocatalyst was dispersed in 100 mL aqueous solution containing 10 mL

triethanolamine. No other cocatalysts or cocatalyst precursors were added unless otherwise stated. After degassing under vacuum to completely remove air, the reaction solution was irradiated by a 300 W Xe-lamp with a cut-off filter ($\lambda > 420$ nm). During the irradiation, the reaction temperature was maintained at 15 °C by cycle water. The generated H₂ was analyzed by an on-line gas chromatography (GC-7900, thermal conductive detector, 5 Å molecular sieve column), using Ar as the carrier.

For comparison, the photocatalytic hydrogen evolution reaction of Pt loaded CN was also performed. The procedure is the same as above except that 3 wt% H₂PtCl₆ (based on Pt) was added before degassing.

The apparent quantum efficiency (AQE) for H₂ evolution was measured by replacing the cut-off filter with a $\lambda_0 \pm 15$ nm band-pass filter. The AQE is calculated from the following equation:

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

Photoelectrochemical measurements

Electrochemical impedance spectra (EIS), photocurrent, and Mott-Schottky plots were measured by a CHI-760E workstation (CH Instruments) in a standard three-electrode system. Ag/AgCl electrode, Pt wire, and the as-prepared sample were used as reference electrode, counter electrode, and working electrode, respectively. 0.2 M Na₂SO₄ aqueous solution was used as the electrolyte. For the preparation of the working electrode, 5 mg sample was first added into 1.00 mL 0.02 wt% Nafion solution. Then the mixture was sonicated for 2 h and 20 μ L of the obtained suspension was spread on to a 1.0 cm² exposed ITO glass. The ITO electrode was air dried overnight. For the photocurrent test, the light source was a 300 W Xe lamp with a cut-off filter ($\lambda > 420$ nm).

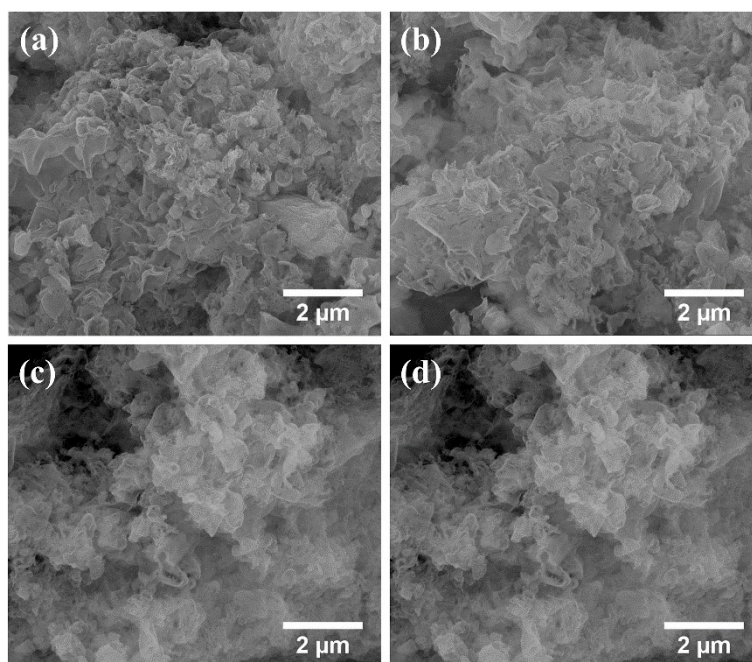


Fig. S1 FESEM images of (a) CN, (b) Ag-CN, (c) C-CN, and (d) Ag-C-CN.

