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Controllable local electronic migration induced charge separation and red-shift emission in carbon nitride for enhanced photocatalysis and potential phototherapy

Zongzhao Sun[a,b], Yabin Jiang[b], Lei Zeng[b] , Xi Zhang[c], Shuchao Hu[c] and Limin Huang*[b]

[a] *School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China.*

[b] *Department of Chemistry, Southern University of Science and Technology, Shenzhen, Guangdong, 518055, China, Email: huanglm@sustech.edu.cn.*

[c] *Department of Biology, Southern University of Science and Technology, Shenzhen, Guangdong, 518055, China.*

Experimental methods

Preparation of samples

Graphitic carbon nitride (CN) was synthesized according to the previous work. Typically, 10 g urea was placed in an alumina crucible with a cover by thermally decomposing at 550 ^{o}C for 2 h in static air with a ramp rate of 5 ^{o}C min^{-1}. After cooling down, the prepared yellow product was ground and collected for further use.

Benzaldehyde grafted graphitic carbon nitride (CNB) was obtained by following that 10 g urea and 2 ml ethanol including 30 mg benzaldehyde were mixed thoroughly to form the mash, and then put in an alumina crucible with a cover by thermally decomposing at 550 ^{o}C for 2 h at a heating rate of 5 ^{o}C min^{-1}. After cooling to room temperature naturally, the obtained powder was ground and collected for further use.

Fluorobenzaldehyde grafted graphitic carbon nitride (CNF-2) was obtained as the same to CNB except for using about 35.1 mg (~30 μL) fluorobenzaldehyde for a comparable stoichiometric ratio. Other CNF samples (CNF-1, CNF-3, CNF-4) were prepared with various volumes (10, 50, 80 μL) of fluorobenzaldehyde following the above procedure.

Preparation of samples suspensions

5 mg as-prepared CNF simples were mixed with 1 ml deionized water in the mortar to be ground for 20 min. Then the mixtures were transferred to the beaker with additional 4 ml water for 5 h

ultrasonic exfoliation. The obtained suspensions were finally diluted into 50, 100, 200, 400, 750 μg/ml, respectively. All equipment has been disinfected for experimental requirements.

Characterization

Transmission electron microscopy (TEM) was performed on a FEI Tecnai F30 microscope at 300 kV. X-ray diffraction (XRD) was carried out on a Rigaku smartlab system at 45 kV and 200 mA with Cu-Kα radiation. Raman spectra were obtained from thermo Fisher DXR at 532 nm excitation. Fourier transform infrared (FT-IR) spectra were collected on Bruker VERTEX 70 spectrophotometers. Surface chemical analysis was recorded by XPS with Al K X-rays radiation operated at 300W (XPS: Kratos XSAM800 spectrometer, USA). Solid-state ^{13}C NMR was performed with Bruker Advance III 600 Spectrometer. N_2 adsorption-desorption isotherms were conducted with a Micromeritics Model ASAP 2020 instrument at 77 K for surface area analysis. UV–vis absorbance spectra were obtained on a Scan UV–vis spectrophotometer (PerkinElmer, Lambda 750S) at the range of 200–800 nm. The steady-state photoluminescence spectra were acquired by an Edinburgh spectrometer at λ_{ex} = 380 nm. The EPR spectra were carried out by a Bruker EMXPlus-10/12-3.8k spectrometer at a microwave frequency of 9.8 GHz under dark and UV light treatment, respectively.

Photoelectrochemical Analysis

Photoelectrochemical analysis, including Mott-Schottky plot, transient photocurrent response and electrochemical impedance spectroscopy (EIS) were performed on a CHI 660 electrochemical workstation with a three electrode cell consisting of Pt wire, Ag/AgCl electrode and 0.1 M Na_2SO_4 aqueous solution as counter electrode, reference electrode and supporting electrolyte, respectively. Working electrodes were obtained by transferring photocatalyst suspensions (5 mg in 1 mL ethanol with 100 μL 0.05% wt Nafion solution) onto glassy carbon electrode using a dispensing method. Mott-Schottky tests were obtained with the potentials ranging from 0 V to 1 V (vs. Ag/AgCl) at 1000 Hz and 1500 Hz, respectively. The visible light for photocurrent was generated by a full automatic 10W LED lamp with 420~430 nm. And the frequency for EIS was set from 1 MHz to 0.01 Hz.

