Electronic Supplementary Information

Critical role of hydrogen bond between microcrystalline cellulose and g-C₃N₄ enables highly efficient photocatalysis

Zhaoqiang Wangᵃ⁺†, Guixiang Dingᵃ⁺†, Juntao Zhangᵃ, Xianqing Lvᵃ, Peng Wangᵇ, Li Shuaiᵃ, Chunxue Liᶜ⁺*, Yonghao Niᵃ⁺*, and Guangfu Liaoᵃ⁺*

ᵃ National Forestry and Grassland Administration Key Laboratory of Plant Fiber Functional Materials, College of Materials Engineering, Fujian Agriculture and Forestry University, Fuzhou 350002, China.
bShandong Chambroad Petrochemicals Co., Ltd, Binzhou, Shandong 256500, China.
cCollege of Ecological Environment and Urban Construction, Fujian University of Technology, Fuzhou 350118, China.

*Corresponding authors. E-mail addresses: chunxueli@fjut.edu.cn (C. Li); yonghao@unb.ca (Y. Ni); liaof@mail2.sysu.edu.cn (G. Liao)
†These authors contributed equally to this work.
Experimental

Experimental materials

All the reagents were of analytical grade and used as received without further purification, Urea (CH₄N₂O, AR 99) was produced from Tianjin Jinhui Taiya Chemical Reagent Co., LTD. Microcrystalline cellulose (MCC), Tetracycline hydrochloride (C₂₂H₂₄N₂O₈·HCl, TC, AR 99) Bisphenol A (BA, AR 99), O-chlorophenol (OCH, AR 98) and 2-Mercaptobenzothiazole (MB, AR 98) was supplied by Aladdin Reagent (Shanghai) Co, Ltd.

Preparation of CN

In a typical synthesis, the urea was ground and dried and calcined in the Muffle furnace at 550 °C for 240 min with heating rate of 2.5 °C min⁻¹. The obtained powder was treated with nitric acid until neutral. After drying at 100 °C for 12 h, sample was calcined in the Muffle furnace at 500 °C for 240 min with heating rate of 5 °C min⁻¹. Remove at room temperature, grind, dry and noted g-C₃N₄ as CN.

Preparation of MCC modified CN

MCC/CN was prepared through dimple physical blending method. In a typical experimental, MCC-X/CN hybrid, where X = 0.01, 0.03, 0.05 and 0.1 g of MCC w.r.t the amount of CN (0.2 g) was dispersed in 100 ml deionized water with vigorous stirring for 24 h. After filtering out the mixture, the samples were dried at 40 °C for 24 h.

Characterization

The scanning electron microscopic (SEM) images were taken on Ultima IV. High-resolution TEM (HRTEM) images were obtained on Jem-2100F. X-ray diffraction (XRD) pattern of samples were carried out via the ULTIMA IV ultima IV
diffractometer under Cu Kα radiation at a scanning rate of 5 °C min⁻¹ (Japan). UV-vis absorption spectra of samples are measured by U-4150 UV-vis spectrometer (Japan) and Fourier transform infrared spectroscopy (FTIR, Bruker Vertex 70, Germany). The X-Ray photoelectron spectroscopy (XPS) measurements were performed on a VG Microtech Multi lab ESCA3000 spectrometer with a non-monochromatised Mg-Ka X-ray source and energy of 0.8 eV. The binding energy correction was performed by the C1s reference peak of carbon atom at 284.9 eV. The calculation was based on the density functional theory (DFT). All the DFT calculations of model CN, MCC/CN and MCC/CN-Pt were performed with Gaussian 16 (C 01) package suite. The structure of all molecules was optimized by using B3LYP method, the 6-31G (d) basis set was employed for all atoms and water was used to represent the solvents. The frequency calculations were also conducted at the same level of theory to ensure all the optimized structures were at a local minimum on the potential energy surface (PES) and then the generated wave functional files were used to calculate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies. Then, We adopted the TDDFT method, at the B3LYP/6-31G (d) level, to calculate the oscillator strength of the excited states of CN, MCC/CN and MCC/CN-Pt. Adsorption energy analysis were conducted under the MP2 method and the adsorption energy of CN and CN-H were calculated based on the equation: 

\[ E_{\text{ads}} = E_{\text{total}} - E_{\text{sub}} - E_H, \]

where the \( E_{\text{sub}} \) and \( E_H \) represent the optimal structures of fragmented CTPs and its corresponding energies, respectively. \( E_{\text{total}} \) is the total energy of the optimal substrates absorbed by \( \text{H}^+ \).

