

Electronic Supplementary Information

**Bio-templated Fabrication of the Metal-Free Boron Carbon Nitride
Tubes for Visible Light Photocatalysis**

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Experimental section

Materials. Urea, boric acid, glucose, triethanolamine (TEOA) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were purchased from China Sinopharm Chemical reagent Co. Ltd. All the chemical reagents were used in this work without further purification. Kapok tree fibres were purchased from natural plant extracts workshops (Guangxi, China). KFs are chemically composed of 13% lignin, 23% pentosan and 64% cellulose.

Solvent-treatment of kapok (KFs): To fabricate the nanocomposite, we used Kapok tree fibres (KFs)¹ as both the template and the carbon source or part of the carbon source. The commercial KFs were cleaned by acetone and ethanol for several times to remove wax from the surface, and then dried at 60 °C overnight to evaporate the residual liquids under vacuum.

Biotemplated fabrication of BCN tubes (BCNTs): BCN was synthesized according to ref². Herein, we develop such a carbon-doping synthesis strategy by using a pyrolysis method. Boric acid (1g), urea (2g) and different amounts of glucose were dissolved in deionized water (18ml) and the mixture was stirred at 50 °C for 0.5h. Then KFs (1g) were added to the mixture and soaked at 50 °C for 20min, followed by the vigorous sonication at room temperature for 30min, and then drying at 60 °C for 24h to remove the residual liquids under vacuum. After drying, the mixture was put into a tube furnace in an ammonia atmosphere at 1250 °C for 5h with a ramp rate of 5 °C min⁻¹. The obtained samples were named as BCNTs-x, where x (0, 1.0, 2.0, and 3.0) is represents the weight of glucose.

Characterization: Powder X-ray diffraction (XRD) measurements were carried out on a Bruker D8 Advance X-ray diffractometer with Cu-K α 1 radiation ($\lambda=0.1541$ nm). Fourier transform infrared (FT-IR) spectra were performed on a thermo Nicolet Nexus 670 FTIR spectrometer with KBr as the diluents. The UV-Vis diffuse reflectance spectra (DRS) were measured on a Varian Cary 500 Scan UV-Visible system with an integrating sphere using BaSO₄ as a reference. Thermal stability of as-prepared catalysts was verified by thermogravimetric analyzer under nitrogen atmosphere (Netzsch STA 449F3) at a heating rate of 5 °C min⁻¹. Raman spectroscopic measurements were operated on a Renishaw in Via Raman System 1000 with a 532 nm Nd:YAG excitation source at room temperature. Nitrogen adsorption-desorption isotherms were performed at 77 K using Micromeritics ASAP 3035 equipment. The

pore size distribution was estimated with Brrett-Joyner-Halenda (BJH) and the specific surface area (SSA) was determined with the Beunauer-Emmett-Teller (BET) method. The scanning emission microscope (SEM) measurements were carried out by using Hitachi S4800 Field Emission Scanning Electron Microscope. Transmission electron microscopy (TEM) was obtained using Tecnai G²F20 microscopy. X-Ray photoelectron spectroscopy (XPS) data were collected on a Thermo Scientific ESCALAB250 instrument with a monochromatized Al K α line source (200 W). All binding energies were referenced to the C 1s peak at 284.6 eV of surface adventitious carbon. Electron paramagnetic resonance (EPR) measurements were recorded on a Bruker model A300 spectrometer. Electrochemical measurements were conducted with a BAS Epsilon Electrochemical System in a conventional three electrode cell, using a Pt plate as the counter electrode and an Ag/AgCl electrode (3 M KCl) as the reference electrode, the working electrode was obtained by dip-coating catalyst slurry on FTO glass, the active area is confined to 0.25 cm².

