Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Sb-doped polymeric carbon nitride with charge-capture centers for efficient charge separation and photocatalytic performance in H_2 evolution and environmental remediation

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S1. Preparation of CN-Sb_2O_3 and CN-$SbCl_3$

For preparation of CN-Sb_2O_3, 10.0 mg of urea and 7.6 mg of Sb_2O_3 were dispersed in 10 mL of H_2O, after which the suspension was evaporated at 80 °C under stirring until completely dried. The solid was further dried at 60 °C for 24 h in an oven. Afterwards, the dried sample was put in a crucible with a lid and heated at 550 °C for 4h in the N_2 atmosphere with a temperature ramp of 5 °C/min. After cooling naturally to the room temperature, the sample was dispersed in 200 mL of H_2O and stirred for 24 h. The final product was obtained after filtration, washing with water and dried at 60 °C for 24 h.

For preparation of CN-$SbCl_3$, 10.0 mg of urea and 11.8 mg of $SbCl_3$ were dissolved in 80 mL of ethanol, after which the solution was evaporated at ~80 °C under stirring until completely dried. The solid was further dried at 60 °C for 12 h in an oven. Afterwards, the dried sample was put in a crucible with a lid and heated at 550 °C for 4h in the N_2 atmosphere with a temperature ramp of 5 °C/min. After cooling naturally to the room temperature, the sample was dispersed in 200 mL of H_2O and stirred for 24 h. The final product was obtained after filtration, washing with water and dried at 60 °C for 24 h.

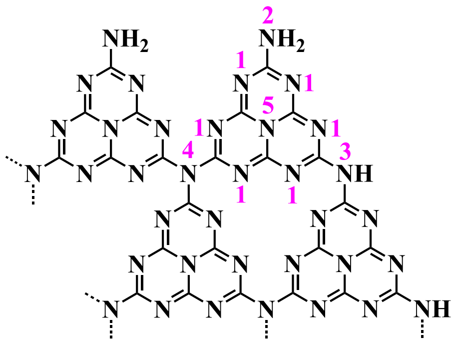

Fig. S1 Possible interacting sites of polymeric carbon nitride with metal ions. The numbers "1", "2 and 3", and "4 and 5" mark N–C_2, N–H, and N–C_3, respectively.

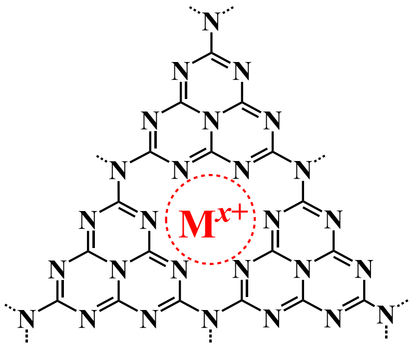

Fig. S2 Coordination interactions of the metal ion with N–C_2.

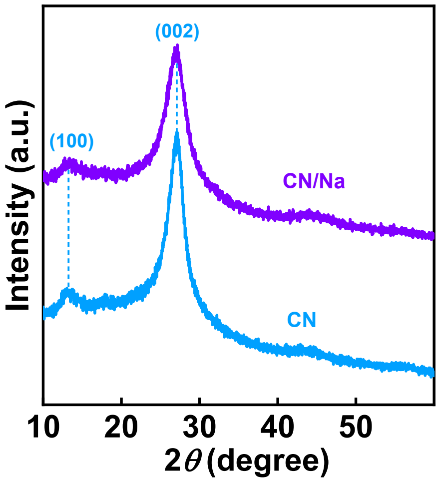

Fig. S3 XRD patterns of samples.

As shown in Fig. S3, CN/Na shows similar (100) and (002) peaks as CN.