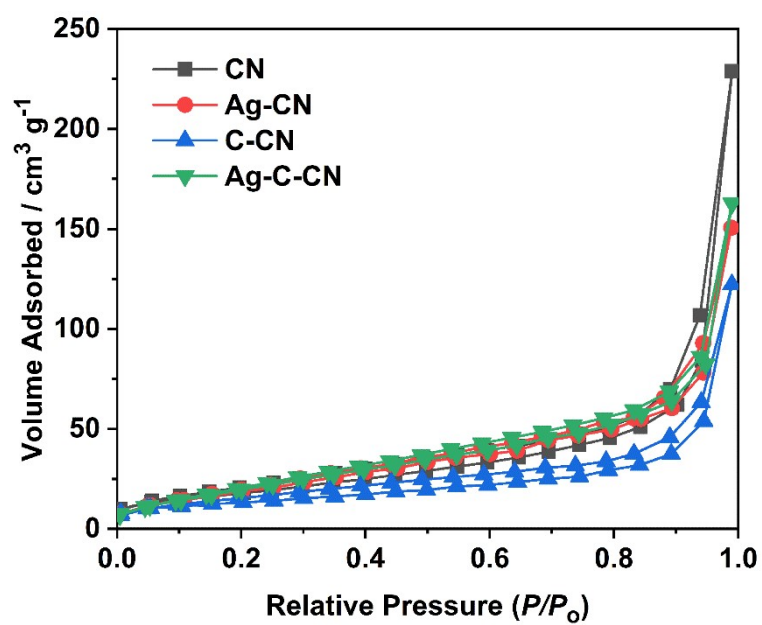
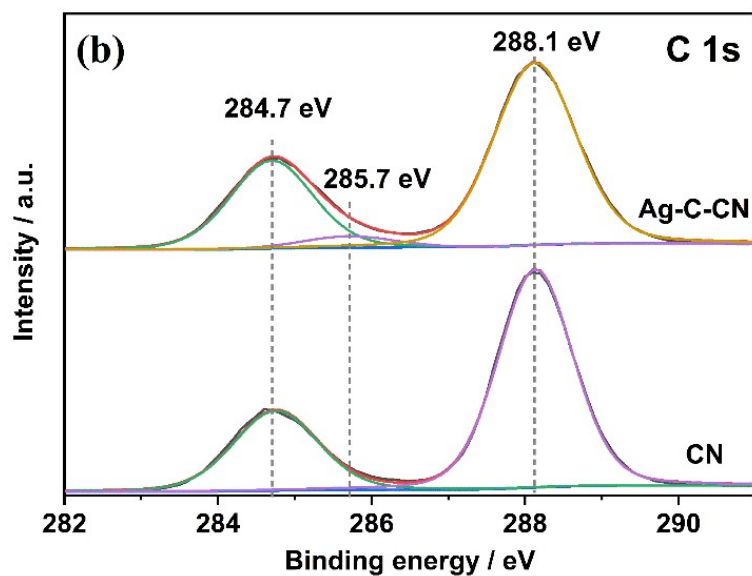
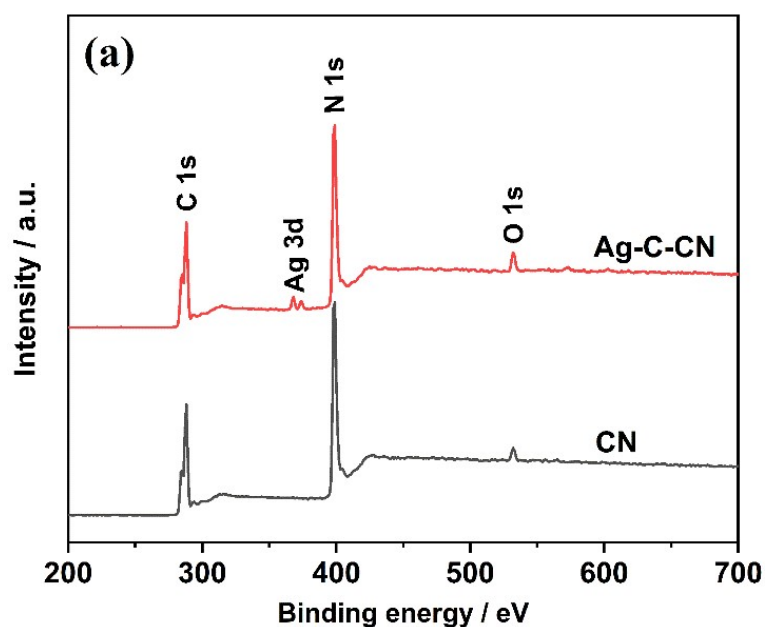


Fig. S2 N₂ sorption isotherm curves of CN, Ag-CN, C-CN, and Ag-C-CN.

Table S1 Elemental compositions and BET specific surface areas of CN, C-CN, Ag-CN, and Ag-C-CN.

