Supporting Information

Facile synthesis and microstructure modulation of crystalline polymeric carbon nitride for highly boosted photocatalytic hydrogen evolution

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The preparation of crystalline PCN with granule-shape using NaCl: The granular crystalline PCN using NaCl was prepared by the mixed-calcination method with using NaCl (shown in Scheme S1a). In detail, 6 g melamine and 10 g NaCl were mixed, loaded in an aluminum-foil-wrapped crucible and heated to 630 °C for 2 h with a heating rate of 15 °C/min in air. After natural cooling, the as-obtained yellow solid was washed with deionized water to remove the NaCl till the specific conductance of filtrate approaching zero and then freeze-dried, which was denoted as NaCCN.

The preparation of crystalline PCN with box-shape using NaCl: The crystalline PCN with box-shape using NaCl was synthesized by the vapor deposition approach (shown in Scheme S1b). Typically, 5 g NaCl was loaded on the top of a ceramic cylinder placed in the crucible, and x g (x=5, 15, 30, 60) melamine was dispersed around the cylinder on the bottom of crucible. Then, the crucible was wrapped with aluminum-foil, heated at 630 °C for 2 h at a heating rate of 15 °C/min in air and naturally cooled down to room temperature. The resulted yellow powder on the top of ceramic cylinder was washed with deionized water to remove the NaCl till the specific conductance of filtrate approaching zero. Subsequently, the obtained yellow product was freeze-dried and denoted as NaCCNB-x (x=5, 15, 30, 60).
Scheme S1. Schematic illustration of (a) the mixed-calcination method and (b) the vapor-deposition approach using NaCl.

Electrochemical measurement

The photocurrent response and electrochemical impedance spectra (EIS) were tested by standard three-electrode electrochemical analyzer on the CHI 760E (CH Instruments Ins.). Typically, 20 mg photocatalyst was dispersed in 60 mL acetone solution including 40 mg elemental iodine. Then, the above solution was sonicated for 5 min. Two fluorine-doped tin oxide (FTO) glasses with area of 1 cm$^2$ were served as cathode and anode of direct-current power supply with voltage of 10 V. Then, the photocatalyst film would be coated on the surface of FTO glass. In the detailed measurement, photocatalyst-coated FTO glass was used as working electrode, and platinum wire and Ag/AgCl as counter electrode and reference electrode, respectively. The 300 W Xenon lamp was served as visible light resource and 0.1 M Na$_2$SO$_4$ solution as electrolyte.

Table S1

The parameters for apparent quantum efficiency (AQE) calculation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>Mole number of H$_2$ evolution</td>
<td>Determined in the test (mol)</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro constant</td>
<td>6.022×10$^{23}$ mol$^{-1}$</td>
</tr>
<tr>
<td>h</td>
<td>Planck constant</td>
<td>6.626×10$^{-34}$ J s</td>
</tr>
<tr>
<td>c</td>
<td>Speed of light</td>
<td>3×10$^8$ m s$^{-1}$</td>
</tr>
<tr>
<td>P</td>
<td>Power of lamp</td>
<td>23.5 mW cm$^{-2}$</td>
</tr>
<tr>
<td>S</td>
<td>Irradiated area</td>
<td>38.465 cm$^2$</td>
</tr>
<tr>
<td>t</td>
<td>Reaction time</td>
<td>Determined in the test (s)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength of monochromatic light</td>
<td>Determined in the test (400, 420, 450, 500 and 600 nm)</td>
</tr>
</tbody>
</table>
Fig. S1 (a) \( \text{N}_2 \) adsorption-desorption isotherms and (b) BJH pore size distribution curves of all samples.

Fig. S2 Kubelka-Munk transformed function of (a) KCCNB-5, KCCNB-15 and KCCNB-60; (b) the hydrogen production rate of KCCNB-30 under different monochromatic light irradiation.
Fig. S3 SEM images of (a) BCN, (b) NaCl, (c) NaCCNB-15-coated NaCl, (d) NaCCNB-5 (e) NaCCNB-30; (f) NaCCNB-60; (g) and (h) TEM images of NaCCNB-15.
Fig. S4 Element mapping images of (a) NaCCN/NaCl mixture, (b) NaCCNB-15-coated NaCl and (c) KCCNB-15.

Fig. S5 FTIR spectra of all samples.
Fig. S6 XPS spectra of BCN, NaCCNB-15 and NaCCN: (a) survey, (b) C 1s, (c) N 1s and (d) Na 1s.

Fig. S7 (a) N$_2$ adsorption-desorption isotherms and (b) BJH pore size distribution curves of all samples.
Fig. S8 Kubelka-Munk transformed function of (a) NaCCNB-5, NaCCNB-30 and NaCCNB-60; (b) the hydrogen production rate of NaCCNB-15 under different monochromatic light irradiation.

Fig. S9 (a) Photocatalytic HER time-courses of all samples; (b) cycling HER test on NaCCNB-15.