Supporting Information

Precisely tunable thickness of graphitic carbon nitride nanosheets for visible-light-driven photocatalytic hydrogen evolution

Yuanzhi Hong\textsuperscript{a}, Changsheng Li\textsuperscript{a}, Di Li\textsuperscript{b}, Zhenyuan Fang\textsuperscript{c}, Bifu Luo\textsuperscript{c}, Xu Yan\textsuperscript{a}, Hongqiang Shen\textsuperscript{a}, Baodong Mao\textsuperscript{c}, Weidong Shi\textsuperscript{c}\textsuperscript{*}

\textsuperscript{a}School of Materials Science and Engineering, Jiangsu University, Zhenjiang, 212013, P. R. China
\textsuperscript{b}Institute for Energy Research, Jiangsu University, Zhenjiang, 212013, P. R. China
\textsuperscript{c}School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, P. R. China

E-mail: swd1978@ujs.edu.cn (W. Shi)

Figure and Table Captions

**Figure S1** SEM images of the different precursors: (a) pristine melamine; (b) MSA-0.5; (c) MSA-1.5; (d) MSA-2.5.

**Figure S2** XRD patterns of the different precursors: (a) pristine melamine; (b) MSA-0.5; (c) MSA-1.5; (d) MSA-2.5.

**Figure S3** (a) XRD patterns of the MSA-2.5 and the simulated patterns; (b) single crystalline structure of as-synthesized MSA-2.5 precursor.

**Figure S4** The average thickness of as-prepared BGCN, GCN0.5, GCN1.5 and GCN2.5 samples with error bars.

**Figure S5** PL emission spectra of as-prepared samples. The inset is their PL QYs.

**Figure S6** The high-resolution N1s XPS spectra of as-prepared samples: (a) BGCN, (b) GCN0.5, (c) GCN1.5, and (d) GCN2.5.

**Figure S7** The FT-IR spectra of as-formed MSA precursors.

**Figure S8** The PL QYs vs. HER of as-prepared GCN nanosheets.

**Figure S9** Time courses of photocatalytic hydrogen evolution over the GCN2.5 nanosheets under different wavelength numbers: (a) 400 nm, (b) 420 nm, (c) 450 nm, and (d) 550 nm.

**Figure S10** Time courses of photocatalytic hydrogen evolution over the ultrathin GCN nanosheets prepared from the thermal oxidation etching.

**Table S1** Summary of the previously reported GCN nanosheets photocatalysts for HER rate, surface area, and increased HER fold than BGCN.
Figure S1 SEM images of the different precursors: (a) pristine melamine; (b) MSA-0.5; (c) MSA-1.5; (d) MSA-2.5.
SEM image (Figure S1) reveals that pristine melamine exhibits the stone-like particles with an average diameter of 25 μm. The as-prepared MSA-0.5 shows the non-standard stick structure with a length of around 50 μm, whereas the MSA-1.5 shows the irregular cube structure with a length of 150-200 μm. When further increased the HCl content, the MSA-2.5 depicts the hexagonal rod-like architecture with smooth surface in a length of around 200 μm. XRD spectra (Figure S2) illustrates that the crystal structure of the as-obtained MSA precursors were obviously changed with increasing the HCl amount. The results indicate that the morphology and crystal structure of the as-made melamine-based supramolecular aggregates are strongly influenced by the HCl concentration.

**Figure S2** XRD patterns of the different precursors: (a) pristine melamine; (b) MSA-0.5; (c) MSA-1.5; (d) MSA-2.5.
Figure S3 (a) XRD patterns of the MSA-2.5 and the simulated patterns; (b) single crystalline structure of as-synthesized MSA-2.5 precursor. Packing analysis using the single crystalline precursor shows that melamine molecules are held together by the hydrogen bonds to forming the melamine-based supramolecular structure. There is no HCl found in the precursor structure, suggesting the HCl plays an induced role on the synthesis of the melamine supramolecular.
**Figure S4** The average thickness of as-prepared BGCN, GCN0.5, GCN1.5 and GCN2.5 samples with error bars.

**Figure S5** PL emission spectra of as-prepared samples. The inset is their PL QYs.
Figure S6 The high-resolution N1s XPS spectra of as-prepared samples: (a) BGCN, (b) GCN0.5, (c) GCN1.5, and (d) GCN2.5.
**Figure S7** The FT-IR spectra of as-formed MSA precursors.

**Figure S8** The PL QYs vs. HER of as-prepared GCN nanosheets.
Figure S9 Time courses of photocatalytic hydrogen evolution over the GCN2.5 nanosheets under different wavelength numbers: (a) 400 nm, (b) 420 nm, (c) 450 nm, and (d) 550 nm.

The apparent quantum efficiency (AQE) of GCN2.5 nanosheets for H₂ evolution had been measured by the following equation:

\[
AQE = \frac{2 \times \text{the number of evolved } H_2 \text{ molecules}}{\text{the number of incident photos}}
\]

where the average intensity of irradiation at \( \lambda = 400 \text{ nm} \) was determined to be 72.0 mW.cm\(^{-2} \) by a CEL-NP2000 optical power densitometer, and the irradiation area was 24.6 cm\(^2 \). The amount of H₂ molecules of GCN2.5 nanosheets generated in 5 h was 76.5 μmol. Thus, the apparent quantum efficiency of the GCN2.5 photocatalyst was determined as 0.144% at 400 nm.
**Figure S10** Time courses of photocatalytic hydrogen evolution over the ultrathin GCN nanosheets prepared from the thermal oxidation etching.

**Table S1** Summary of the previously reported GCN nanosheets photocatalysts for HER rate, surface area, and increased HER fold than BGCN.

<table>
<thead>
<tr>
<th>Samples</th>
<th>HER rate (μmol h(^{-1}) g(^{-1}))</th>
<th>Surface area (m(^2) g(^{-1}))</th>
<th>Increased HER fold than BGCN</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCN nanosheets</td>
<td>650</td>
<td>306</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1860</td>
<td>384</td>
<td>9.3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>205.8</td>
<td>2.6</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>80</td>
<td>3.1</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1171</td>
<td>42</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>503.8</td>
<td>44.4</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>552.9</td>
<td>99.7</td>
<td>6.8</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td><strong>524</strong></td>
<td><strong>170</strong></td>
<td><strong>9</strong></td>
<td>This work</td>
</tr>
</tbody>
</table>
References