Sample	C / wt %	N / wt %	H / wt %	C/N molar ratio	$S_{\text{BET}} / \text{m}^2 \cdot \text{g}^{-1}$
CN	34.25	59.32	1.61	0.674	65
C-CN	34.03	58.75	1.58	0.676	47
Ag-CN	31.41	54.03	1.37	0.678	69
Ag-C-CN	31.61	54.10	1.33	0.682	77



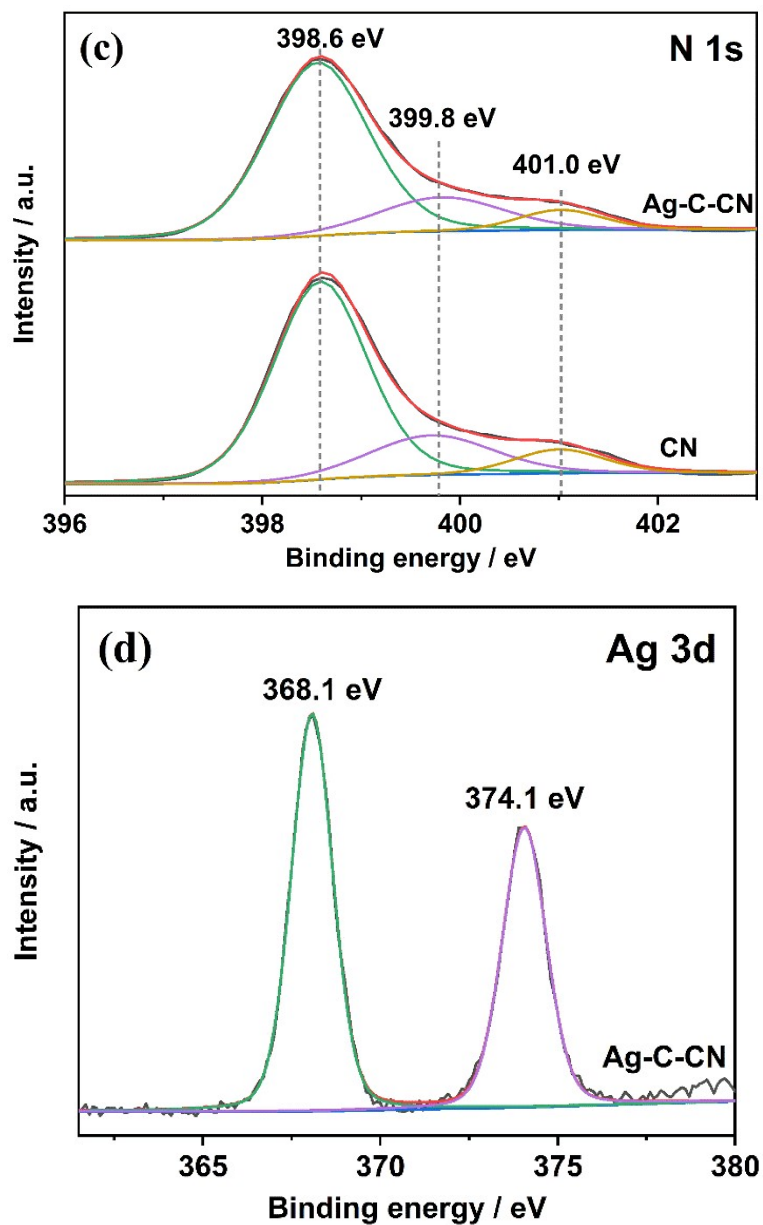


Fig. S3 (a) XPS survey spectra, (b) high-resolution C 1s spectra, and (c) N 1s spectra of CN and Ag-C-CN. (d) XPS high-resolution Ag 3d spectrum of Ag-C-CN.