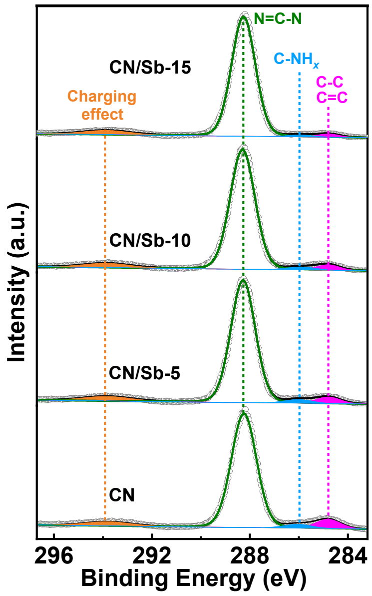

Fig. S4 C 1s core-level XPS spectra of samples.

In Fig. S4, peaks of CN at ~284.8, 286.0, 288.3, and 293.9 eV are assigned to adventitious carbon, C atoms in C–NH$_x$ and N=C–N bonds, and charging effect of heterocycles, respectively [1]. Corresponding peaks of CN/Sb-*n* show similar BE positions.

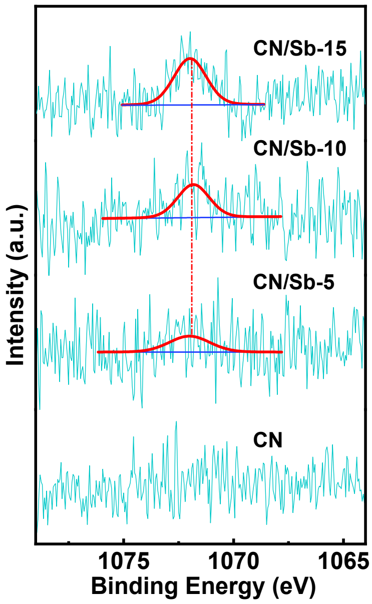

Fig. S5 Na 1s core-level XPS spectra of samples.

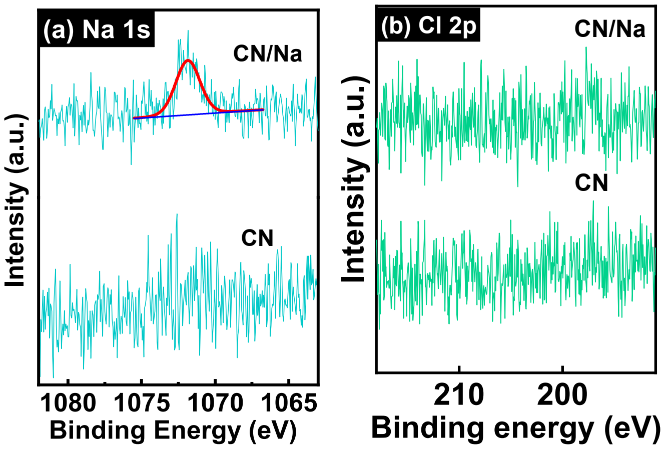

Fig. S6 (a) Na 1s and (b) Cl 2p core-level XPS spectra of CN and CN/Na.

The Na 1s core-level XPS spectrum of CN/Na shows one peak at the BE of ~1071.9 eV (Fig. S6a), but its Cl 2p spectrum shows no peaks (Fig. S6b), suggesting successful doping of Na^+ ions in CN/Na without residual of Cl.

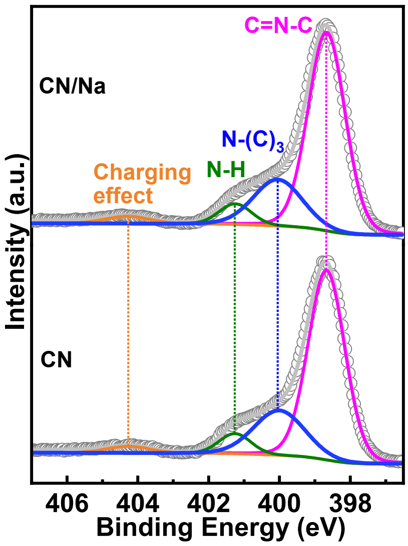

Fig. S7 N 1s core-level XPS spectra of CN and CN/Na.

