Supplementary Information

## One-pot preparation of micro-fibrillated cellulose fiber (MCF) through the synergistic action of g-C<sub>3</sub>N<sub>4</sub> and diluted acid

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1. Differences in absorbability of  $g-C_3N_4-400$ ,  $g-C_3N_4-500$  and  $g-C_3N_4-600$  (Fig. S1).



Fig. S1 Adsorption of  $g-C_3N_4$ -400,  $g-C_3N_4$ -500 and  $g-C_3N_4$ -600 onto 0.05 g cotton cellulose after stirring for 12 h. The  $g-C_3N_4$ -500 were the only sample that can completely adsorbed onto cotton cellulose and eventually formed a transparent solution. This suggests that the  $g-C_3N_4$ -500 has the strongest cellulose affinity.

2. The Zeta potential and the content of pyrrolic N of  $g-C_3N_4$ -400,  $g-C_3N_4$ -500 and  $g-C_3N_4$ -600 (Fig. S2).



Fig. S2 The Zeta potential and the content of pyrrolic N of  $g-C_3N_4$ -400,  $g-C_3N_4$ -500 and  $g-C_3N_4$ -600.

The Zeta potential of g-C<sub>3</sub>N<sub>4</sub>-400, g-C<sub>3</sub>N<sub>4</sub>-500 and g-C<sub>3</sub>N<sub>4</sub>-600 was measured to be +13.2 mV, +11.3 mV and +7.4 mV, while the content of pyrrolic N was calculated to be 44.5%, 33.8% and 30.4%, respectively. The positive surface charges of the g-C<sub>3</sub>N<sub>4</sub> are from the amine groups which act as proton acceptors because of the free lone pair of electrons on the nitrogen atom. Actually, the pyrrolic N as the strongest proton acceptor is the main source of the Zeta potential of g-C<sub>3</sub>N<sub>4</sub>, which could explain the g-C<sub>3</sub>N<sub>4</sub>-600 with the highest content of pyrrolic N (44.5%) have the highest Zeta potential (+13.2 mV). However, the Zeta potential of g-C<sub>3</sub>N<sub>4</sub>-500 (+11.3 mV) is similar to g-C<sub>3</sub>N<sub>4</sub>-600, but the content of pyrrolic N of g-C<sub>3</sub>N<sub>4</sub>-500 is relatively low. This indicates that the nitrogen (may form pyridinic N and graphitic N) with strongest electronegativity in g-C<sub>3</sub>N<sub>4</sub>-500 can be extra strong

proton acceptors which improve the Zeta potential of g-C<sub>3</sub>N<sub>4</sub>-500.

3. Optical microscope image of cellulose after adsorbing  $g-C_3N_4$ -400,  $g-C_3N_4$ -500 and  $g-C_3N_4$ -600 in 0.02 M H<sub>2</sub>SO<sub>4</sub> aqueous solution (Fig. S3).



Fig. S3 Optical microscope image of cellulose after adsorbing  $g-C_3N_4-400$  (a),  $g-C_3N_4-500$  (b) and  $g-C_3N_4-600$  (c) in 0.02 M H<sub>2</sub>SO<sub>4</sub> aqueous solution.

The pure cellulose in 0.02M H<sub>2</sub>SO<sub>4</sub> aqueous solution was negatively charged. The Zeta potential of pure cellulose measured to be -0.4 mV. And after adsorbing g-C<sub>3</sub>N<sub>4</sub> the Zeta potential became positive, which was measured to be +4.6 mV, +4.3 mV and +0.9 mV for adsorbing g-C<sub>3</sub>N<sub>4</sub>-400, g-C<sub>3</sub>N<sub>4</sub>-500 and g-C<sub>3</sub>N<sub>4</sub>-600, respectively. There is no doubt that g-C<sub>3</sub>N<sub>4</sub>-600 own the lowest cellulose affinity, which could also be confirmed by the optical microscope image of cellulose after adsorbing g-C<sub>3</sub>N<sub>4</sub>. The Zeta potential of cellulose after adsorbing g-C<sub>3</sub>N<sub>4</sub>-400 and g-C<sub>3</sub>N<sub>4</sub>-500 is almost the same, but the Zeta potential of pure g-C<sub>3</sub>N<sub>4</sub>-500 is lower than that of pure g-C<sub>3</sub>N<sub>4</sub>-400, which means more g-C<sub>3</sub>N<sub>4</sub>-500 was adsorbed on the surface of cellulose in 0.02 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. This indicates that g-C<sub>3</sub>N<sub>4</sub>-500 have the highest cellulose affinity.

 HPLC chromatogram and <sup>1</sup>H-NMR spectrum of concentrate reaction solution after the preparation of MCF (Fig. S4).



**Fig. S4** (a) HPLC chromatogram and (b) <sup>1</sup>H-NMR spectrum of concentrate reaction solution after the preparation of MCF.

