Bamboo fiber molecular-assisted engineering realizes carbon-doped g-C_3N_4 for efficient photocatalytic degradation of tetracycline

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Experimental section

1. Materials and Methods

Chemicals. The bamboo used is called Bambusa ventricosa McClure, which is common in Guangxi, China. Urea was purchased from Tianjin Aopusheng Chemical Co., Ltd., China. Tetracycline (TC), p-benzoquinone(p-BQ), sodium hydroxide, and ethanol were purchased from Shanghai Macklin Biochemical Technology Co., Ltd., China. Nafion™ perfluorinated resin solution, and sodium sulfate anhydrous were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., China. Isopropyl alcohol (IPA), and acetone were purchased from Chengdu Kelong Chemical Co., Ltd., China. Silver nitrate and ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) were provided from Sinopharm Chemical Reagent Co., Ltd., China. All chemicals were of analytical grade and were employed without any additional purification treatment. The pH values were adjusted by 0.5 mM NaOH and H_2SO_4. Deionized water (18.2 MΩ) from the Millipore Milli-Q water purification system was used to prepare all the solutions in the experiments.

Preparation of C-doped g-C_3N_4. Pretreatment of bamboo: The whole bamboo was cut into small pieces with scissors and then grinded into powder in an agate mortar for

30 minutes. Preparation of C-doped g-C_3N_4: the C-doped g-C_3N_4 named as **CCN-x** (x is the mass percentage of bamboo powder to urea, x= 0.5, 1, 2.5, 5) were prepared by high-temperature calcination of pretreated bamboo powder and urea. Briefly, 50 g of urea and different amount of pretreated bamboo powder were mixed in water homogenously through sonication for 10 mins. They were isolated by centrifugation and washed with ethanol and D. I. water for three times alternately. Then, they were dried at 60 °C for 2 hrs under vacuum. After that, the mixtures were transferred into a 100 mL covered alumina dry pot and heated at 400 °C for 2.5 hrs under air atmosphere in a muffle furnace, then at 550 °C for 2 hrs. The grey powders were obtained after cooling down to the room temperature, which was taken out, grinded into powder and stored for further use. For comparison, the pure g-C_3N_4 (named **CN**) with yellow powder was also prepared by high-temperature calcination of urea at the same condition.

Characterization. The crystal structure, and surface chemical structure of the samples were studied by X-ray diffraction (XRD, MiniFlex 600, Japan) and Fourier transform infrared spectroscopy (FT-IR, Spectrum GX, Perkin-Elmer, USA). UV-VIS spectrophotometer (UV-VIS DRS, Lambda 1050+, Perkin-Elmer, USA) was used to check the light absorption characteristics. Scanning electron microscope (SEM, SUPRA 55 Sapphire, Carl Zeiss, Germany) and high-resolution transmission electron microscope (HRTEM, JEM 2100F, Japan) were used to observe the surface morphology. X-ray photoelectron spectroscopy (XPS, Scientific K-Alpha, Thermo, USA) was carried out to check the composition of valence states of elements.

Brunauer Emmett Teller (BET, ASAP 2460, Micromeritics, USA) technique was used to measure the surface area and porous properties of the samples. The dynamics of photogenerated carriers were studied by steady-state photoluminescence (PL, FL-4600, Hitachi, Japan) spectroscopy at a directional wavelength of 350 nm using a fluorescence spectrophotometer. Unpaired spins or paramagnetic centers were detected by electron paramagnetic resonance (EPR, EMXplus-6/1, Bruker, Germany) spectroscopy. The photoelectrochemical property was carried out by an electrochemical analyzer (CHI660E, Shanghai Chenhua).