Photocatalytic hydrogen evolution: Photocatalytic hydrogen production was carried out in a Pyrex top-irradiation reaction vessel linked to a glass closed gas system. Hydrogen production was performed by dispersing 50 mg of catalyst powder in an aqueous solution (100 mL) containing triethanolamine (10 vol.%) as sacrificial electron donor. 1 wt.% Pt was loaded on the surface of photocatalyst by the in-situ photodeposition approach using H₂PtCl₆ dissolved in the reactant solution. The reactant solution was evacuated several times to remove air completely before irradiation under a 300 W Xe-lamp and a water-cooling filter. The wavelength of the incident light was controlled by using appropriate long pass cut-off filters. The temperature of the reaction solution was controlled at room temperature by a flow of cooling water. The generated gases were analyzed by gas chromatography equipped with a thermal conductive detector (TCD).

The apparent quantum efficiency (AQE) for hydrogen evolution was measured in the same experiment set-up, using monochromatic LED lamps as incident light source with band pass filter of 405 nm. The irradiation area was 3 × 3 cm², and the intensity was estimated to be 15.9 mW cm⁻¹ (ILT 950 spectroradiometer). The AQY was calculated as $AQY = Ne/Np * 100\% = 2MN_Ahc/SPt\lambda * 100\%$, where Np is the amount of incident photons, Ne is the amount of reaction electrons. M is the amount of H₂ molecules, N_A is Avogadro constant, h is the Planck constant, c is the speed of light, S

is the irradiation area, P is the intensity of the irradiation, t is the photo-irradiation time, and λ is the wavelength of the monochromatic light.²

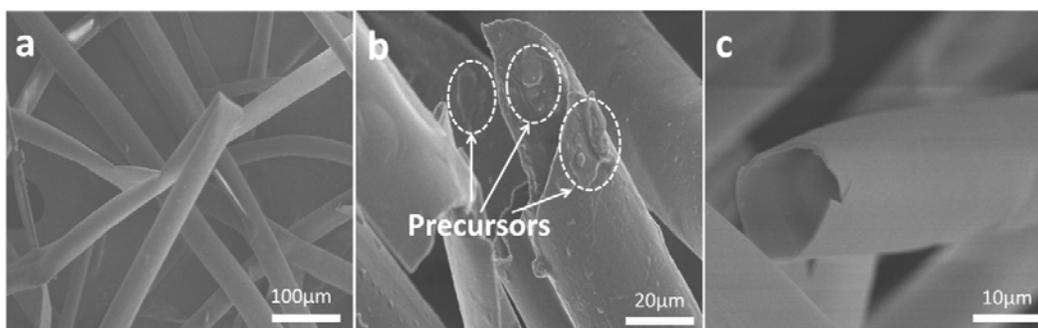


Fig. S1 SEM images of (a) KFs, (b) KFs filled with precursors after drying, and (c) the formation of BCNTs-2 after heating KFs filled with precursors (heating at 1250 °C for 5h in NH₃ atmosphere).

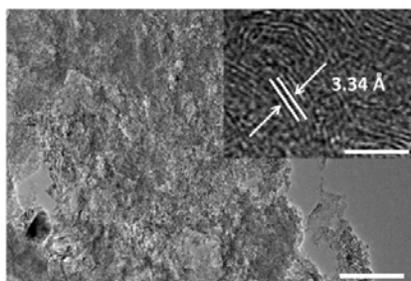


Fig. S2 (c) HRTEM image of the BCNTs-2 sample. Scale bar, 200 nm, inset scale bars, 5 nm.

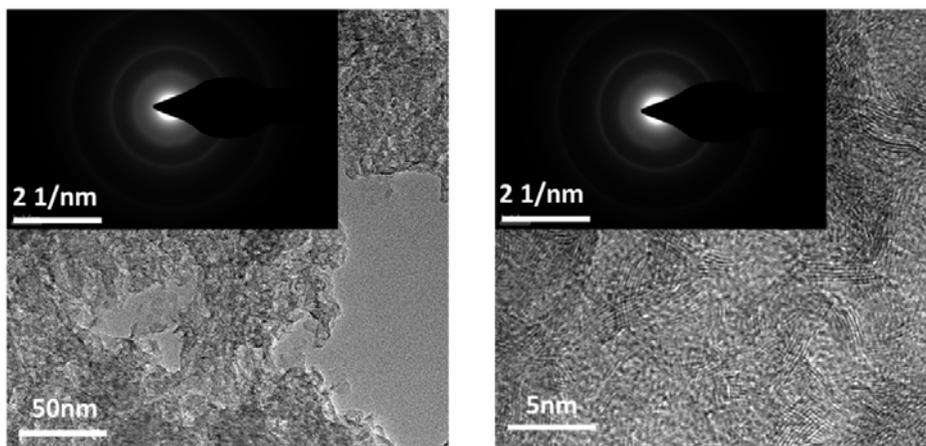


Fig. S3 TEM and selected-area electron diffraction images of BCNTs-2 sample.