Photocatalytic hydrogen evolution

Photocatalytic hydrogen evolution tests were carried out in an online photocatalytic hydrogen production system (CEL-SPH2N, CEAULIGHT, Beijing). Typically, 20 mg catalyst was suspended in 50 mL of aqueous solution containing 10 ml triethanolamine as the sacrificial electron donor and 3% wt $H_2PtCl_6 \cdot 6H_2O$ as co-catalyst. The suspension was thoroughly degassed and irradiated by a 300 W Xe lamp (CEAULIGHT CEL-HXF300, Beijing) with a 420 nm filter. The photocatalytic H_2 evolution rate was determined by using an online gas chromatograph (GC D7860, TCD detector, N_2 carrier, 5 Å molecular sieve column, Shanghai Jinghe Chromatograph Co., Ltd). The average intensity of irradiation was measured by a Coherent Fieldax-TO spectroradiometer for the wavelength-dependent apparent quantum yield (AQY) using the 420, 450, 500, 600 nm band-pass filter. And the AQY was estimated as follow:

AQY (%) = 2*number of evolved H_2 molecules/number of incident photons

For a stability test, the system was evacuated every 5 h and repeated 4 times (i.e., a 20 h recycling experiment with intermittent evacuation every 5 h).

Cytotoxicity assay

Typically, the cytotoxicity of CNF suspensions was studied by a 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) cell-viability assay. HeLa cells were activated and seeded into 96-well plates with the number of 6000−7000. After 24 h of incubation with 5% CO_2 at 37 °C, the cells were treated with different amounts of CNF colloidal dispersions (50, 100, 200, 400, 750 μg/ml), and cultured for another 24 h. After that, 20 μL of the as-prepared MTT solution was added to each well and incubated for 4 h at 37 °C. Finally, the cells were lysed by adding 150 μL of DMSO with the plate shaken for 5 minutes. The absorbance was recorded by a microplate reader regulating to 490 nm. In vitro cytotoxicity assay for phototherapy was carried out at the same condition except for adding two contrastive groups treated with 500 nm light for 30 min.

Cell imaging tests

20 μL of CNF colloidal dispersion was added into 6-well cell culture plates containing HeLa cells at a density of 2×104 cells per well. The plate was then incubated for 1 h at 37 °C in 5% CO_2 atmosphere. After that, the cells were fixed with 4% paraformaldehyde for 30 min, and then washed with PBS for three times. The coverslips were mounted on glass slides with glycerinum and examined using a confocal fluorescence microscopy (Zeiss 710 microscope).

Computational methodology

All calculations were performed with the Gaussian 09 program[1] and the M06-2X/def2-TZVP method was used to optimize geometric structures. The g-C_3N_4 was modeled using a $C_6N_{10}H_6$

planar cluster where the dangling bonds of the N atoms were terminated with H atoms to obtain neutral cluster. Due to the influence of size and edge, the properties of finite size model estimation may differ from those of real systems to some extent. However, it can be expected that the results obtained from the current model are qualitatively reliable in predicting local chemical properties. The isosurface maps of valence-electron density were visualized using VESTA software[2]. The natural charges are obtained by natural bond orbital analysis (NBO)[3].