The reaction conditions including microwave radiation combined with the use of dilute acids and elevated pressure have been proved to be an effective method of removing lignin and hemicellulose. After microwave treatment under 0.02 M  $H_2SO_4$  aqueous solution, hemicelluloses and part of amorphous cellulose will be degraded in the environment of weak acids, and lignin will be decomposed at elevated pressure and temperature. We analyzed the composition of the reaction solution after the preparation of MCF from wood as raw material by <sup>1</sup>H-NMR and HPLC. Soluble sugars and aromatic compounds can be detected in the reaction solution by HPLC and <sup>1</sup>H-NMR, respectively, which are the main products of degradation of lignin and hemicellulose. The results further proves that lignin and hemicellulose have indeed been removed.

 The XRD pattern of obtained MCF from leaf, viscose, corncob, algae, paper, grass, wood and cotton (Fig. S5).



Fig. S5 The XRD pattern of obtained MCF from leaf, viscose, corncob, algae, paper, grass, wood and cotton. The red dotted lines at  $10.6^{\circ}$ ,  $13.2^{\circ}$ ,  $17.9^{\circ}$ ,  $19.5^{\circ}$ ,  $22.2^{\circ}$  and  $27.5^{\circ}$  represent the peaks of g-C<sub>3</sub>N<sub>4</sub>. The blue and red dotted lines at  $15.8^{\circ}$  and  $22.1^{\circ}$  are attributed to cellulose I and cellulose II, respectively.

6. The FT-IR spectra of obtained MCF from cotton, wood, grass, paper, algae, corncob, viscose and leaf (Fig. S6).



**Fig. S6** The FT-IR spectra of obtained MCF from cotton, wood, grass, paper, algae, corncob, viscose and leaf (from the top to the bottom). The FT-IR spectra of MCF from different sources are similar which means that the lignin and hemicellulose are moved by the acid.

7. The SEM micrograph of viscose cellulose after microwave treatment under 0.02 M  $H_2SO_4$  aqueous solution and pure g-C<sub>3</sub>N<sub>4</sub>-500 suspension (Fig. S7).



Fig. S7 The SEM micrograph of viscose cellulose after microwave treatment under  $0.02M H_2SO_4$  aqueous solution (a) and pure g-C<sub>3</sub>N<sub>4</sub>-500 suspension (b).

The SEM micrograph of viscose cellulose after microwave treatment under 0.02M  $H_2SO_4$  aqueous solution can be seen in Fig. S7a. Although the surface of viscose cellulose was severely etched after reacted in 0.02 M  $H_2SO_4$  aqueous, no microfibrils were found. However, the microfibrils can been seen in the surface of viscose fiber with the addition of g-C<sub>3</sub>N<sub>4</sub>-500 (Fig. S7b), which confirms that microfibrils are generated through the interaction between g-C<sub>3</sub>N<sub>4</sub> and cellulose.

8. XRD of raw cellulose materials and  $g-C_3N_4$ -500 before and after reaction (Fig. S8).



**Fig. S8** XRD of raw cellulose materials and g-C3N4-500 before and after reaction. The stability of  $g-C_3N_4$  can be verified by repeated experiments for MCF preparation. Large pieces of wood (5 mm×5 mm×0.2 mm) was used in the repeated experiments for the residuals of wood can be easily removed by a 20 Mesh sieve. In the repeated experiment,  $g-C_3N_4$  was reused and the MCF can also be found after reaction. This shows that the  $g-C_3N_4$  does have the potential to be reused. In addition, the XRD was used to study the structural stability of  $g-C_3N_4$ . The diffraction peaks of the residuals from repeated experiments appearing at 27.5° and 13.2° are consistent with initial  $g-C_3N_4$ -500, which shows that the  $g-C_3N_4$  is stable during the hydrolysis.

9. The natural sunlight-driven photocatalysis of Rhodamine B by the residue containing  $g-C_3N_4$ -500 (Fig. S9).



**Fig. S9** Photocatalytic degradation of Rhodamine B by the residue containing  $g-C_3N_4$ -500 (left), pure  $g-C_3N_4$ -500 (middle) and blank (right) after natural sunlight exposure for 10 min (a), 20 min (b), 30 min (c) and 40 min (d). The natural sunlight-driven photocatalysis was measured from Nov. 8 to Nov. 20 2021 in our laboratory (N 29°55′26″ E 121°37′38″) in Ningbo city, Zhejiang province, China. In this experiment, 0.02g catalyst was suspended into 5 mL mixed dye aqueous solution (RhB: 10 mg/L, pH=7) without stirring.

10.Optical microscope image of residue containing g-C<sub>3</sub>N<sub>4</sub>-500 (Fig. S10).



**Fig. S10** Optical microscope image of residue containing  $g-C_3N_4$ -500. The  $g-C_3N_4$ -500 in the residue is adsorbed on the surface of the viscose which induces a better dispersion of  $g-C_3N_4$ -500. This exposes more catalytic active sites which provides an explanation for the increase in the rate of photocatalytic degradation.