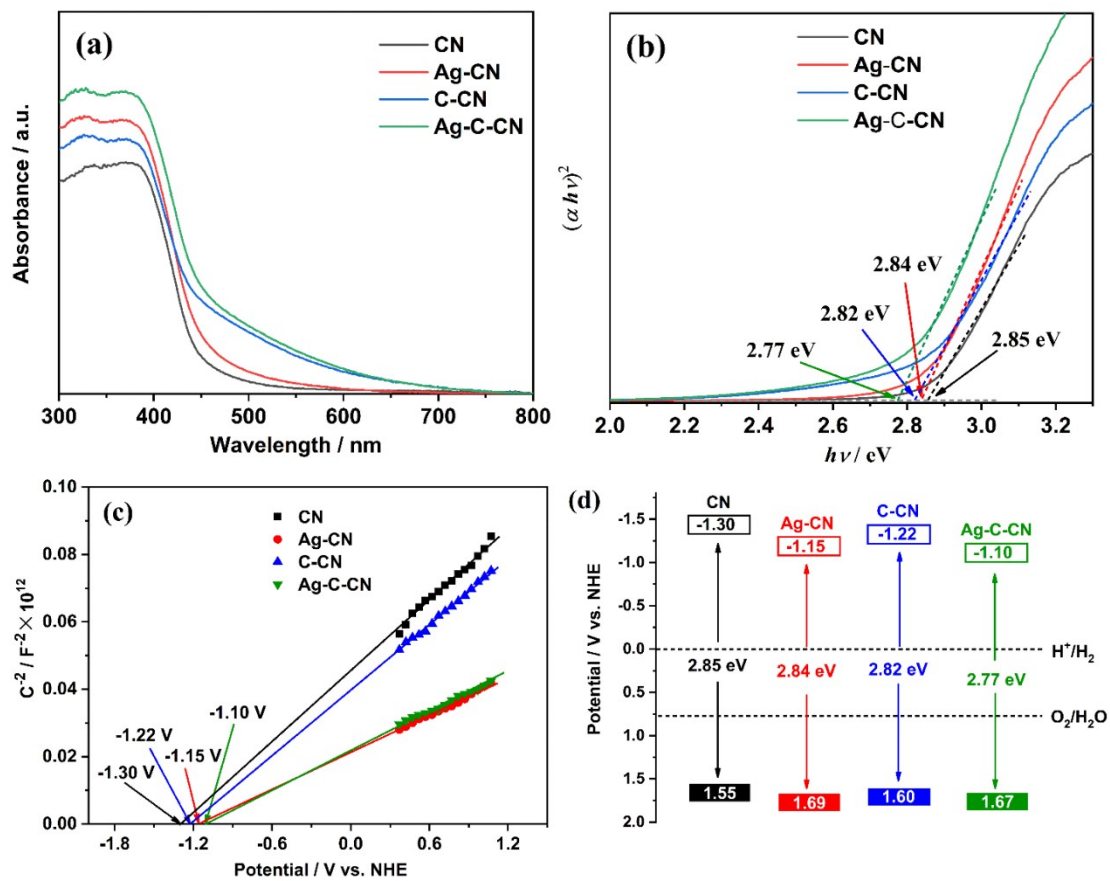


Fig. S4 (a) UV-vis DRS, (b) the corresponding Tauc plots, (c) Mott-Schottky plots, and (d) band structure alignments of CN, Ag-CN, C-CN, and Ag-C-CN.

Table S2 Comparison of photocatalytic H₂ evolution activity of Ag-C-CN with other Ag/carbon nitride based materials.

Catalysts	HER / μmol·h ⁻¹	Catalysts mass / mg	AQE	Pt cocatalyst	Ref.
Ag QDs/g-C ₃ N ₄	0.9	50	-	without	S1
Ag _{1.0} /g-C ₃ N ₄	2.2	10	-	without	S2
Ag/Ag ₂ Ta ₄ O ₁₁ /g-C ₃ N ₄	5.0	50	0.60	without	S3
Ag/ND/g-C ₃ N ₄	7.9	50	-	without	S4
g-C ₃ N ₄ /Ag/MoS ₂	10.4	100	-	without	S5
1.2%-Ag/CNF	2.3	25	-	3.0 wt%	S6
Ag-g-C ₃ N ₄ -2	31.2	50	-	1.0 wt%	S7
Ag-C-CN	28.2	50	4.9	without	this work

Note: The photocatalytic H₂ evolution reactions were carried out in the presence of triethanolamine as sacrificial agent under visible light irradiation (300 W Xe-lamp with a cut-off filter). The AQE of H₂ evolution is calculated at 420 nm.

Optimization of Ag concentration in Ag-CN

The Ag-CN samples were prepared by calcining the mixture of urea and silver acetate: 15 g urea and a certain amount of silver acetate (50, 100, and 200 mg) were thoroughly ground. The resulting mixture was put into a 50 mL crucible and then heated in a muffle furnace at 550 °C for 4 h. The ramp rate was 2.2 °C·min⁻¹. The obtained products are labelled as Ag_x-CN ($x = 50, 100, 200$), where x refers to the initial mass (mg) of silver acetate added. As shown in Fig. S5, Ag100-CN sample exhibits the highest visible-light-induced H₂ evolution rate.