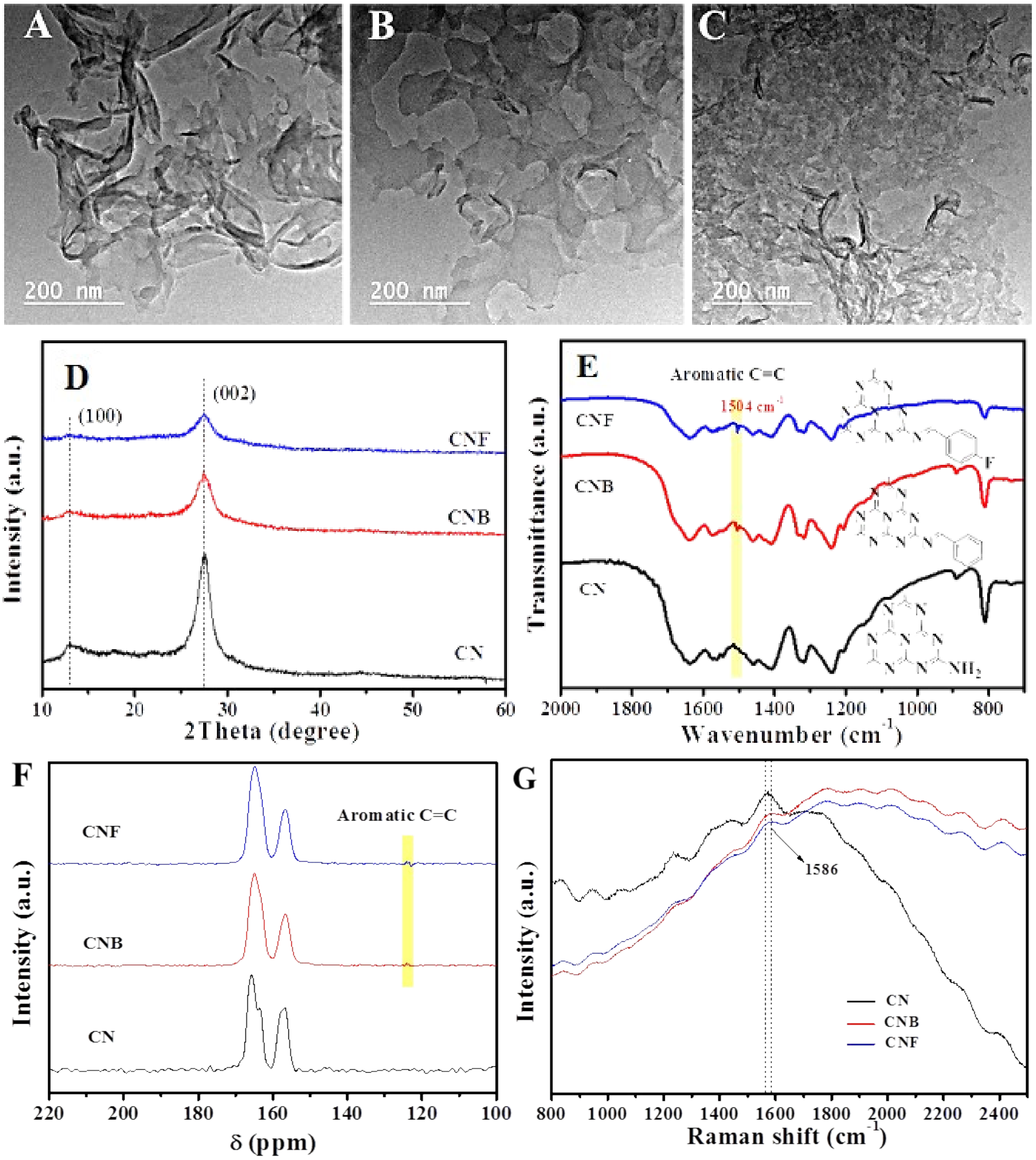


Fig. S1. Typical TEM images of three different samples: A) CN, B) CNB and C) CNF. D) XRD patterns and E) High-resolution FT-IR spectra with the inserts of possible corresponding structures. F) Solid-state ^{13}C NMR and G) Raman spectra of CN, CNB and CNF.