As shown in N 1s core-level spectra (Fig. S7), peak positions of CN/Na are similar to those of CN. The C=N–C peak of CN/Na does not show obvious shift to high BE relative to that of CN as reported [2-4], because of the too low doping concentration of Na^+ ions in CN/Na.

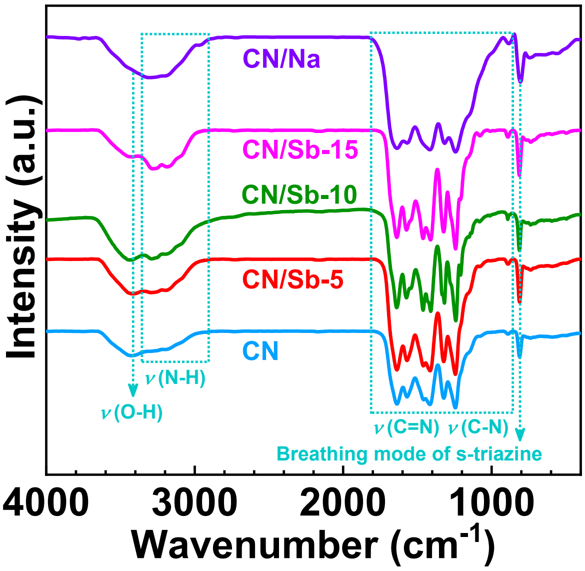

Fig. S8 FT-IR spectra of samples.

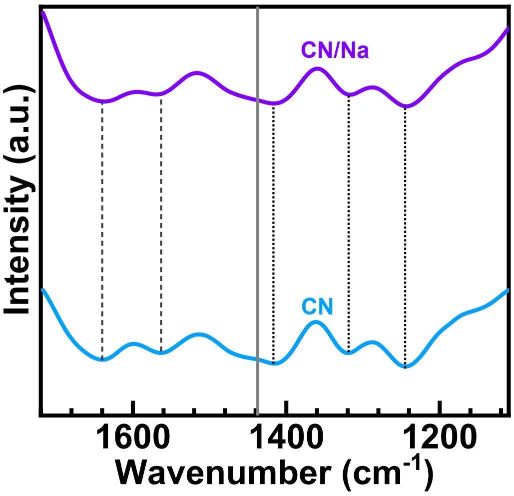

Fig. S9 FT-IR spectra of samples.

Equation S1:

$$\mathrm{CO(NH_2)_2 + NaSb^{V}O_3 \xrightarrow{\Delta} ((C_3N_4)_{\mathit{x}}\text{-}NH)_3\text{-}Sb^{III} + Na^+ + N_2\uparrow + CO_2\uparrow + H_2O\uparrow + NH_3\uparrow}$$

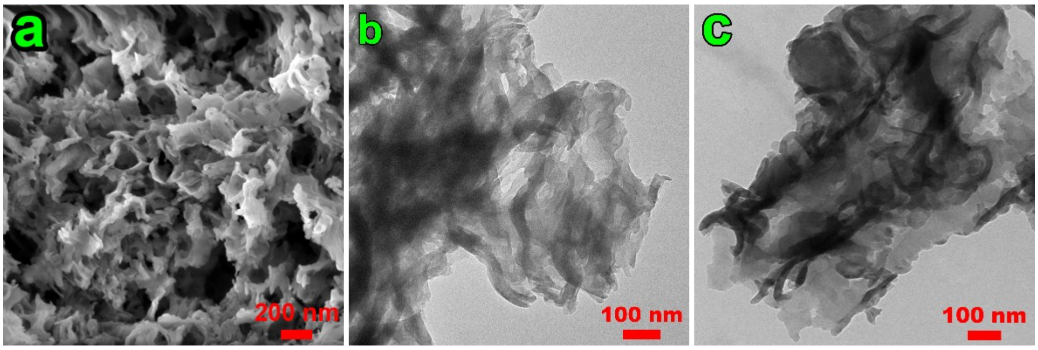

Fig. S10 (a) SEM and (b and c) TEM images of (a and b) CN and (c) CN/Sb-15.