**Photocatalytic degradation test**

Firstly, TC, BA, OCH and MB were used as the target molecules to evaluate the photocatalytic degradation activity of the samples. The photocatalyst (10 mg) was added into target molecules aqueous solution (50 ml) with a concentration of 20 mg/L, and stirred in the dark for 60 min until the adsorption-desorption equilibrium. The photocatalytic degradation was performed by using 300 W Xenon Lamp (Beijing Perfectlight) and UV cut-off filter (\( \lambda > 420 \text{ nm} \)). The concentration of supernatants
were determined at the characteristic absorption wavelengths of TC (357 nm), BA (278 nm), OCH (279 nm), MB (322 nm) by U-3900 ultraviolet-visible spectrophotometer with an interval of 15 min. The photo-degradation efficiency and rate constant were obtained as follows:\(^1\)

\[
\eta = \frac{C_0 - C}{C_0} \times 100%  
\]

(1)

\[
\ln \frac{C_0}{C} = K_{app} t 
\]

(2)

where \(C_0\) was the initial concentration, \(t\) was the reaction time, \(C\) was the concentration at time \(t\), and \(K_{app}\) was the first-order rate constant (min\(^{-1}\)).

**Photocatalytic H\(_2\) evolution activity measurements**

The photocatalytic H\(_2\) evolution activity of the obtained samples was evaluated under Labsolar-6A (Beijing Perfectlight). Typically, 25 mg of sample powder is dispersed in an aqueous solution (100 mL) containing triethanolamine (10 vol\%) as a sacrifice-electron donor, with the addition of 1.5 ml H\(_2\)PtCl\(_6\) (3 wt\%). The suspension solution was added into a 150 mL double layered Pyrex reaction cell linked to a circulating cold bath (5 \(\degree\)C). A 300 W Xenon Lamp source (PLS-SXE 300/UV) and UV cut-off filter (\(\lambda > 420\)) were used for H\(_2\) evolution. The catalyst suspensions were stirred constantly in order to prevent the settling down of the catalyst. Subsequently, an online meteorological chromatograph was used to detect the H\(_2\) precipitation rate under visible light irradiation.

**Photoelectrochemical test**

Photoelectrochemical measurements were conducted in a conventional three-electrode cell system using Chen hua electrochemical station (Shang Hai). The fluorine-doped tin oxide (FTO) transparent conductive film glass deposited with samples, Pt wire, and Ag/AgCl electrode were respectively used as working electrodes, counter electrode, and reference electrode. 0.5 M Na\(_2\)SO\(_4\) aqueous solution (pH = 6.8) was
used as the electrolyte. In the work, 5.0 mg photocatalyst was well dispersed in 50 μL Nafion PFSA Polymer Dispersions D520 (5%) and 2 ml N, N-dimethylamide ultrasonic for 30 min in an ultrasonic cleaner. Then, evenly drop on the FTO with the glue head dropper, bake in the oven at 40 °C for 5 h, remove the FTO and insert it into the working electrode of the three electrodes. In addition, the photocurrent response of the photocatalysts as light on and off was measured without bias voltage or photocurrent-time curves and electrochemical impedance.

**Apparent quantum yield (AQY) measurements**

Under the same photocatalytic conditions, using 300W Xenon lamp as light source, monochromatic band-pass filters (420, 450, 500, 550 nm) were used to obtain the required single incident wavelength, and the AQY of H2 precipitation was measured. The average light intensity was measured by optical power meter (PL-MW2000), and the specific light intensity of 420, 450, 500 and 550 nm was 3.80, 3.84, 2.89 and 4.14 mW cm⁻², respectively. After that, catalyst solution was irradiated for 1 h. The AQY was calculated by using the equation:\(^2\)

\[
AQY (\%) = \frac{2 \times \text{amount of H}_2 \text{ molecules}}{(\text{Number of incident electrons})} \times \frac{(2 \times M \times A \times h \times c)}{(P \times S \times T \times \lambda)} \times 100\%
\]

(3)

where M is the amount of H2 molecules (mol), A is the Avogadro constant (6.02×10²³ mol⁻¹), h is the Planck constant (6.626×10⁻³⁴ m² kg s⁻¹), c is the speed of light (3×10⁸ m s⁻¹), P is the intensity of irradiation light (W cm⁻²), S is the irradiation area (cm²), T is the photoreaction time (s), \(\lambda\) is the wavelength of the monochromatic light (nm).
Figures

Fig. S1. (a-b) Molecular structure of CN and MCC.
**Fig. S2.** SEM images of (a) CN and (b) MCC-0.05/CN.