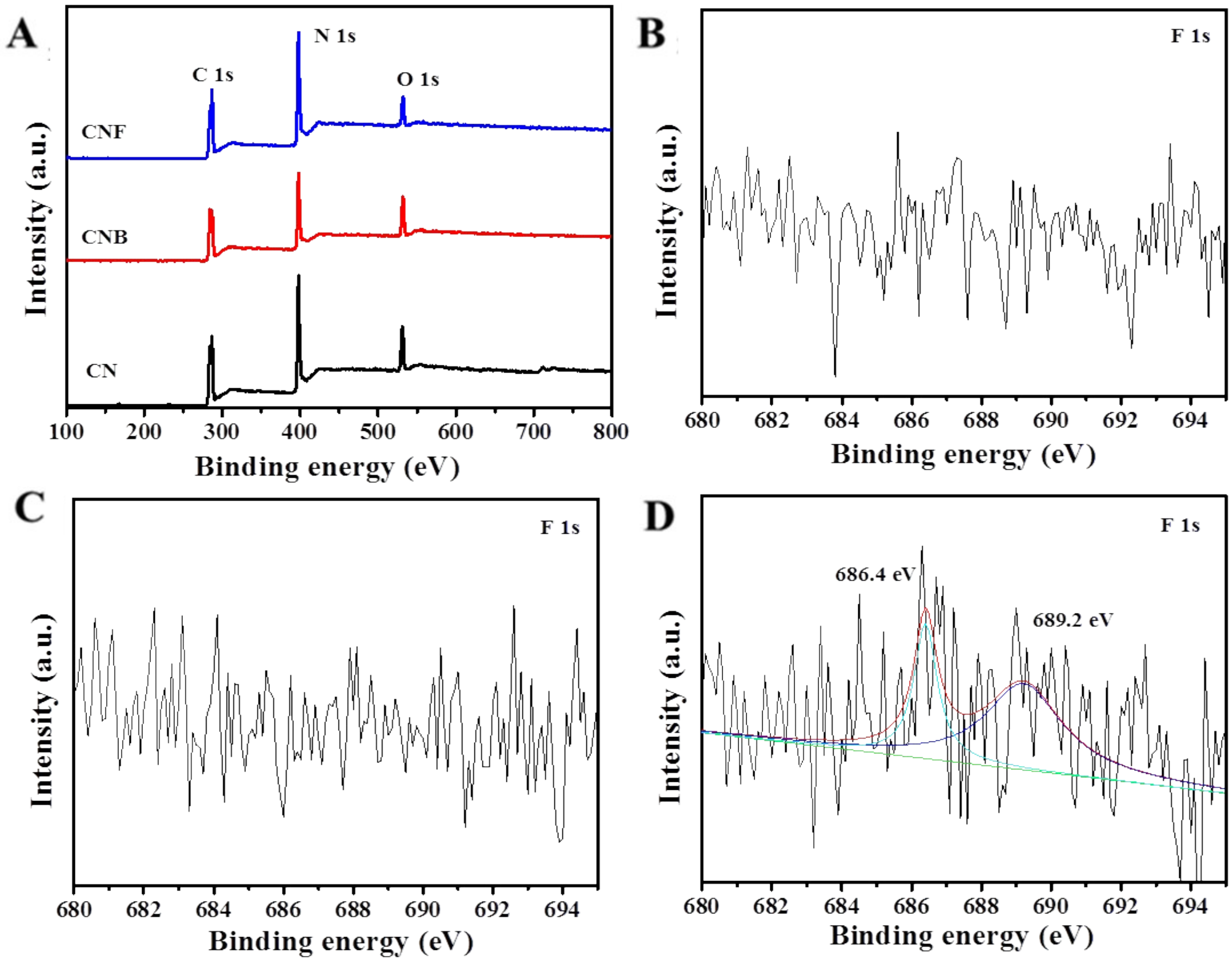


Fig. S2. A) XPS survey spectra and B), C) and D) F 1s XPS spectra of three different samples: CN, CNB and CNF, respectively.