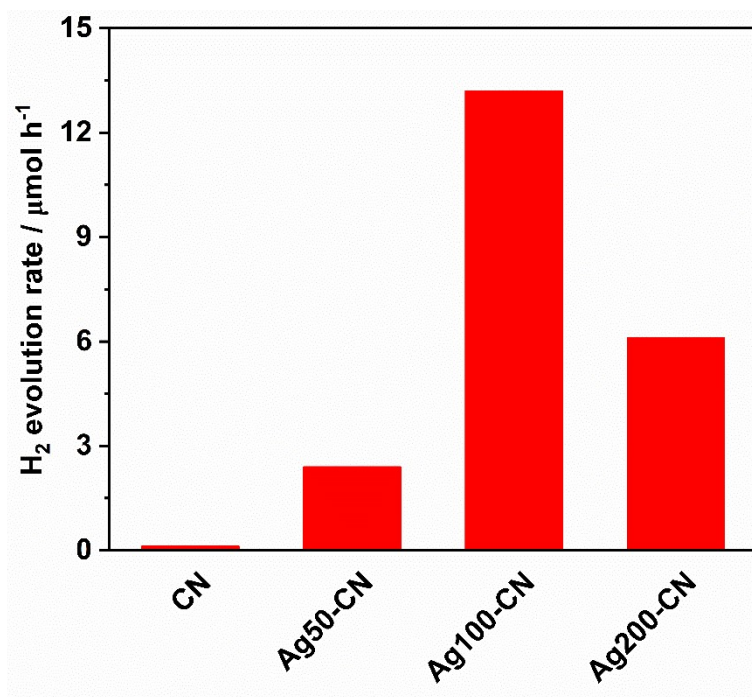


Fig. S5. Photocatalytic H₂ evolution rates of CN and Ag_x-CN ($x = 50, 100, 200$) under visible light irradiation ($\lambda > 420$ nm).

Optimization of carbon dopants concentration in Ag-C-CN

Based on the above results, the optimized amount of silver acetate added is 100 mg, thus the Ag100-C-CN samples with different carbon doping levels were prepared as follows: 15 g urea, 100 mg silver acetate, and a certain amount of ascorbic acid (5, 10, 15, and 20 mg) were thoroughly ground. The resulting mixture was put into a 50 mL crucible and then heated in a muffle furnace at 550 °C for 4 h. The ramp rate was 2.2 °C·min⁻¹. The obtained products are labelled as Ag100-C_x-CN ($x = 5, 10, 15, 20$), where

x refers to the initial mass (mg) of ascorbic acid added. As shown in Fig. S6, Ag100-C10-CN sample exhibits the highest visible-light-induced H₂ evolution rate.

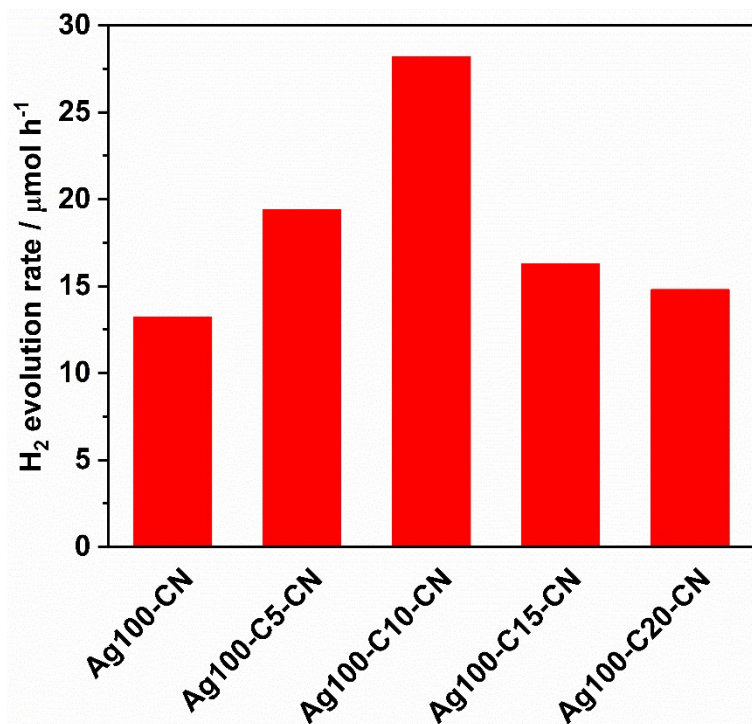


Fig. S6 Photocatalytic H₂ evolution rates of Ag100-CN and Ag100-C x -CN ($x = 5, 10, 15, 20$) under visible light irradiation ($\lambda > 420$ nm).

