A “Pillared” Process to Construct Graphitic Carbon Nitrides
Based Functionalized Mesoporous Materials

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1. Experimental Section

Preparation of pillared g-C$_3$N$_4$ nanosheets by nanoparticles

All reagents were analytical grade and used without further purification.

**Synthesis of g-C$_3$N$_4$ nanosheets:** g-C$_3$N$_4$ was synthesized by heating dicyandiamide in a muffle roaster at 600 $^\circ$C and holding the sample at the same temperature for another 4 h in air.$^{51,52,53}$ g-C$_3$N$_4$ nanosheets were prepared according to a previously reported method.$^{53}$ The as-prepared g-C$_3$N$_4$ (4 g) was mixed with 52 g of H$_2$SO$_4$ (98 wt.%) and 20 g of oleum (with free SO$_3$ 20 wt.% ~ 25 wt.%) in a 100 mL of flask and stirred at 140 $^\circ$C for 3 h. Then the mixture was then heated up to 170 $^\circ$C and held at that temperature for another 3 h before being cooled down to ambient temperature. After that, the mixture was injected into 800 mL of deionized water at 80 $^\circ$C under vigorous stirring, and a suspension was formed. When temperature was lowered down to room temperature, the suspension was filtered with the filtrate collected for further experiments.

**Synthesis of silica sol solution($\alpha$):** As a typical procedure for the synthesis of silica sol solution,$^{54}$ 0.85 g of HNO$_3$ (68 wt.%), 36 g of H$_2$O, and 17.5 g of C$_2$H$_5$OH were mixed together and a colorless solution was obtained after stirring for 2 min. Then, 20.8 g of tetraethyl orthosilicate (TEOS) was added dropwise to the above solution. The mixture was further vigorously stirred at 70 $^\circ$C for 3 h, and a homogeneous colorless solution was obtained. The silica sol solution obtained with method was referred to $\alpha$.

**Synthesis of silica sol solution($\beta$):** In another procedure, 0.43 g of HNO$_3$ (68 wt.%), 5.76 g of H$_2$O, and 37.95 g of C$_2$H$_5$OH were mixed together and a colorless solution was obtained after stirring for 2 min. Then, 20.8 g of TEOS was added dropwise to the above solution. The mixture was further vigorously stirred at 70 $^\circ$C for 3 h, and a homogeneous colorless solution was obtained, which was referred to $\beta$. The size of $\alpha$ silica sol was bigger than that of $\beta$ silica sol according to the literature.$^{54}$

**Synthesis of SiO$_{2-x}$/g-C$_3$N$_4$ composites:** In a typical synthesis, the silica sol solution ($\alpha$ ($\beta$) samples 2.58 (3.74), 6.45 (9.36), 10.32 (14.98) and 14.19 g (20.6 g) corresponding to 0.2, 0.5, 0.8 and 1.1 g of silicon dioxide, respectively) was added into 100 mL of the as-prepared CNS filtrate and stirred for 2 min. Then the mixture was poured into 100 g of diluted ammonia solution (5 wt.%). After being held in an ice-water bath for about 0.5 h, the solid products were separated by
filtration, washed by water and ethanol, and dried in vacuum at 60 °C. The final products were obtained after calcination at 300 °C for 4 h. The samples were referred to as SiO$_2$-xN/g-C$_3$N$_4$ where $x$ and $N$ denote the ten times weight of silicon dioxide and the silica sol used, respectively.

*Adsorption experiments:* Cu$^{2+}$ and Cd$^{2+}$ were used as the pollutants of heavy metal ions pollutants, while malachite green (MG) and methyl blue (MB) were employed as organic pollutant. A mixture of Cu(NO$_3$)$_2$ and Cd(NO$_3$)$_2$ aqueous solution (100 mL, 10 mg/L) was administered to flow through a tube (4 mm inner diameter) which was filled with 0.5 g of adsorbent. The residual metal ions in the solution were measured by Inductively Coupled Plasma Optical Emission Spectrometry (Agilent 725-ES, ICP). MG and MB (20 mg/L, 50 mL) were mixed with the adsorbent (30 mg), and the adsorption process was monitored by a UV-vis spectrophotometer (Shimadzu 2550).

**Characterization of samples**

Nitrogen adsorption-desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 analyzer. Before measurements, the samples were degassed in vacuum at 150 °C for at least 6 h. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method, and the pore size distributions were determined using Barett-Joyner-Halenda (BJH) model based on the desorption branch.