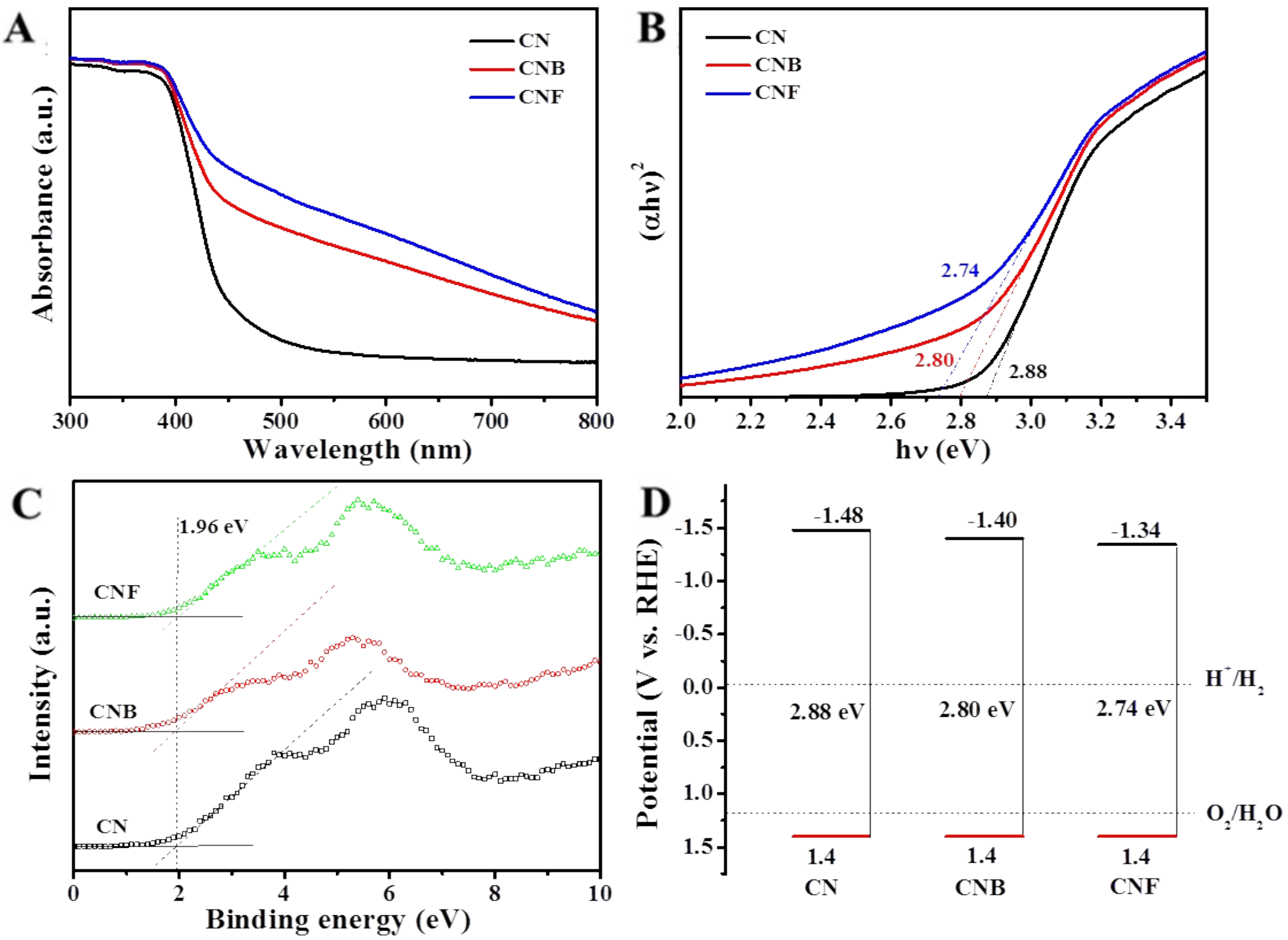
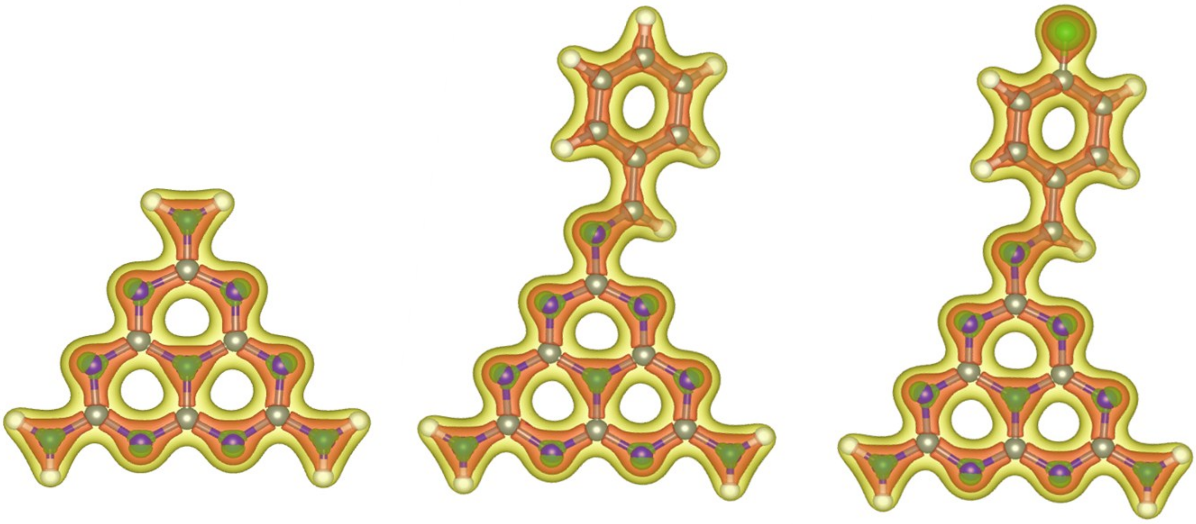