**Fig. S3.** (a-b) SEM images of MCC.
Fig. S4. Valence spectra of different photocatalysts.

As showed in Fig. S3, the bandgap ($E_g$) was calculated according to Tauc/David-Mott model described by the equation $(\alpha \nu)^{1/2} = A(\nu - E_g)$, where $\hbar$ is the Planck constant, $\nu$ is the frequency of vibration, $\alpha$ is the absorption coefficient, $E_g$ is the bandgap, $A$ is a proportional constant. The bandgap energies of the CN and MCC-X/CN were estimated to be 2.78, 2.77, 2.73, 2.72 and 2.76 eV, respectively. The valence band ($E_{VB}$) of the CN and MCC-X/CN were determined using valence band X-ray photoelectron spectroscopy (VB-XPS). The $E_{VB}$ position of the CN and MCC-X/CN were estimated to be 2.27, 2.07, 2.07, 1.97 and 2.15 eV via the VB-XPS spectrum. Moreover, the CB positions of the CN and MCC-X/CN were determined to be -0.61, -0.70, -0.76, -0.85 and -0.9 eV according to the empirical formula:

$$E_{CB} = E_{VB} - E_g. \quad (4)$$
Fig. S5. (a) FTIR spectra of MCC-0.05/CN before and after five cycles during photocatalytic TC degradation experiment. (b) FTIR spectra of MCC-0.05/CN before and after five cycles of during photocatalytic H₂ evolution experiments.
**Fig. S6.** (a) XRD spectra of MCC-0.05/CN before and after five cycles during photocatalytic TC degradation experiment.
Fig. S7. Degradation dynamic curves of TC, BA, OCH, MB.

For investigating the universal applicability of the MCC-0.05/CN sample for degrading the other various organic pollutants, the photocatalytic degradation experiments of some typical persistent pollutants are further carried out, such as BA, OCH, and MB. As the degradation dynamic curves shown in Fig. S5, the maximal degradation rate of BA, OCH and MB are obtained over the MCC-0.05/CN sample, which reach up to 46.5%, 55.7% and 65.8%, respectively. The results indicate that the MCC-0.05/CN sample has the superior universality for unselective degrading the various organic pollutants
Fig. S8. ESR spectra of ·OH and ·O$_2^-$ in the dark and after light irradiation (a, b) for the pristine MCC-0.05/CN.

ESR spectra are detected to capture the signals of generated radicals (·OH and ·O$_2^-$) under light irradiation with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapping agent and further revealing the photocatalytic mechanism of MCC-0.05/CN.
Fig. S9. Photocatalytic degradation curves for TC.

In order to compare the impact of platinum on the degradation of tetracycline, control experiments were conducted using the best samples. The experimental conditions were kept consistent, and 1 mL H$_2$PtCl$_6$ (3 wt%) was added to one set of experiments. Figure S8 illustrated that the degradation rate of the catalyst increased from 69.8% to 86.6% when platinum was introduced. The results showed that platinum accelerates the degradation of tetracycline.
Fig. S10. (a, b) TD-DFT-calculated absorption spectra and oscillator strengths for the model system of CN and MCC/CN at the initial state; (c) Calculated HOMO/LUMO energy levels of MCC/CN-Pt; (d) HOMO/LUMO distributions of MCC/CN-Pt; (e) Calculated free energy diagrams of H₂ production catalyzed by CN and MCC/CN model system.
# Tables