Photocatalytic activity tests. The light source was generated by a 350 W xenon lamp and passed through a filter ($\lambda > 420$ nm) to simulate visible light. TC was used as a model organic pollutant to evaluate the photocatalytic activity of the prepared samples. 7.5 mg of the photocatalyst sample was dispersed into 15 mL of TC solution (20 mg/L), and stirred thoroughly for 30 mins in a dark environment to reach adsorption-desorption equilibrium. Photodegradation was carried out in a photoreactor (Xujiang Electrochemical Plant, XPA-7, Nanjing, China). 1 mL of suspension was taken out at regular intervals, and the photocatalyst was separated using a water membrane filter with a pore size of 0.22 μm. The absorbance of the TC solution at a wavelength of 356 nm was measured by using UV-visible spectrophotometry. Since there is a linear relationship between the concentration of the reactant and the absorbance, the degradation rate can be calculated through the absorbance. The specific formula is as follows: $X=(A_0-A_t)/A_0\times100\%$, where A_0 and A_t represents the absorbance of the reactant when the light time is 0 and the time is t after being placed in the dark, respectively. Specific quenchers, such as p-BQ (1mM), IPA (1mM) and EDTA-2Na (0.5 mM) were added to the photocatalytic system to determine the superoxide radicals ($\bullet O_2^-$), hydroxyl radical (•OH) and hole (h^+) radicals involved.

Electrochemical experiment. An electrochemical workstation was used to record the photocurrent response (i-t), Mott-Schottky curve (M-S), and electrochemical impedance spectroscopy (EIS) of the samples. The test was carried out in a traditional three-electrode with platinum wire as the counter electrode and Ag/AgCl (3 M KCl) as the reference electrode. The prepared sample (5 mg photocatalyst, 20 μL Nafion) was coated on 5 × 25 × 1.1 mm ITO conductive glass as the working electrode. The electrolyte is sodium sulfate (Na_2SO_4, 0.5 M). To analyze the impedance and band gap of the samples, EIS and M-S tests were performed in the frequency range of 0.01 ~ 1000 k and 1000 Hz respectively. To measure the transient photocurrent of the sample, the xenon lamp was turned on or off every 25 seconds.

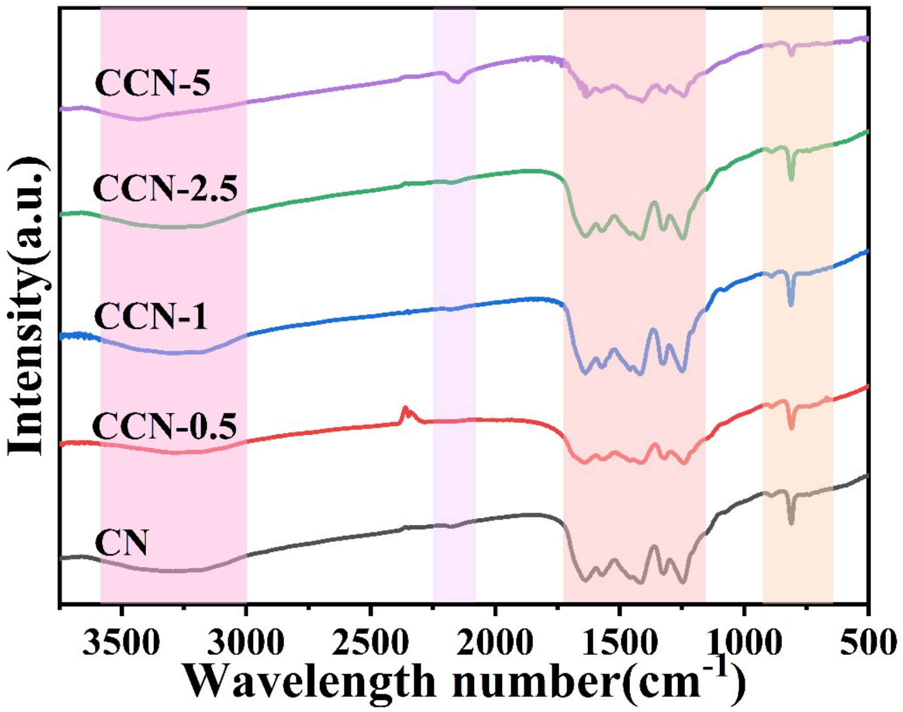

Fig S1. FT-IR images of **CN** and **CCN-x**.