Fig. S3. A) UV–vis absorption spectra, B) Plots of transformed Kubelka-Munk function versus photon energy and C) VB-XPS spectra of three different organic semiconductors: CN, CNB and CNF, with D) the corresponding diagram of band structure.



CN **CNB** **CNF**

Fig. S4. Isosurface maps of valence-electron density, the iso-value of yellow, red and green surface is 0.10 eV/Å^3, 0.25 eV/Å^3 and 0.50 eV/Å^3 respectively.

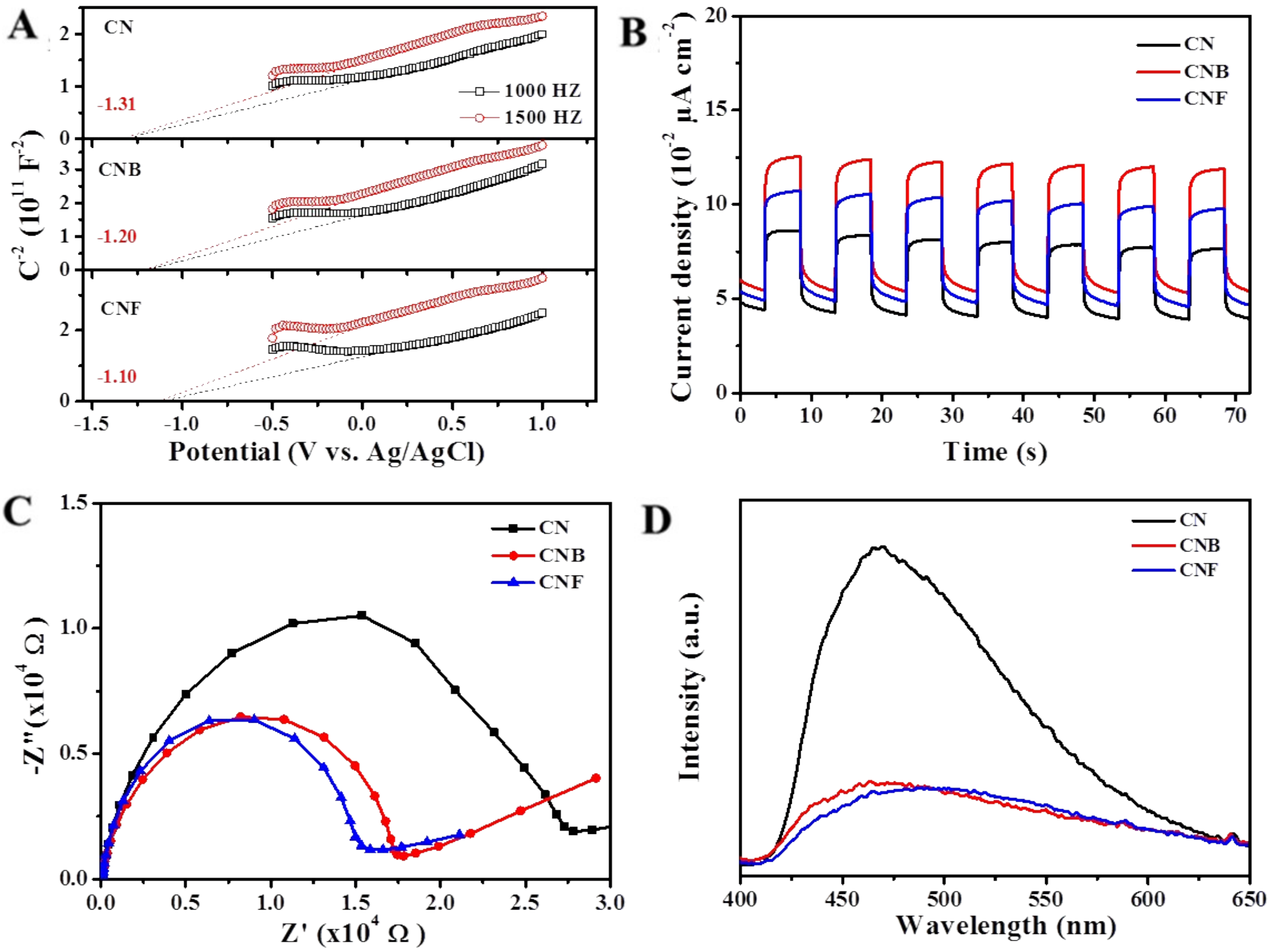


Fig. S5. A) Mott-Schottky plots under different frequency 1000 Hz and 1500 Hz. B) Periodic on/off photocurrent responses under 420±10 nm light treatment, C) Electrochemical