**Table S1.** The activity comparison of the photocatalytic TC degradation of CN-based photocatalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Efficiency</th>
<th>$^aK_{\text{app}}$</th>
<th>Catalyst; TC</th>
<th>Conditions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO/g-C$_3$N$_4$</td>
<td>78.4 (50 min)</td>
<td>0.1490</td>
<td>20 mg; 20 mg /L</td>
<td>Xl 300 W ($\lambda \geq 400$ nm)</td>
<td>[4]</td>
</tr>
<tr>
<td>B-PCN</td>
<td>81.3 (120 min)</td>
<td>0.0170</td>
<td>10 mg; 40 mg/L</td>
<td>Xl 300 W ($\lambda \geq 420$ nm)</td>
<td>[5]</td>
</tr>
<tr>
<td>Nv@g-C$_3$N$_4$</td>
<td>78.0 (120 min)</td>
<td>0.0100</td>
<td>50 mg; 20 mg/L</td>
<td>LED 50 W</td>
<td>[6]</td>
</tr>
<tr>
<td>WO$_3$/g-C$_3$N$_4$ @MWCNs</td>
<td>79.5 (120 min)</td>
<td>0.0172</td>
<td>20 mg; 20 mg/L</td>
<td>Halogen lamp 500 W ($\lambda \geq 420$ nm)</td>
<td>[7]</td>
</tr>
<tr>
<td>Ag/g-C$_3$N$_4$</td>
<td>83.0 (120 min)</td>
<td>-</td>
<td>100 mg; 20 mg/L</td>
<td>Xl 300 W ($\lambda \geq 420$ nm)</td>
<td>[8]</td>
</tr>
<tr>
<td>WO$_3$/g-C$_3$N$_4$</td>
<td>70.0 (120 min)</td>
<td>0.0120</td>
<td>50 mg; 25 mg/L</td>
<td>Xl 300 ($\lambda \geq 420$ nm)</td>
<td>[9]</td>
</tr>
<tr>
<td>BrCN</td>
<td>75.0 (150 min)</td>
<td>0.0179</td>
<td>250 mg; 10mg/L</td>
<td>LED lamp 38.5 W ($\lambda &gt; 450$ nm)</td>
<td>[10]</td>
</tr>
<tr>
<td>CQDs/ g-C$_3$N$_4$</td>
<td>78.6 (240 min)</td>
<td>0.0064</td>
<td>50 mg; 10 mg/L</td>
<td>Xl 250 W ($\lambda \geq 420$ nm)</td>
<td>[11]</td>
</tr>
<tr>
<td>ZnSnO$_3$/CN</td>
<td>85.0 (120 min)</td>
<td>0.0131</td>
<td>25 mg; 10 mg/L</td>
<td>Xl 300 W ($\lambda \geq 400$ nm)</td>
<td>[12]</td>
</tr>
<tr>
<td>CFs/g-C$_3$N$_4$/BiOB</td>
<td>86.1 (120 min)</td>
<td>0.0150</td>
<td>15 mg; 20 mg/L</td>
<td>Xl 300 W ($\lambda \geq 400$ nm)</td>
<td>[13]</td>
</tr>
<tr>
<td>h-BN/WO$_3$/g-C$_3$N$_4$</td>
<td>88.5 (120 min)</td>
<td>0.0130</td>
<td>50 mg; 10 mg/L</td>
<td>Xl 300 W ($\lambda \geq 420$ nm)</td>
<td>[14]</td>
</tr>
<tr>
<td>V$_2$O$_5$/g-C$_3$N$_4$</td>
<td>75.0 (120 min)</td>
<td>-</td>
<td>50 mg; 10 mg/L</td>
<td>Xl 300 W ($\lambda \geq 420$ nm)</td>
<td>[15]</td>
</tr>
<tr>
<td>NCNT/mpg-C$_3$N$_4$</td>
<td>67.1</td>
<td>-</td>
<td>20 mg; 10 mg/L</td>
<td>Xl 300 W ($\lambda \geq 400$ nm)</td>
<td>[16]</td>
</tr>
<tr>
<td>Bi$_2$WO$_6$/g-C$_3$N$_4$</td>
<td>73.0 (60 min)</td>
<td>0.0345</td>
<td>50 mg; 10 mg/L</td>
<td>Xl 250 W ($\lambda \geq 420$ nm)</td>
<td>[17]</td>
</tr>
<tr>
<td>HDMPO-g-C$_3$N$_4$</td>