In this work, we take Ag100-CN and Ag100-C10-CN as the optimized samples for the discussion. **The Ag-CN and Ag-C-CN samples in the manuscript are Ag100-CN and Ag100-C10-CN, respectively.** For comparison, C-CN sample was also prepared, and the corresponding synthetic procedure is described in the experimental section.

Synthesis and photocatalytic H₂ evolution test of Ag/C-CN

The photocatalytic hydrogen evolution reaction was carried out in a top-irradiation reaction vessel connected to a glass closed system: 50 mg C-CN was dispersed in 100 mL aqueous solution containing 10 mL triethanolamine. Then 6.1 mg AgNO₃ (7.7 wt%, based on Ag) was added (The ratio of Ag(I) added was the same as that of the Ag-C-CN sample). After degassed under vacuum to completely remove air, the reaction solution was irradiated by a 300 W Xe-lamp with a cut-off filter ($\lambda > 420$ nm). During the irradiation, the reaction temperature was maintained at 15 °C by cycle water. The generated H₂ was analyzed by an on-line gas chromatography (GC-7900, thermal conductive detector, 5 Å molecular sieve column), using Ar as the carrier. After the photoreaction, the resulting solid was collated by filtration, washed with water and ethanol several times, dried at 60 °C overnight. The obtained sample is Ag loaded C-CN, which is labelled as Ag/C-CN.

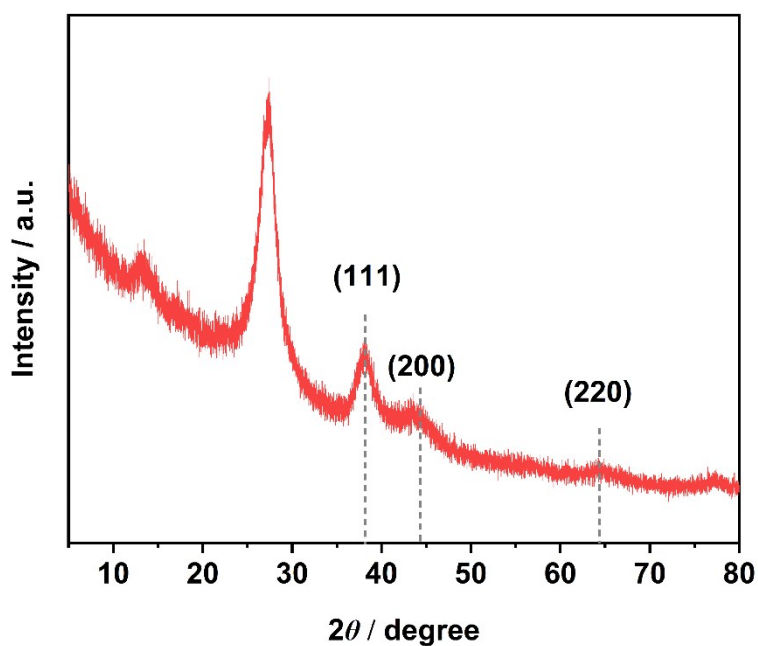


Fig. S7 XRD pattern of Ag/C-CN.