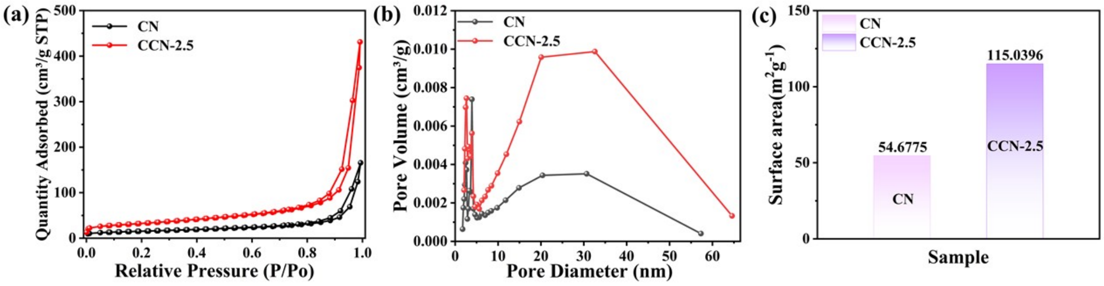

Fig S2. (a) N_2 adsorption and desorption isotherms; (b) pore size distribution; (c) specific surface area of **CN** and **CCN-2.5**.

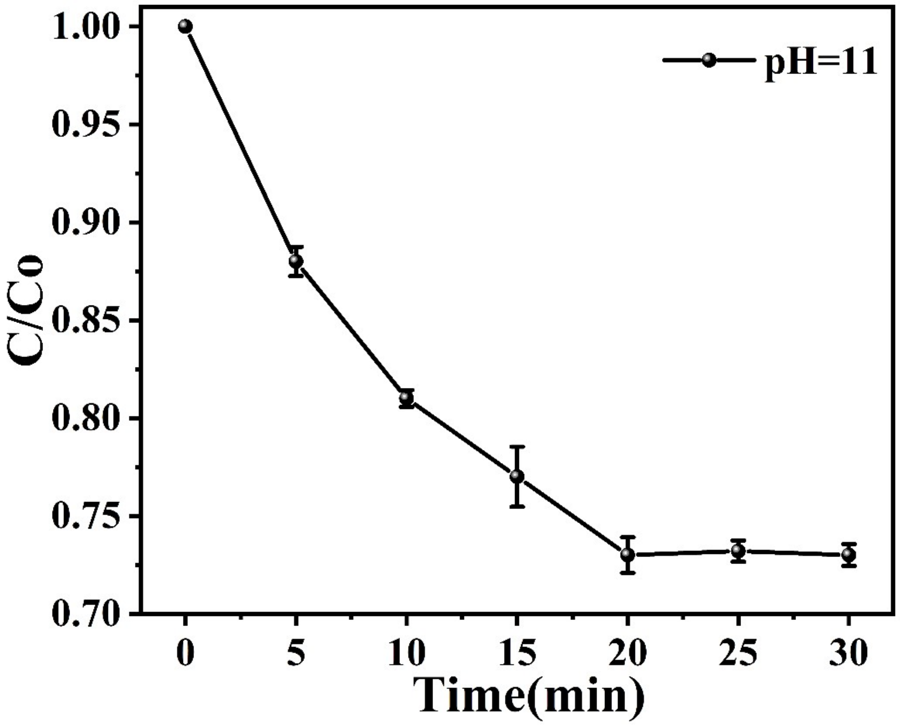

Fig S3. Adsorption experiment of **CCN-2.5** on TC at pH=11.