impedance spectroscopy (EIS) Nyquist plots in the dark, and D) Photoluminescence spectra (excitation wavelength = 380 nm) for CN, CNB and CNF.

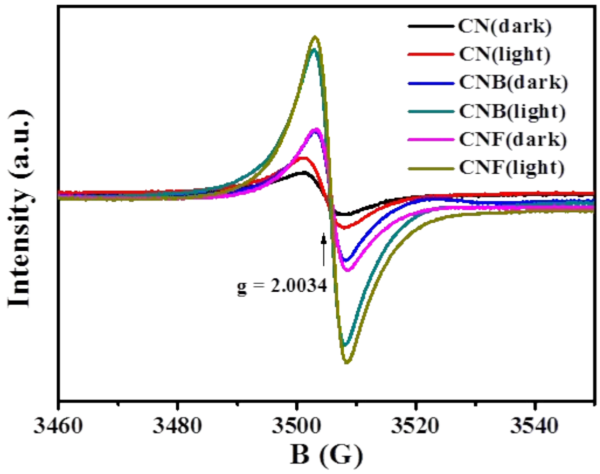


Fig. S6. A) Room-temperature EPR spectra for three different samples: CN, CNB and CNF measured with and without light irradiation.

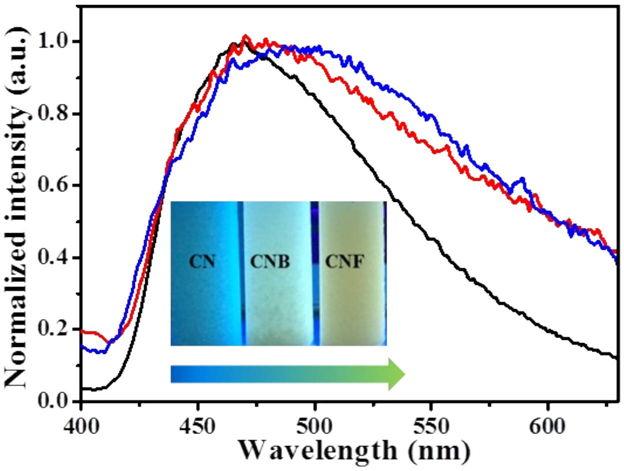


Fig. S7. Normalized photoluminescence spectra (excitation wavelength = 380 nm) for CN, CNB and CNF with the luminescence picture (insert) under UV light.

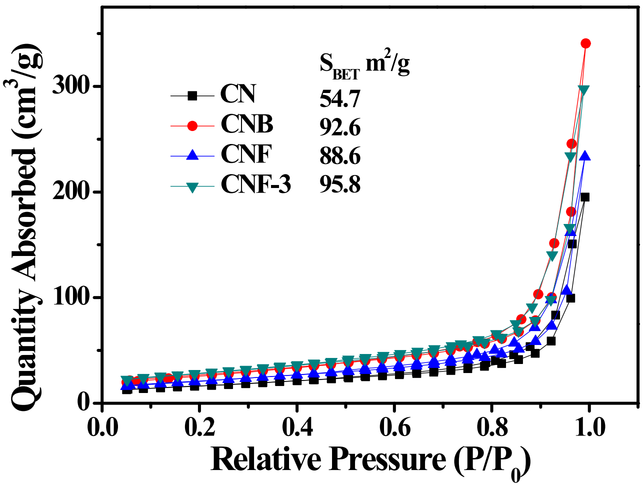


Fig. S8. N_2 isothermal adsorption-desorption curves of CN, CNB, CNF and CNF-3.