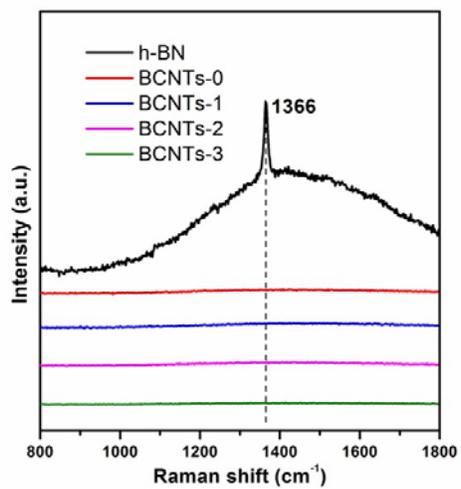


Fig. S4 Raman spectra of BCNTs-x samples.

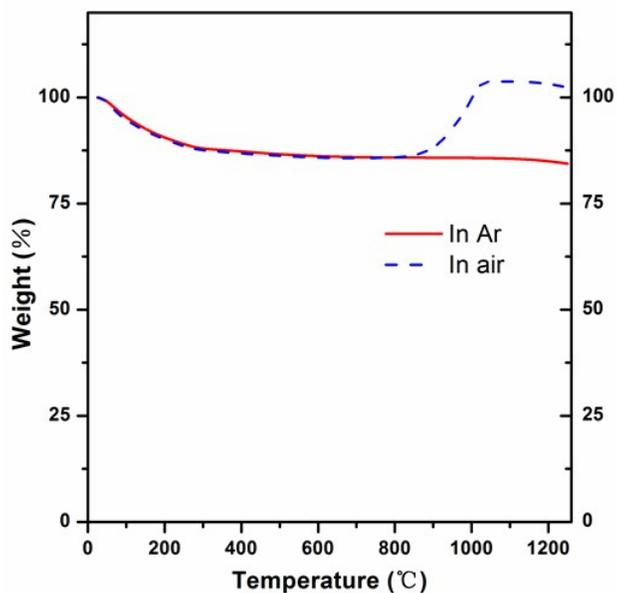


Fig. S5 The thermogravimetric analysis of BCNTs-2 sample. A large mass loss below 200 °C was observed in TG curve, which is due to the evaporation of a lot of absorbed water. There is not obvious weight loss from 200 to 1250 °C, indicating the high thermal stability of BCNTs in Ar atmosphere. When operating in air, we detect that the material is stable up to 800 °C, and the weight is gradually increasing above 800 °C attributed to the oxidation of BCNTs to relevant oxides, like B₂O₃.