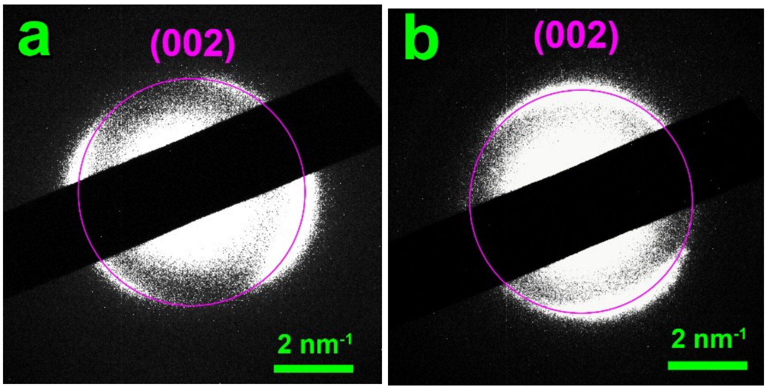

Fig. S11 SAED images of (a) CN and (b) CN/Sb-15.

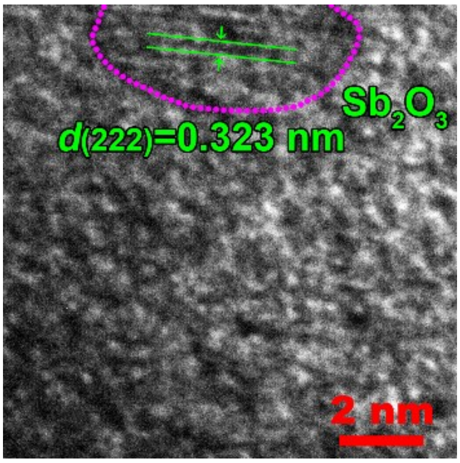

Fig. S12 The HRTEM image of CN/Sb-15.

The lattice fringe spacing of ~0.323 nm in Fig. S12 corresponds to the (222) crystal facet of Sb_2O_3.

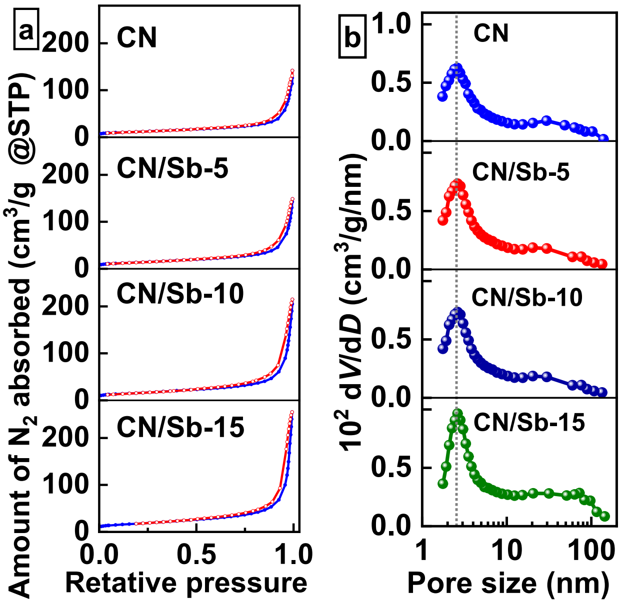

Fig. S13 (a) N_2 sorption isotherms and (b) pore size distribution curves calculated from adsorption branches of the isotherms by a BJH method.

