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-Sb₂O₃ and CN-SbCl₃

For preparation of CN-Sb₂O₃, 10.0 mg of urea and 7.6 mg of Sb₂O₃ were dispersed in 10 mL of H₂O, 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 4 h in the N₂ atmosphere with a temperature ramp of 5 °C/min. After cooling naturally to the room temperature, the sample was dispersed in 200 mL of H₂O 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-SbCl₃, 10.0 mg of urea and 11.8 mg of SbCl₃ 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 4 h in the N₂ atmosphere with a temperature ramp of 5 °C/min. After cooling naturally to the room temperature, the sample was dispersed in 200 mL of H₂O 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–C₂, N–H, and N–C₃, respectively.

Fig. S2 Coordination interactions of the metal ion with N–C₂.
As shown in Fig. S3, CN/Na shows similar (100) and (002) peaks as CN.

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-$\alpha$ show similar BE positions.
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.
**Equation S1:**

\[
\text{CO(NH}_2\text{)}_2 + \text{NaSb}^\text{IV}\text{O}_3 \overset{\Delta}{\longrightarrow} ([C_3\text{N}_4\text{X}_3\text{-NH}_3]_3\text{Sb}^{\text{III}} + \text{Na}^+ + \text{N}_2 \uparrow + \text{CO}_2 \uparrow + \text{H}_2\text{O} \uparrow + \text{NH}_3 \uparrow
\]

**Fig. S9** FT-IR spectra of samples.

**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.
The lattice fringe spacing of ~0.323 nm in Fig. S12 corresponds to the (222) crystal facet of Sb$_2$O$_3$.

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 ($\lambda_E$).

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

**Fig. S15** The UPS spectrum of CN.

The UPS spectrum shows $E_{\text{fm}}$ and $E_c$ of CN are 2.42 and 17.40 eV, respectively. Then, its $E_{\text{VBM}}$ is calculated to be 6.24 eV. The electrochemical potential of $E_{\text{VBM}}$ (vs NHE) for CN is figured out as 1.80 V.
Table S1 Photocatalytic hydrogen evolution rates ($R_H$) and partial experimental conditions for some metal-doped CN.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electron donor</th>
<th>Light source</th>
<th>$R_H$ (mmol g$^{-1}$ h$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN/Sb-10</td>
<td>Triethanolamine (10 vol%)</td>
<td>300 W Xe lamp ($\lambda &gt; 420$ nm)</td>
<td>1.3</td>
<td>This work</td>
</tr>
<tr>
<td>K-doped CN</td>
<td>Triethanolamine (10 vol%)</td>
<td>300 W Xe lamp (2500 &gt; $\lambda &gt; 420$ nm)</td>
<td>1.0</td>
<td>[6]</td>
</tr>
<tr>
<td>Co-doped CN</td>
<td>Triethanolamine (20 vol%)</td>
<td>300 W Xe lamp</td>
<td>0.2</td>
<td>[7]</td>
</tr>
<tr>
<td>Pt-doped CN</td>
<td>Triethanolamine (10 vol%)</td>
<td>300 W Xe lamp ($\lambda &gt; 400$ nm)</td>
<td>0.6</td>
<td>[8]</td>
</tr>
<tr>
<td>Zn-doped CN</td>
<td>Methanol (18.5 vol%)</td>
<td>200 W Xe lamp ($\lambda &gt; 420$ nm)</td>
<td>0.3</td>
<td>[9]</td>
</tr>
<tr>
<td>Na-doped CN</td>
<td>Triethanolamine (10 vol%)</td>
<td>300 W Xe lamp ($\lambda &gt; 420$ nm)</td>
<td>0.2</td>
<td>[10]</td>
</tr>
<tr>
<td>Li-doped CN</td>
<td>Triethanolamine (10 vol%)</td>
<td>350 W Xe lamp ($\lambda &gt; 400$ nm)</td>
<td>0.2</td>
<td>[11]</td>
</tr>
</tbody>
</table>

![Fig. S16 EPR spectra of CN and CN/Sb-10.](image-url)
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, $C/C_0 = 1 - k_0 C_0^{-1}t$, where $k_0$ is the rate constant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adj. $R^2$ for RhB</th>
<th>Adj. $R^2$ for salicylic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>0.9980</td>
<td>0.99995</td>
</tr>
<tr>
<td>CN/Sb-5</td>
<td>0.9993</td>
<td>0.99998</td>
</tr>
<tr>
<td>CN/Sb-10</td>
<td>0.9993</td>
<td>0.99990</td>
</tr>
<tr>
<td>CN/Sb-15</td>
<td>0.9976</td>
<td>0.99994</td>
</tr>
</tbody>
</table>

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