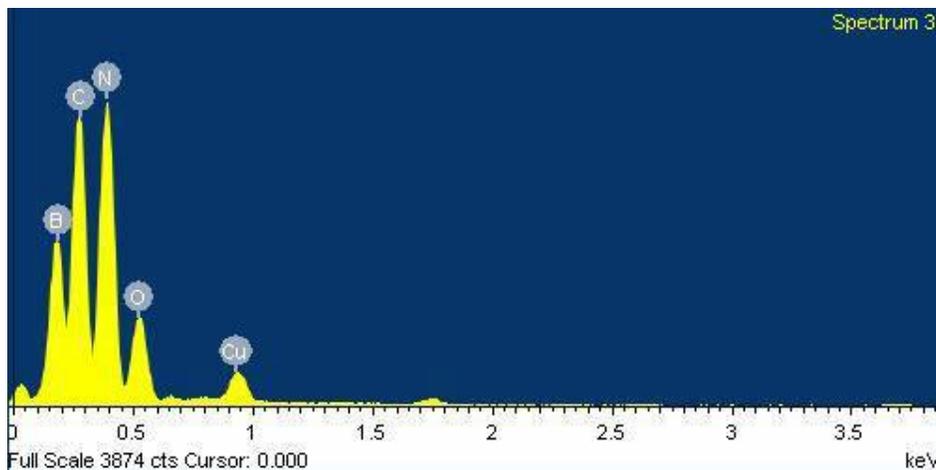


Fig. S6 The energy-dispersive X-ray (EDX) spectroscopy analyses of BCNTs-2 sample. The oxygen is coming from the un-reacted B_2O_3 residues. The Cu is coming from the conductive substrate to load BCNTs-2 sample.

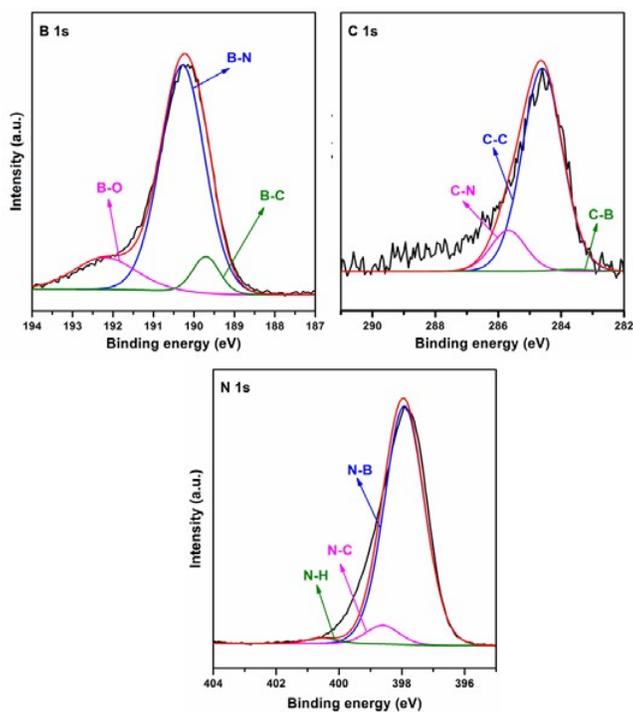


Fig. S7 XPS spectra of the BCNTs-2 sample.

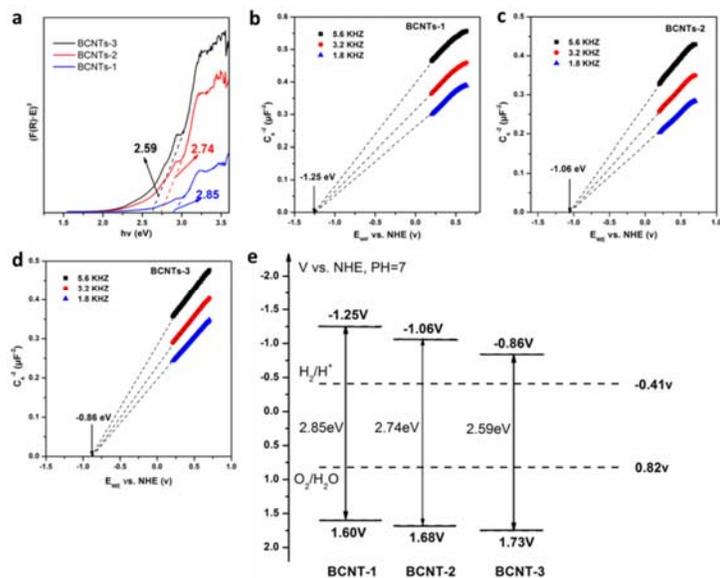


Fig. S8 (a) the $(F(R) \cdot E)^2$ versus E plots of BCNTs-1, BCNTs-2 and BCNTs-3 to determine their band gap energy. (b-d) The determination of the conduction band minimum of the BCNTs samples by Mott-Schottky method. (e) The determined band structure of BCNTs-x with respect to normal hydrogen electrode (NHE), together with the oxidation potential of H_2O to O_2 as well as the reduction level for H^+ to H_2 .

