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Supporting Information

One-step Fabrication of Porous Oxygen-doped g-C_3N_4 with Feeble Nitrogen Vacancies for Enhanced Photocatalytic Performance

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Experimental Section

1. Synthesis porous graphitic carbon nitride (g-C_3N_4)

Melamine purchased from Sigma-aldrich and polyvinylpyrrolidone (PVP) bought from Sinopharm Chemical Reagent Co., Ltd were used directly without further treatment. 1.0 g melamine powders and 1.0 mg (0.1 wt%) PVP were grinded thoroughly in a agate mortar. After that, the mixture was transferred to a 20 mL alumina crucible with a cover and heated at 500 ^oC for 2 hours with a ramp rate of 2 ^oC min^{-1} in a muffle in air subsequently.[1] After cooling down to room temperature naturally, the as-prepared aggregate was ground into powder for further use. For the sake of comparison, g-C_3N_4 samples with different content of PVP powders (0, 0.5 and 5.0 mg) were prepared as the processing method described above and labeled as CN-0, CN-0.05, CN-0.1, CN-0.5 and the yields of the obtained g-C_3N_4 were 49.5%, 49.8%, 51.5% and 54.3%, respectively.

2. Characterization methods

The morphologies and structures of the samples were analyzed by transmission electron microscopy (TEM; TECNAI 30, 300 kV) and scanning electron microscopy (SEM; HITACHI S4800). The BET specific surface areas were measured by N_2 adsorption at 77 K on an Quantachrome Instruments (Autosorb 1-C). The specific surface area of photocatalysts was measured by the adsorption isotherm of nitrogen at 77.350 K on a TriStar II 3020 V1.03 apparatus using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was determined by the desorption branch of the isotherm using the Barrett-Joyner-Halanda (BJH) method. The crystal structure of catalysts was studied by X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer with Cu Kα radiation). Infrared transmission was measured using a Fourier transform infrared (FT-IR) spectrophotometer Spectrum (Nicolet). X-ray photoelectron spectroscopy (XPS) measurements were used to study the surface binding elements and element content. The C 1s peak at 284.6 eV was adopted as an internal reference in this work. UV-vis diffuse reflection spectra were carried out with a UV-vis spectrophotometer (CARY 500). Elemental analyses (C, H, N, O) were tested using an elemental analyzer (vario EL a, Elementar Analysensyteme, Germany). Electrochemical impedance spectroscopy (EIS) measurements were conducted in a standard three electrode system with a Parstat 2273 workstation. The Pt foil and Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. Fluoride tin oxide (FTO) conductor glass with 1.0 cm^2 exposing area was used to prepare the working electrode. 10 mg catalyst was well dispersed in 50 μL naphthol and 200 μL dimethyl formamide (DMF). After ultrasonic treatment for 30 min, 20 μL slurry was doped onto the prepared FTO glass and then dried naturally. We used 0.2 M Na_2SO_4 aqueous solution with 10 vol% triethanolamine (TEOA) as the electrolyte.

3. Photocatalytic reactions evaluation

Photocatalytic H_2 production reaction is performed in a 300 mL top irradiation-type Pyrex cell connected to a gas-closed-circulation and evacuation system. The amount of evolved H_2 was monitored by an online gas chromatography (Shimadzu 2014C, TCD detector, argon as carrier gas, 5 Å molecular sieve column). A 300 W Xe arc lamp (CEL-HXBF300) eliminated ultraviolet light by an optical cutoff filter was used as the visible light source (λ>420 nm) and the average light intensity was 70.47 mW cm^{-2}. 3.0 wt% Pt (H_2PtCl_6 as the precursor) as co-catalyst was loaded on the g-C_3N_4 through impregnation method.[2] 30 mg the prepared catalysts was suspended in 100 mL TEOA (10% v/v) liquid solution. The turbid solutions were put in ultrasonic bath for 10 min before the reaction and stirred during the test procedure in order to eliminate sedimentation. In order to determine the photocatalytic reaction rate, the H_2 product amount was tested every 30 min during 2 h. To test the photocatalytic stability of the obtained CN-0.1, the system was irradiated for 28 h and evacuated every 4 h. Before irradiation, no air was present in the gas-closed-circulation system after evacuation thoroughly by vacuum pump.

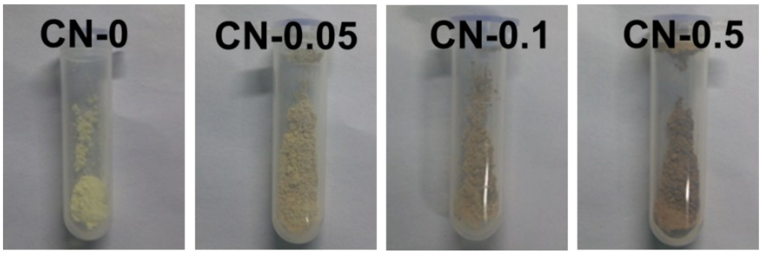

Fig. S1 Photographs of prepared photocatalysts.