<td>74.0 (60 min)</td>
<td>0.0101</td>
<td>10 mg; 20 mg/L</td>
<td>Xl 300 W ($\lambda \geq 420$ nm)</td>
<td>[18]</td>
</tr>
<tr>
<td>Nb$_2$O$_5$/g-C$_3$N$_4$</td>
<td>76.2 (150 min)</td>
<td>0.0096</td>
<td>50 mg; 10 mg/L</td>
<td>Xl 250 W ($\lambda \geq 420$ nm)</td>
<td>[19]</td>
</tr>
<tr>
<td>MCC-0.05/CN</td>
<td>84.24 (90 min)</td>
<td>0.019</td>
<td>10 mg; 20 mg/L</td>
<td>Xl 300W ($\lambda \geq 420$ nm)</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^aK_{\text{app}}$: the first-order rate constant (min$^{-1}$).
**Table S2.** The activity comparison of the photocatalytic H₂ production of CN-based photocatalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>H₂ evolution rate (μmol h⁻¹ g⁻¹)</th>
<th>Reaction conditions</th>
<th>Light source</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP/g-C₃N₄</td>
<td>101</td>
<td>MeOH</td>
<td>Xe (λ ≥ 420 nm)</td>
<td>[20]</td>
</tr>
<tr>
<td>CNQDs/CoPi</td>
<td>234.5</td>
<td>TEOA</td>
<td>Halogen lamp (λ ≥ 420 nm)</td>
<td>[21]</td>
</tr>
<tr>
<td>BP/g-C₃N₄</td>
<td>384.2</td>
<td>TEOA</td>
<td>Xe (λ ≥ 420 nm)</td>
<td>[22]</td>
</tr>
<tr>
<td>NiCoP/g-C₃N₄</td>
<td>159</td>
<td>MeOH</td>
<td>UV-vis light irradiation</td>
<td>[23]</td>
</tr>
<tr>
<td>m-gCN/BP-M</td>
<td>442</td>
<td>TEOA</td>
<td>Solar Light (λ ≥ 420 nm)</td>
<td>[24]</td>
</tr>
<tr>
<td>Zn-MOFs/g-C₃N₄</td>
<td>484.1</td>
<td>TEOA</td>
<td>Xe 300W (λ ≥ 420 nm)</td>
<td>[25]</td>
</tr>
<tr>
<td>MIL-125/g-C₃N₄</td>
<td>606</td>
<td>TEOA</td>
<td>Xe 298W (λ ≥ 420 nm)</td>
<td>[26]</td>
</tr>
<tr>
<td>Co/Mo-MCN.</td>
<td>694.5</td>
<td>TEOA</td>
<td>Xe (λ ≥ 420 nm)</td>
<td>[27]</td>
</tr>
<tr>
<td>BPQDs/g-C₃N₄</td>
<td>271.0</td>
<td>MeOH</td>
<td>Visible-Light</td>
<td>[28]</td>
</tr>
<tr>
<td>BP/g-C₃N₄</td>
<td>571</td>
<td>Lactic acid</td>
<td>Xe 300W (λ ≥ 400 nm)</td>
<td>[29]</td>
</tr>
<tr>
<td>2D BP/2D C₃N₄</td>
<td>259.04</td>
<td>-</td>
<td>Xe 300W (λ ≥ 400 nm)</td>
<td>[30]</td>
</tr>
<tr>
<td>NYFG/C₃N₄ NT</td>
<td>311.6</td>
<td>TEOA</td>
<td>Xe 300W</td>
<td>[31]</td>
</tr>
<tr>
<td>g-C₃N₄-ZnCdS</td>
<td>108.9</td>
<td>Na₂S; Na₂SO₃</td>
<td>Xe 300W (λ ≥ 420 nm)</td>
<td>[32]</td>
</tr>
<tr>
<td>Ag/CoxP/Meso-g-C₃N₄</td>
<td>96.66</td>
<td>-</td>
<td>Xe 300W (λ ≥ 420 nm)</td>
<td>[33]</td>
</tr>
<tr>
<td>MCC-0.05/CN</td>
<td>642.71</td>
<td>TEOA</td>
<td>Xe lamp 300W (λ ≥ 420 nm)</td>
<td>This work</td>
</tr>
</tbody>
</table>
Reference

22. Q. Zhang, S. Huang, J. Deng, D. T. Gangadharan, F. Yang, Z. Xu, G. Giorgi,