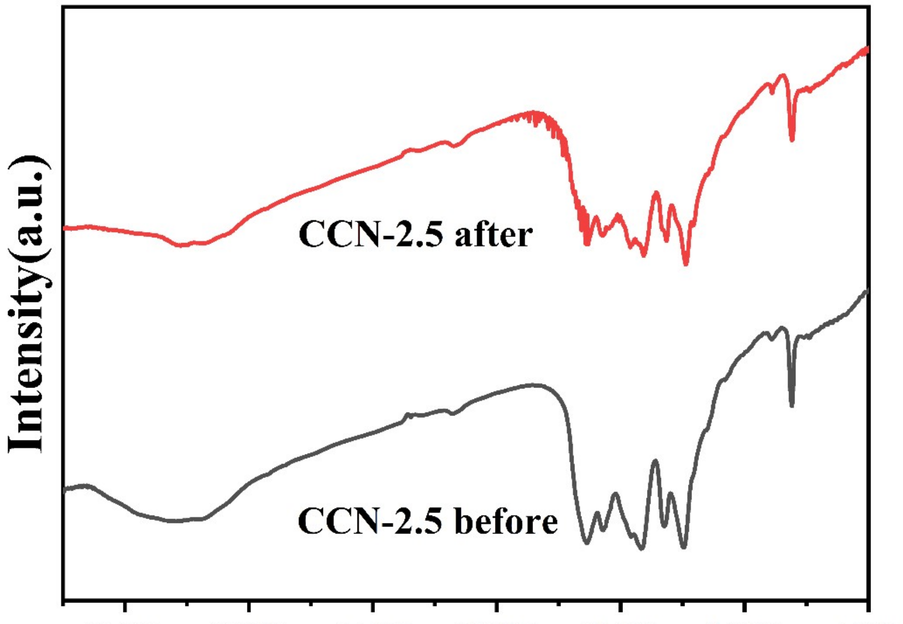

Fig S4. FT-IR images of **CCN-2.5** sample before and after 5 cycles.

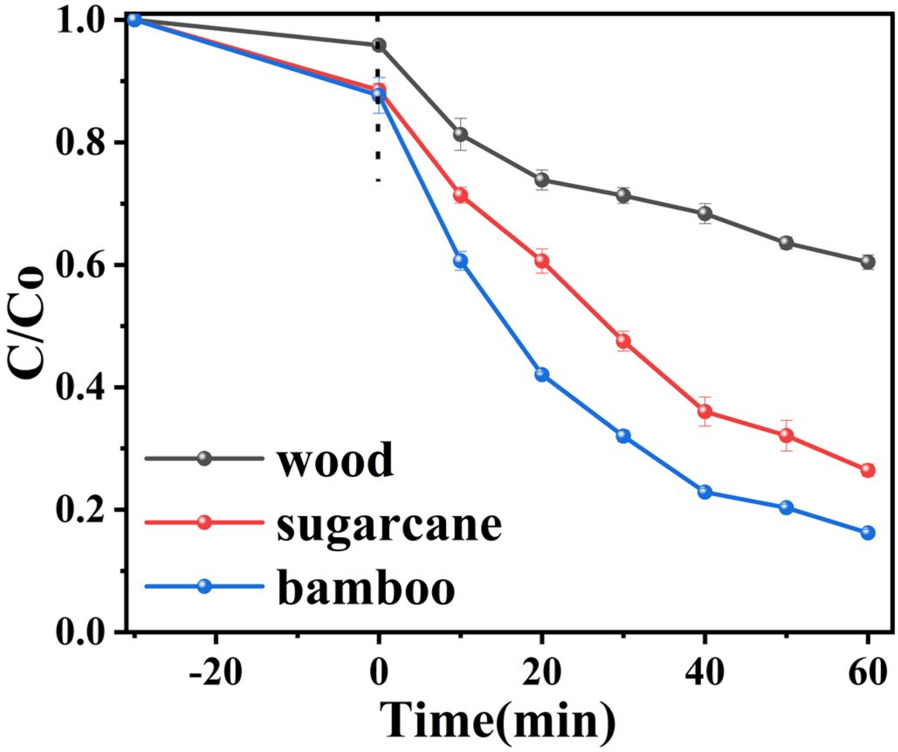

Fig S5. Photocatalytic degradation efficiency of different celluloses as carbon sources.

Table S1 XPS quantitative analysis

Peak BE	CN area CPS.eV	CCN-2.5 area
288.18	116680.71	116432.01
284.80	35400.91	44782.97
286.54	20141.83	20499.25
398.62	224695.12	218574.21
400.24	27904.36	23535.99
401.24	21007.00	21540.68
404.46	19040.83	15950.86

Table S2 Comparison with some existing catalysts

Sample	Pollutant concentration（mg/L）	Sample concentration（g/L）	Time（min）	removal rate（%）	Degradation rate	Ref.
CN-3	20	1.0	240	96.0	0.01007	[1]
CQDs	10	0.5	240	78.6	0.00642	[2]
CNF	20	0.5	70	64.2	0.01420	[3]
CN-Cl-1	10	0.5	120	92.0	0.02010	[4]
PCN	10	1.0	40	30.0	0.00170	[5]
CCN-2.5	20	0.5	60	82.1	0.02653	**This work**

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