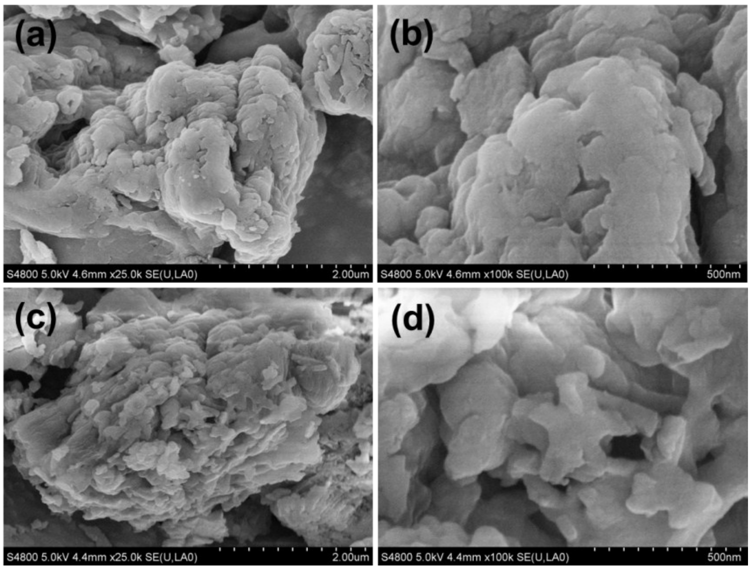

Fig. S2 (a) and (b) SEM imagins of CN-0. (c) and (d) SEM imagins of CN-0.1.

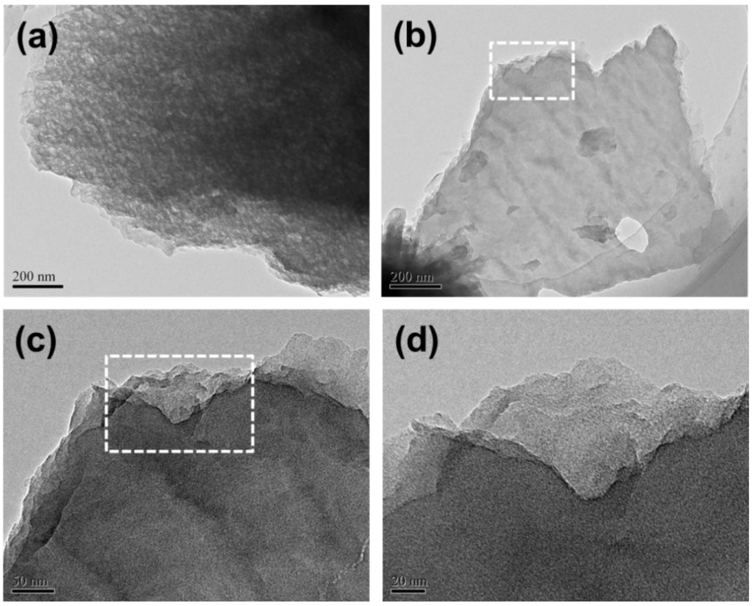

Fig. S3 (a) TEM imagins of CN-0.1. (b), (c) and (d) TEM and HR-TEM imagins of CN-0.

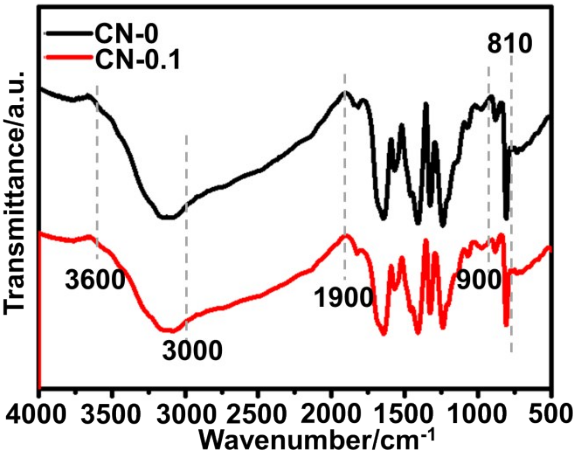

Fig. S4 FT-IR spectra of CN-0 and CN-0.1.