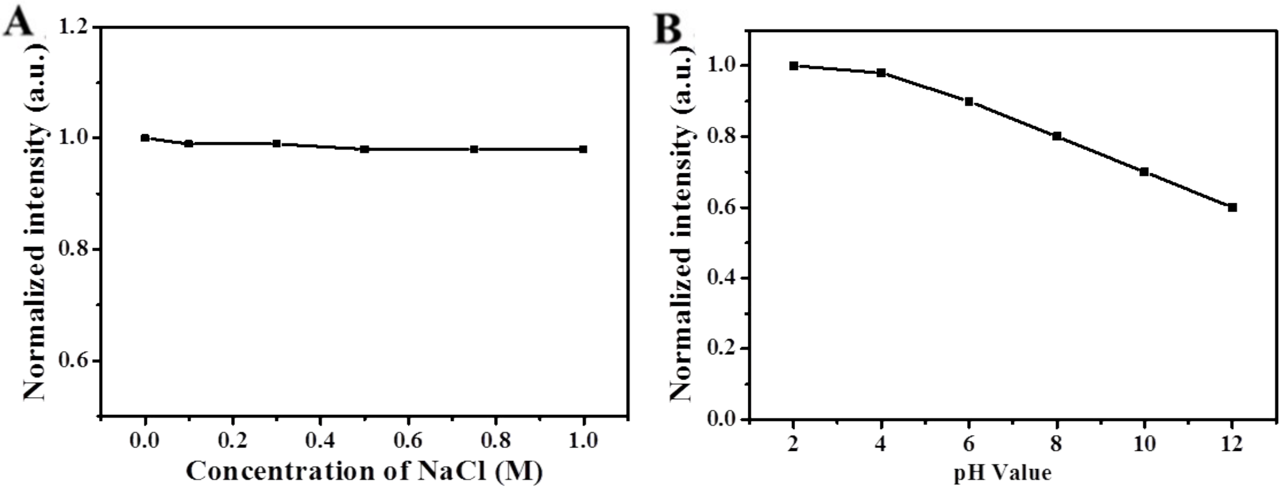


Fig. S9. A) Ion strength and B) pH dependent normalized photoluminescence intensity (excitation wavelength = 380 nm) for exfoliated CNF suspensions.

Table S1 Comparison for the recent similar researches in photocatalytic hydrogen evolution.

Catalysts	**Catalysts mass**	**Cocatalysts**	**Light source**	**Incident light/nm**	**H_2 Rate (μmol/h/g)**	**AQY at 420 nm**	**Ref.**
$g-C_3N_4$ based polymer	100 mg	3wt % Pt	300 W Xe lamp	> 420 nm	4360	4%	1
$g-C_3N_4$ based polymer	100 mg	3wt % Pt	300 W Xe lamp	> 420 nm	2260	_	2
$g-C_3N_4$ based polymer	100 mg	3wt % Pt	300 W Xe lamp	> 420 nm	924	5.5%	3
$g-C_3N_4$ based polymer	100 mg	3wt % Pt	300 W Xe lamp	> 420 nm	1450	_	4
$g-C_3N_4$ based polymer	20 mg	3wt % $H_2PtCl_6 \cdot 6H_2O$ (1wt % Pt)	300 W Xe lamp	> 420 nm	5000	20.98%	This work

Reference:

1. X. Fan, L. Zhang, R. Cheng, M. Wang, M. Li, Y. Zhou and J. Shi, *ACS Catal.*, 2015, **5**, 5008.
2. X. Fan, L. Zhang, M. Wang, W. Huang, Y. Zhou, M. Li, R. Cheng and J. Shi, *Appl. Catal. B Environ.*, 2016, **182**, 68.
3. J. Tian, L. Zhang, X. Fan, Y. Zhou, M. Wang, R. Cheng, M. Li, X. Kan, X. Jin and Z. Liu, *J. Mater. Chem. A*, 2016, **4**, 13814.
4. J. Zhang, G. Zhang, X. Chen, S. Lin, L. Möhlmann, G. Dołęga, G. Lipner, M. Antonietti, S. Blechert and X. Wang, *Angew. Chem.*, 2012, **51**, 3237.