Powder X-ray diffraction (XRD) patterns were recorded with a Shimadzu XD-3D X-ray diffractometer with monochromatized Cu Kα radiation. Fourier transform infrared (FT-IR) spectra were collected on a Nexus 870 spectrophotometer in KBr pellets. X-ray photoelectron spectroscopy (XPS) were collected on a photoelectron spectrometer (VG ESCALAB 210) with a monochromatic X-ray source of Mg Kα ($hν = 1253.6$ eV). Elemental analysis was performed with a VarioE-L cube form Elementar Analysensysteme GmbH to determine nitrogen, carbon, and hydrogen contents in the samples. Transmission electron microscopy (TEM) measurements were performed using a TECNAI G$^2$ F20 field emission transmission electron microscope operated at acceleration voltage of 200 kV. All samples were ultrasonically dispersed in ethanol and drop-cast onto copper grids covered with carbon film before being transferred into the TEM chamber. Thermal gravimetric (TG) analysis were conducted using a Zettsch Sta 449F3 in a continuous flow of air (20 mL/min) from room temperature to 700 °C.
2. Supporting information for XRD

Figure S1. XRD patterns (A) and enlarged partial XRD patterns (B) of bulk g-C₃N₄, acidified g-C₃N₄, recovered g-C₃N₄ that obtained by calcinating acidified g-C₃N₄, and SiO₂-5α-CN.⁵³

3. Flatting effect

As is known, g-C₃N₄ exhibits slight undulating in the plane of tri-s-triazine caused by the sp³ hybridization bridge nitrogen atoms. While when after pillared by SiO₂ nanoparticles, the degree of undulation of g-C₃N₄ decreased, resulted in the stretched properties in-plane and the decrease distance of interlayer packing of g-C₃N₄. We defined this phenomenon as “flatting effect”. There are some other evidences, including the weakened absorption intensity of the N-(C)₃ group in the IR analysis and the decreased thermal stability of SiO₂-CNS compared to the bulk g-C₃N₄.
4. Supporting information for XPS

Figure S3. XPS profile of survey of Si-5α-CN sample

Figure S4. XPS profile of survey (A), N1s (B), C1s (C) of bulk g-C₃N₄
5. Elemental analysis date and the percentage contents of g-C$_3$N$_4$ along with SiO$_2$ contents

Table S1. C, N contents (wt.%) and C/N (molar ratio) of the samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>Si-2α-CN</th>
<th>Si-5α-CN</th>
<th>Si-8α-CN</th>
<th>Si-11α-CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>34.35</td>
<td>19.86</td>
<td>13.05</td>
<td>9.78</td>
</tr>
<tr>
<td>C</td>
<td>19.72</td>
<td>11.19</td>
<td>8.35</td>
<td>6.59</td>
</tr>
<tr>
<td>C/N</td>
<td>0.66</td>
<td>0.66</td>
<td>0.74</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Figure S5. The percentage content of g-C$_3$N$_4$ changed with SiO$_2$ contents ($x$)

Supposed that the materials were composed only by CNS and SiO$_2$, the percentage contents of g-C$_3$N$_4$ (1/y) can be calculated by the following equation:

$1/y = W_c / (W_c + W_s)$

$y = (W_c + W_s) / W_c$

Where $W_c$ and $W_s$ represent the percentage contents of g-C$_3$N$_4$ and SiO$_2$ calculated with the EA data, respectively. The y axis represents the reciprocal of the percentage content of g-C$_3$N$_4$, and the x axis is assigned to the mass of SiO$_2$ used in the experiments. Curve fit analysis shows the equation is the $y=4.7533x+0.8753$. By calculated reciprocal of the slope, the mass of g-C$_3$N$_4$ in the...
samples is about 0.22 g, while 0.5 g of bulk g-C₃N₄ were used as precursors in the experiments. Other g-C₃N₄ has been filtered out during the preparation process of g-C₃N₄ nanosheets.

6. TEM images

![TEM images of g-C₃N₄ nanosheets](image1)

Figure S6. TEM images of g-C₃N₄ nanosheets

![SiO₂ nanoparticles](image2)

Figure S7. SiO₂ nanoparticles of α (A), β (B) and the corresponding size distribution (C) and (D)
7. Textural parameters, TG and DSC thermograms of Si-xN-CN

Table S2. Textural parameters of Si-xN-CN

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) (m²/g)</th>
<th>Pore size (nm)</th>
<th>(V_p) (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-2(\alpha)-CN</td>
<td>259</td>
<td>11.9</td>
<td>0.79</td>
</tr>
<tr>
<td>Si-5(\alpha)-CN</td>
<td>407</td>
<td>11.6</td>
<td>1.21</td>
</tr>
<tr>
<td>Si-8(\alpha)-CN</td>
<td>416</td>
<td>11.6</td>
<td>1.25</td>
</tr>
<tr>
<td>Si-11(\alpha)-CN</td>
<td>444</td>
<td>9.99</td>
<td>1.10</td>
</tr>
<tr>
<td>Si-2(\beta)-CN</td>
<td>227</td>
<td>14.0</td>
<td>0.79</td>
</tr>
<tr>
<td>Si-5(\beta)-CN</td>
<td>324</td>
<td>11.2</td>
<td>0.79</td>
</tr>
<tr>
<td>Si-8(\beta)-CN</td>
<td>324</td>
<td>8.6</td>
<td>0.53</td>
</tr>
<tr>
<td>Si-11(\beta)-CN</td>
<td>355</td>
<td>8.9</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Pore size determined by the desorption branch of isotherm.

Figure S8. TG and DSC thermograms of Si-5\(\alpha\)-CN
8. Supporting information for absorption properties

Figure S9. Absorption spectra of activated carbon for MG

Figure S10. Absorption spectra (A) and adsorption rate (B) of an aqueous solution of MB (20 mg L\(^{-1}\), 50 ml) after treatment with Si-5\(\alpha\)-CN (50 mg) at different time intervals
References