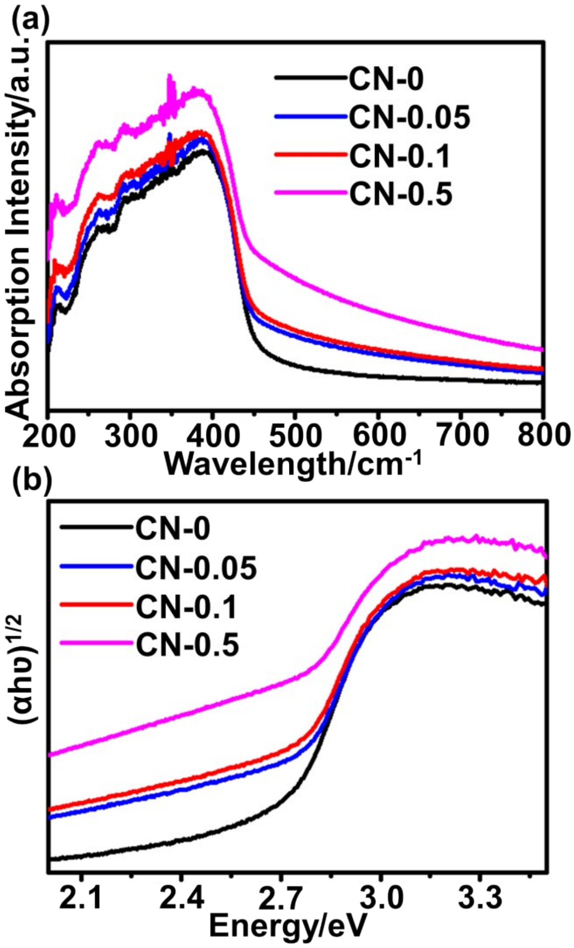

Fig. S5 (a) UV-vis diffuse reflection spectra of CN-x (x = 0, 0.05, 0.1, 0.5). (b) $(ah\upsilon)^{1/2}$ versus $h\upsilon$ curve of CN-x (x = 0, 0.05, 0.1, 0.5).

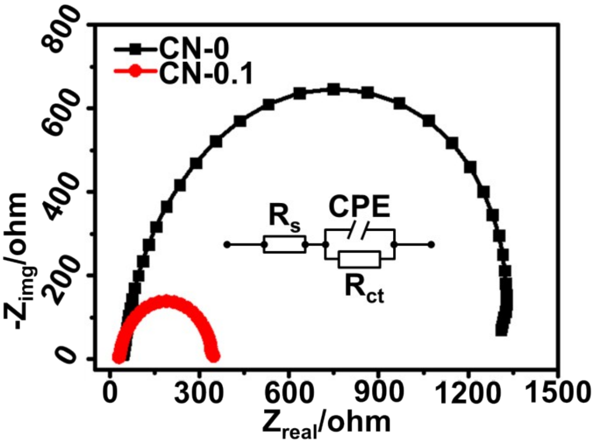

Fig. S6 The EIS results for CN-0 and CN-0.1.

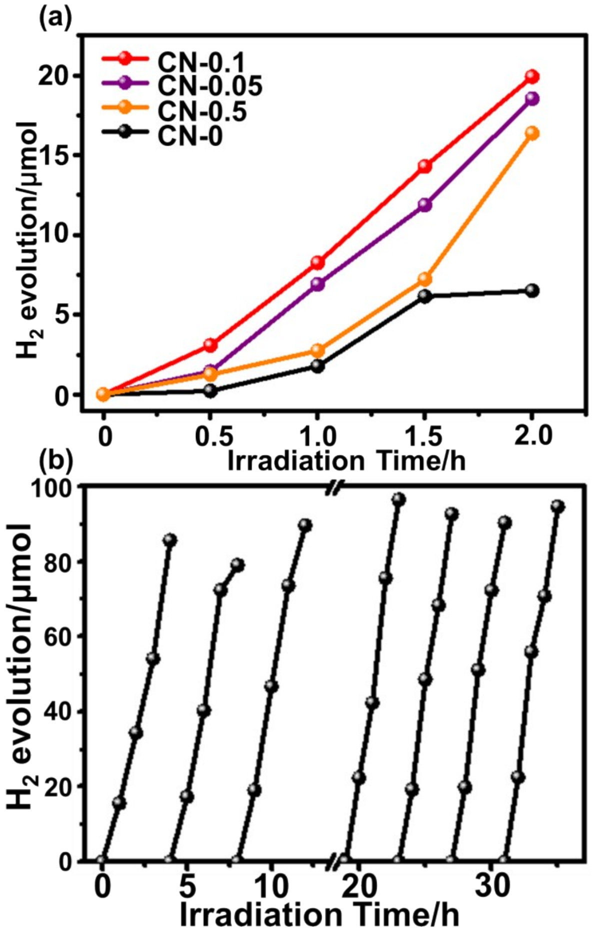

Fig. S7 (a) Photocatalytic H_2 performance within 2.0 h. (b) Photocatalytic durability test for CN-0.1. All the experiments were carried out in the presence of 30 mg catalysts, 3 wt% Pt as the co-catalyst and 10 vol% TEOA functioned as sacrificial agent in aqueous solution at room temperature under visible light irradiation (λ>420 nm).

References

1. Z. Xing, Z. Chen, X. Zong and L. Wang, *Chem. Commun.*, 2014, 50, 6762-676.
2. X. L. Wang, W. Liu, Y. –Y. Yu, Y. Song, W. Q. Fang, D. Wei, X. –Q. Gong, Y. –F. Yao and H. G. Yang, *Nat Commun.*, 2016, 7.