Supporting Information

Excellent Visible Light Photocatalysis of Fluorinated Polymeric Carbon Nitride Solids

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Synthesis of CNF-x Materials

In a typical synthetic procedure, 3 g dicyanamide and 0.5 g NH₄F was added into the aqueous solution and the mixture was heated in an oil bath at 60 °C until removal of water and formation of a white solid. The white solid was then transferred into a crucible and heated over 4 h to reach a temperature of 550 °C and tempered at this temperature for 4 h. This was followed by cooling the sample naturally to room temperature.

**Caution**: HF is highly corrosive and toxic. Care should be taken to ensure that the oven is putted in the cabinet and never blocked, and the exhausting gas should be fed through NaOH solution bath cooling traps system to collect the remnant toxic gas.

Characterization of CNF-x Materials

WAXS spectra were recorded on a Bruker D8 Advance diffractometer and the FTIR spectra were recorded on a BioRad FTS 6000 spectrometer, equipped with an attenuated total reflection (ATR) setup. The UV/Vis spectra were recorded on a Varian Cary 500 Scan UV/Vis system. SEM images were performed on a Zeiss DSM 940A. TEM was performed on a FEI Tencai 20 microscope. Elemental analyses were performed on a Vario EL Elementar (Elementar Analyzen-system, Hanau, Germany). X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo ESCALAB250 instrument with a monochromatized AlKa line source (200). All binding energies were referenced to the C₁s peak at 288.2 eV corresponding to a C-N-C coordination in g-C₃N₄. BET surface area was obtained from 77 K N₂ adsorption-desorption isotherms using an ASAP 2010. Samples were outgassed at 200 °C for 10 h to a residual pressure <10⁻⁴ Pa.
Photocatalytic reactions:

**Oxidation of benzene:** CNF-x (50 mg) was milled and then suspended in a mixture of acetonitrile (4 ml), water (4 ml), benzene (0.8 ml), and hydrogen peroxide (30 wt%, 0.51 ml). The resulting biphasic system was stirred at 60 °C for 4 h in the dark. At the end of the reaction, ethanol (5 ml) was poured into the mixture at 4 °C to quench the reaction and turn the biphasic system to a single-phase one. To carry out the photochemical reaction, a 500 W Xenon lamp together with a 420 nm cut-off filter was used as a visible light source for the irradiation of reaction system, with otherwise the same experimental conditions as those in the dark. The products of the reactions were analyzed by a HPLC (Agilent 1200 Series) with toluene as the internal standard.

**Photocatalytic Hydrogen Evolution with Visible Light:** Reactions were carried out in a Pyrex top irradiation-type vessel connected to a glass closed gas circulation system. H₂ production was performed by dispersing 0.1 g of catalyst powder in an aqueous triethanolamine solution (TEA, 10 vol. %, 100 ml) as the sacrificial electron donor. In the case of deposition of Pt, an appropriate amount of H₂PtCl₆ (3 wt. %) was dissolved in the reactant solution. The reactant solution was evacuated several times to remove air completely prior to irradiation under a 500 W HBO lamp fitted with a water filter. The wavelength of the incident light was controlled by using a λ=420 nm cut-off filter. The temperature of the reactant solution was maintained at room temperature. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector.

**Method of calculation**

All the calculations were performed with the Gaussian 03 program.¹ The hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation functional with the 6-31G* and 6-31++G** basis sets were employed.²³ The model molecules melem and fluorine doped melem were first optimized at the B3LYP/6-31G* level and fully characterized as minima by frequency analysis. Subsequent geometry optimizations were performed at the B3LYP/6-31++G** level starting from the B3LYP/6-31G* geometries, followed by frequency calculations to verify the reasonability of the optimized structures.
\[
\text{NH}_4\text{F} \rightarrow \text{F}^- + \text{H}^+ + \text{NH}_3
\]

**Scheme S1.** NH$_4$F reaction.

**Table S1.** \(\frac{n_C}{n_N}\) based on the element analysis of CNF-x.

<table>
<thead>
<tr>
<th>Entry</th>
<th>CNF-0.5</th>
<th>CNF-1.0</th>
<th>CNF-2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{n_C}{n_N})</td>
<td>0.75</td>
<td>0.75</td>
<td>0.76</td>
</tr>
</tbody>
</table>

**Table S2.** Conversion of \(\text{H}_2\text{O}_2\) in the oxidation of benzene.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(\text{H}_2\text{O}_2) Conv. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>g-C$_3$N$_4$</td>
</tr>
<tr>
<td>2</td>
<td>CNF-0.05</td>
</tr>
<tr>
<td>3</td>
<td>CNF-0.1</td>
</tr>
<tr>
<td>4</td>
<td>CNF-1.0</td>
</tr>
<tr>
<td>5</td>
<td>CNF-2.0</td>
</tr>
</tbody>
</table>
Figure S1. The atomic orbital compositions of the frontier molecular orbitals and optimized geometry of uncodensed form (CN) and fluorine doped form.

It is worth noticing that even in the uncodensed form (CN) the amino groups are planar, indicating sp$^2$ hybridiztion. However, incorporation of fluorine resulting in a partial conversion of C-sp$^2$ to C-sp$^3$, which partly destroyed the in-plane order of the CN (Figure S5).
Obviously a final clarification of the exact positioning of F in the structure relies on more detailed experimental characterization. In the present state we can only claim the incorporation in the resulting doped carbon nitride via C-F bonds, while the characteristic structural properties of polymeric g-C$_3$N$_4$, such as the original graphitic structure, C-N heterocycle units, and C/N composition, were essentially retained.
Figure S3. Energy diagrams of the molecular orbital (MO) energies of uncodensed form (CN) and fluorine doped form (CN-F1 and CN-F2). The vertical lines and values indicate the energy of HOMO-LUMO gap (in eV). Only sixteen occupied and sixteen unoccupied MOs are listed.
Figure S4. N$_2$ adsorption-desorption isothermal curves.

Figure S5. SEM images of polymeric g-C$_3$N$_4$, melon, (a) and CNF-0.5 (b).

SEM images indicate the typical slate-like, stacked lamellar texture of the unmodified melon (Figure 3, a). However, both the sheets and stacks of the texture were broken up, and a more open texture was observed in CNF-2.0 (Figure S3, b), due to fluorination. The BET results indicate a surface area of CNF-2.0 of 38 m$^2$/g, as compared to the surface area of 8 m$^2$/g of the unmodified parental material (Figure S2). Thus, both the morphology and surface area were modified by the presence of fluorine. Already the textural changes are expected to promote heterogeneous photocatalysis. This textural effect adds on the chemical effect, brought by fluorine doping.
Figure S6. Typical TEM pictures of CNF-1.0 (above) and CNF-2.0 (below).
Figure S7. FTIR spectra of CNF-0.5 before and after reaction.

Figure S8. Cycling runs in the photocatalytic oxidation of benzene to phenol under visible-light irradiation ($\lambda>420$, using CNF-0.5 as photocatalyst).
Supporting References:

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