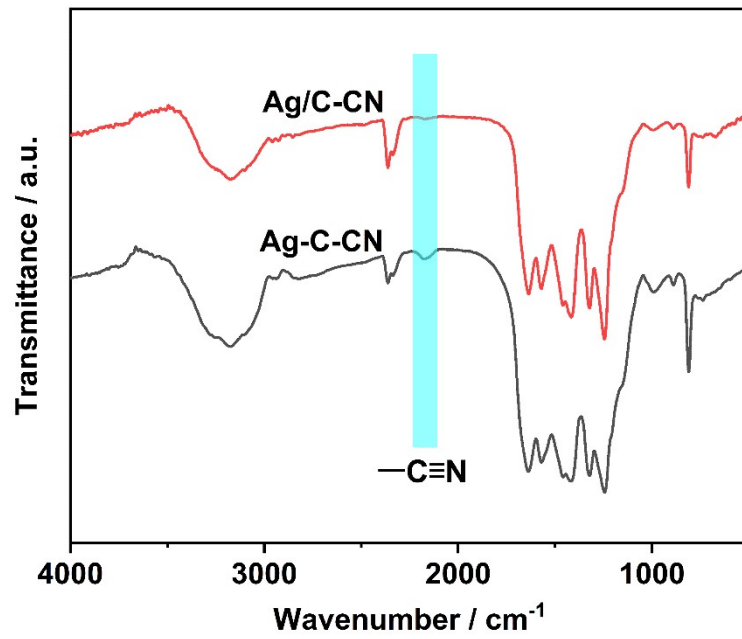


Fig. S8 FT-IR spectra of Ag-C-CN and Ag/C-CN.

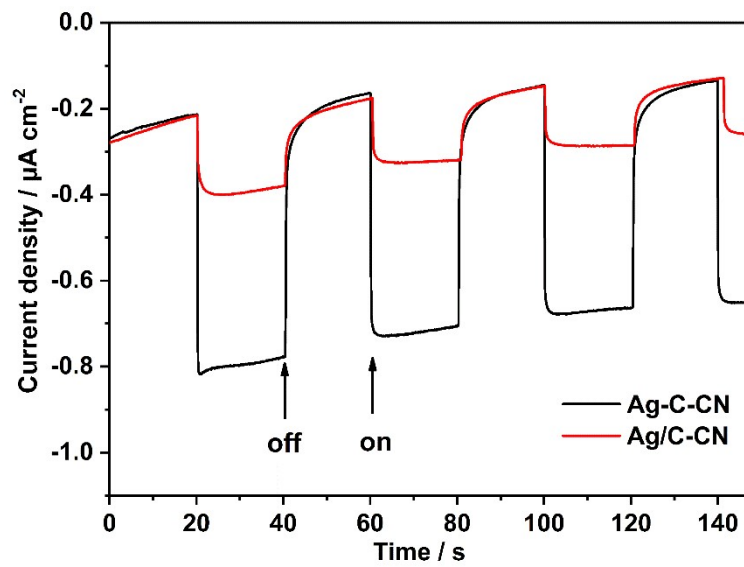


Fig. S9 Transient photocurrent responses of Ag-C-CN and Ag/C-CN.

Table S3 The fitting parameters of the time-resolved transient PL decay curves for Ag-C-CN and Ag/C-CN.

Sample	A ₁ / %	τ ₁ / ns	A ₂ / %	τ ₂ / ns	τ _{avg.} / ns
Ag-C-CN	78.76	2.88	21.24	22.7	3.54
Ag/C-CN	62.32	3.00	37.68	23.0	4.46

References

- S1. T. Chen, W. Quan, L. Yu, Y. Hong, C. Song, M. Fan, L. Xiao, W. Gu and W. Shi, *J. Alloys Compd.*, 2016, **686**, 628-634.
- S2. I. Majeed, U. Manzoor, F. K. Kanodarwala, M. A. Nadeem, E. Hussain, H. Ali, A. Badshah, J. A. Stride and M. A. Nadeem, *Catal. Sci. Technol.*, 2018, **8**, 1183-1193.
- S3. Y. H. Wu, M. T. Song, Z. L. Chai and X. J. Wang, *J. Colloid Interface Sci.*, 2019, **550**, 64-72.
- S4. L. X. Su, Q. Lou, C. X. Shan, D. L. Chen, J. H. Zang and L. J. Liu, *Appl. Surf. Sci.*, 2020, **525**, 146576.
- S5. D. Lu, H. Wang, X. Zhao, K. K. Kondamareddy, J. Ding, C. Li and P. Fang, *ACS Sustain. Chem. Eng.*, 2017, **5**, 1436-1445.
- S6. F. He, S. Wang, H. Zhao, Y. Wang, J. Zhang, Q. Yan, P. Dong, Z. Tai, L. Chen, Y. Wang and C. Zhao, *Appl. Surf. Sci.*, 2019, **485**, 70-80.
- S7. J. Wang, J. Cong, H. Xu, J. Wang, H. Liu, M. Liang, J. Gao, Q. Ni and J. Yao, *ACS Sustain. Chem. Eng.*, 2017, **5**, 10633-10639.