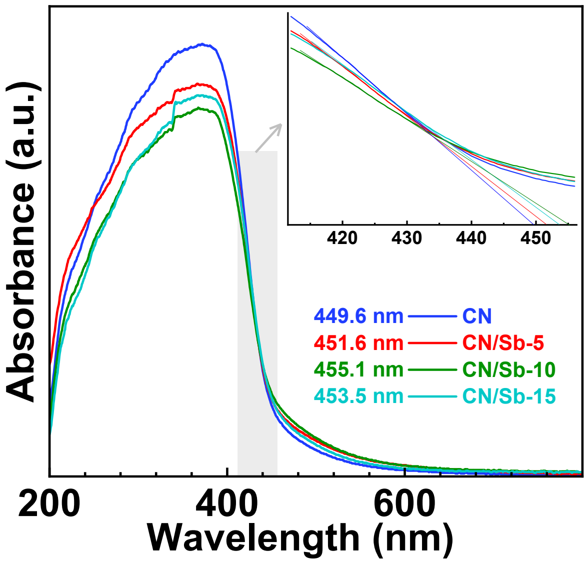

Fig. S14 UV-vis diffuse reflectance spectra of samples and (Inset) corresponding enlarged parts of the spectra. Numbers in the figure are absorption edges (λ_E).

Lines in the inset in Fig. S14 shows λ_E of the samples, and their corresponding energy bandgaps (E_g) can be calculated via the equation [5], $E_g = 1240.7/(\lambda_E/\text{nm})$ (eV).

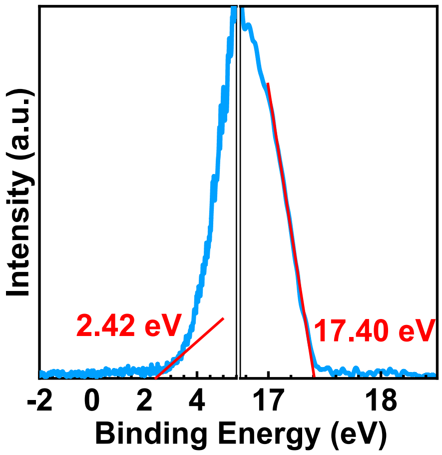

Fig. S15 The UPS spectrum of CN.

The UPS spectrum shows E_{Fm} and E_c of CN are 2.42 and 17.40 eV, respectively. Then, its E_{VBM} is calculated to be 6.24 eV. The electrochemical potential of E_{VBM} (*vs* NHE) for CN is figured out as 1.80 V.

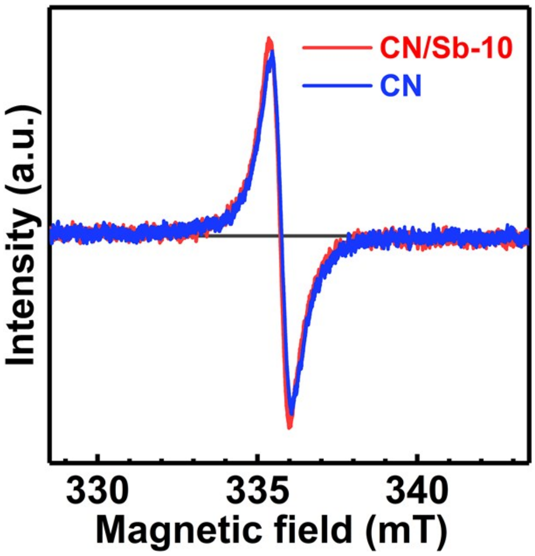

Fig. S16 EPR spectra of CN and CN/Sb-10.

Table S1 Photocatalytic hydrogen evolution rates (R_H) and partial experimental conditions for some metal-doped CN.

Sample	Electron donor	Light source	R_H (mmol g^{-1} h^{-1})	Ref.
CN/Sb-10	Triethanolamine (10 vol%)	300 W Xe lamp (λ> 420 nm)	**1.3**	**This work**
K-doped CN	Triethanolamine (10 vol%)	300 W Xe lamp (2500 > λ > 420 nm)	1.0	[6]
Co-doped CN	Triethanolamine (20 vol%)	300 W Xe lamp	0.2	[7]
Pt-doped CN	Triethanolamine (10 vol%)	300 W Xe lamp (λ > 400 nm)	0.6	[8]
Zn-doped CN	Methanol (18.5 vol%)	200 W Xe lamp (λ > 420 nm)	0.3	[9]
Na-doped CN	Triethanolamine (10 vol%)	300 W Xe lamp (λ> 420 nm)	0.2	[10]
Li-doped CN	Triethanolamine (10 vol%)	350 W Xe lamp (λ> 400 nm)	0.2	[11]
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Table S2 Adjusted coefficients of determination (Adj. R^2) for fitting results of RhB photodegradation data (Fig. 9c) to a pseudo-first-order kinetics model, $-\ln(C/C_0) = kt$ where t, C_0, C, and k are the reaction time, the initial organic concentration, the organic concentration at t, and the rate constant, respectively, and for fitting results of salicylic acid photodegradation data (Fig. 9d) to a pseudo-zero-order kinetics model, $C/C_0 = 1 - k_0C_0^{-1}t$, where k_0 is the rate constant.