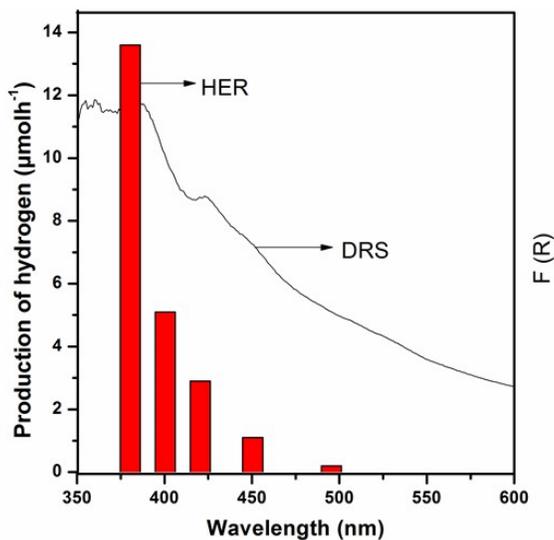


Fig. S9 Wavelength-dependent of HER by Pt/BCNTs-2.

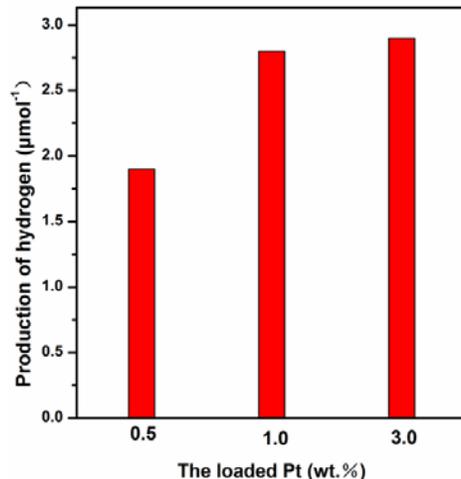


Fig. S10 Photocatalytic activity for hydrogen production from water over BCNTs-2 loaded with different amount of Pt.

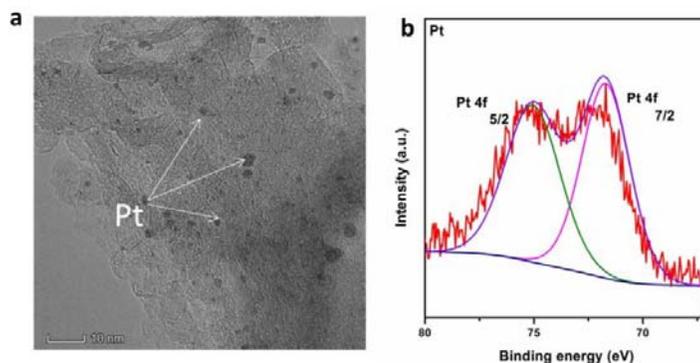


Fig. S11 (a) TEM image of the Pt/BCNTs-2 sample recovered after the photocatalytic reaction. (b) XPS spectrum of Pt for Pt/BCNTs-2 after used for the photochemical hydrogen production under visible light illumination. TEM image of Pt/BCNTs-2 sample shows that there are some dark spots formed on the BCNTs-2 surface due to the deposition of Pt nanoparticles as hydrogen evolution site and cocatalyst. In addition, this evidence is confirmed by the XPS spectrum of used BCNTs-2 sample, and the BE of Pt 4f is observed.³

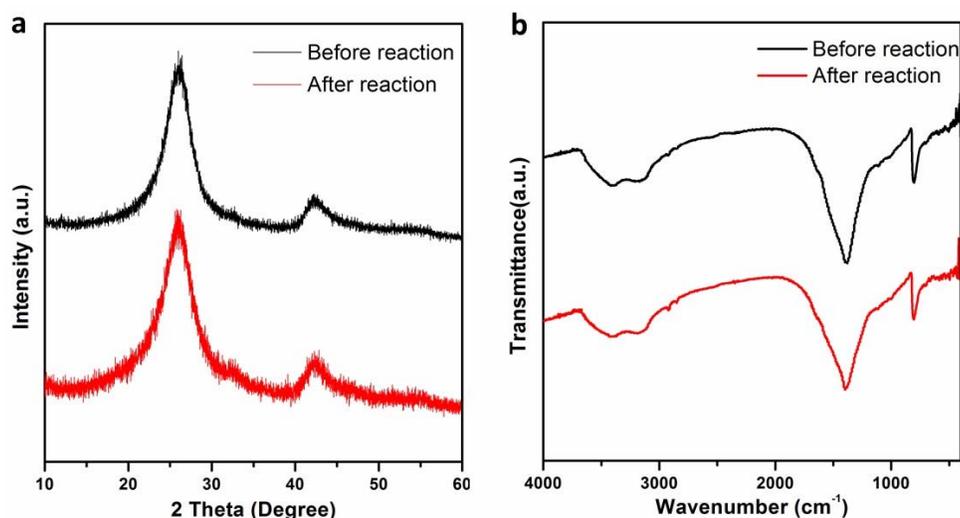


Fig. S12 (a) Powder XRD patterns of the BCNTs-2 sample before (black line) and after reaction (red line). (b) FT-IR spectra of the BCNTs-2 sample before (black line) and after reaction (red line).

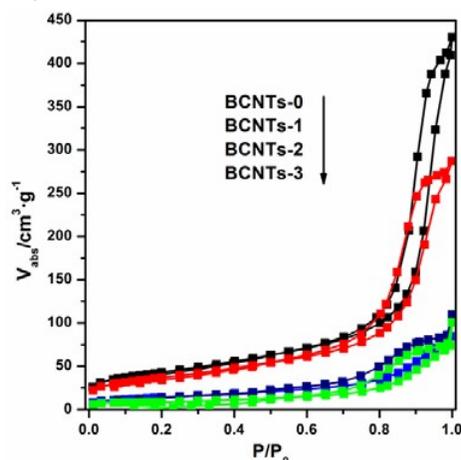


Fig. S13 N₂ adsorption and desorption isotherms of BCNTs samples.

Table S1. Elemental analysis results from XPS for BCNTs samples.

Sample	Boron (Wt. %)	Carbon (Wt. %)	Nitrogen (Wt. %)	Oxygen (Wt. %)
BCNT-0	43.8	7.4	36.7	12.1
BCNT-1	41.8	10.3	37.3	10.6
BCNT-2	39.3	12.5	36.4	11.8
BCNT-3	39.5	15.6	32.4	12.5

Table S2. AQE for photocatalytic hydrogen evolution over 1.0 wt% Pt-loaded BCNTs-x samples, using LED lamps as the incident light (405 nm).

Sample	AQE (%)
BCNTs-0	0.05
BCNTs-1	0.14
BCNTs-2	0.32
BCNTs-3	0.18

Table S3. The BET surface areas of the BCNTs-x and their catalytic activity for hydrogen evolution rate from water by 1.0wt% Pt loaded BCNTs samples under visible light ($\lambda > 420$ nm).

Sample	HER ^[a] ($\mu\text{mol}\cdot\text{h}^{-1}$)	Specific surface area ($\text{m}^2\cdot\text{g}^{-1}$)
BCNTs-0	1.1	151
BCNTs-1	2.1	131
BCNTs-2	2.8	51
BCNTs-3	2.3	29

It is worth noting that there is no clear relationship between hydrogen evolution rate and the specific surface area (SSA) of BCNTs samples. This is because the reaction rate in most solid-liquid phase heterogeneous photocatalysis is primarily restricted by charge separation rather than mass transfer as in gas-solid phase heterogeneous photocatalytic system.

- 1 X. Tao, J. Wang, C. Liu, H. Wang, H. Yao, G. Zheng, Z. W. Seh, Q. Cai, W. Li, G. Zhou, C. Zu and Y. Cui, *Nat. Commun.*, 2016, **7**, 11203.
- 2 C. Huang, C. Chen, M. Zhang, L. Lin, X. Ye, S. Lin, M. Antonietti and X. Wang, *Nat. Commun.*, 2015, **6**, 7698.
- 3 D. Zheng, C. Huang and X. Wang, *Nanoscale*, 2015, **7**, 465.