Sample	Adj. R^2 for RhB	Adj. R^2 for salicylic acid
CN	0.9980	0.99995
CN/Sb-5	0.9993	0.99998
CN/Sb-10	0.9993	0.99990
CN/Sb-15	0.9976	0.99994

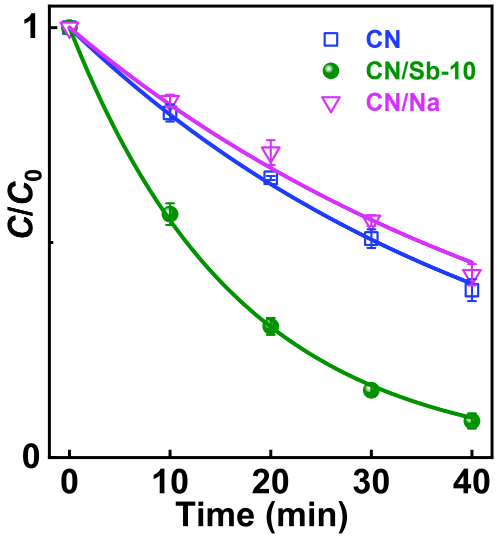

Fig. S17 Photodegradation of RhB on various samples.

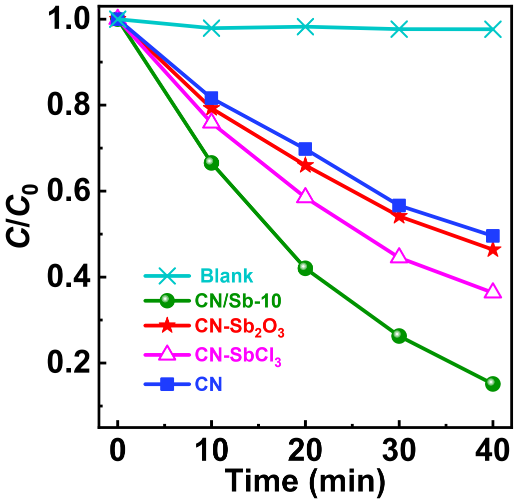

Fig. S18 RhB photodegradation on various samples.

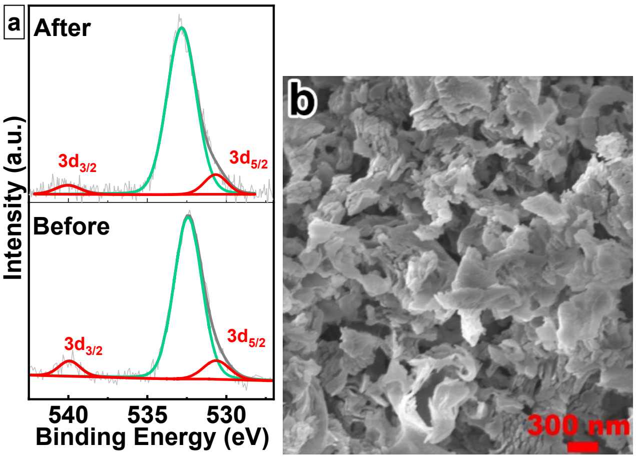

Fig. S19 (a) Sb 3d XPS core-level spectra of CN/Sb-10 before and after the cyclic experiments; and (c) the SEM image of CN/Sb-10 after the cyclic experiments.

References

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