Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Facile implantation of imidazole-ring into carbon nitride for efficient photocatalytic hydrogen production

Siyuan He, Guanchao Wang and Zhongkui Zhao*

State Key Laboratory of Fine Chemicals, Department of Catalysis Chemistry and Engineering,
School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China.

**Corresponding author：E-mail:* *zkzhao@dlut.edu.cn*

Materials

Urea (>99%) was purchased from Tianjin Damao Chemical Reagent Factory. 1-methylimidazolium chloride (Mim, >95%), chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_20$, >37.5 wt%, Pt basis), and triethanolamine (TEOA) were provided by Aladdin. Imidazole (>99%) was supplied by Tianjin Guangfu Fine Chemical Research Institute. Dichloromethane (CH_2Cl_2, >99.5%) was obtained from Tianjin Jindongtianzheng Fine Chemical Reagent Factory. All chemical reagents were utilized without additional purification as they were received.

Preparation of PImM

The polymer was prepared according to our previous work.[1] Generally, 5 g of imidazole and 25 mL of CH_2Cl_2 were loaded into the autoclave and stirred at 300 rpm. Then, the mixture was subsequently polymerized for 10 hours at 1.5 MPa and 95 ^{o}C. Following cooling to atmospheric temperature, the residual CH_2Cl_2 was eliminated via rotary evaporation at 60 ^{o}C. Finally, the yellow and stickypolymer was obtained and labeled as PImM.

Preparation of PI-CN

The PI-CN is prepared by thermal polycondensation of the precursor urea and PImM. The experimental procedure involved melting 20 g of urea in a flask at 140 ^{o}C, followed by adding 200 mg PImM to form a homogeneous solution. The mixture was ground and then placed to a crucible with a lid once it had reached atmospheric temperature. Finally, the crucible was positioned in the center of a muffle furnace, heated to 600 ^{o}C with a heating rate of 5 ^{o}C min^{-1}, and maintained for 3 hours. The brown powders obtained by washing five times with deionized water to remove chloride ions and drying at 60 ^{o}C, labeled as PI-CN. By varying the amount of PImM (x mg, x = 100, 150, 200, 250, 300), a series of CN were prepared, named as PI-CN$_x$.

Preparation of BCN

The preparation of bare carbon nitride was the same as the PI-CN except that PImM was not added. The obtained light yellow powders were grounded and labeled as BCN.

Preparation of MI-CN

The preparation of Mim implanted carbon nitride was the same as the PI-CN except that Mim instead of PImM. The obtained yellow powders were labeled as MI-CN$_x$.

Characterizations of Materials

The morphology of the samples was observed using scanning electron microscopy (SEM) with a JEOL JSM-5600LV instrument, while the transmission electron microscopy (TEM) characterization was performed on a JEOL-2100F (JEOL, Akishima Shi, Japan) field-emission transmission electron microscope (FETEM) operating at an acceleration voltage of 80kV. To analyze the samples' crystal structure, X-ray diffraction (XRD) was carried out using a Rigaku Corporation SmartLab 9kW instrument with a CuKα radiation source operating at 40 kV and 40 mA. Fourier transform infrared (FT-IR) spectra were obtained using a Bruker EQUINOX55 infrared spectrometer. The chemical state of the samples was examined using X-ray photoelectron spectroscopy (XPS) with an ESCALAB 250 XPS system equipped with an AlKα X-ray source. N_2 adsorption/desorption isotherms were measured at 77 K using a Beishide instrument. UV-Vis diffuse reflectance spectra (DRS) were obtained with a Lambda 750S spectrometer, utilizing barium sulfate as the reference material. Photoluminescence (PL) spectra were collected using a Hitachi F-7000 fluorescence spectrometer. Finally, electron paramagnetic resonance (EPR) experiments were conducted at a temperature of 25 ^{o}C using a Bruker model A300 spectrometer.

Photoelectrochemical Measurements

The catalysts obtained were deposited onto ITO conductive glass (2 cm × 2 cm) by utilizing the spin-coating technique. Specifically, a slurry was formed by dispersing 10 mg of the catalyst in 400 µL of terpineol through ultrasonication. In each iteration, 50 µL of the slurry was added to the center of the conductive glass and then spun at 2000 rpm for 30 seconds, followed by drying at 65 ^{o}C for 5 minutes. This spin-coating process was repeated five times before the samples were employed for electrochemical analyses.

Electrochemical impedance spectroscopy (EIS), Mott-Schottky plots, and photocurrent measurements were conducted using an electrochemical workstation (CHI660E, Shanghai Chen Hua, China) in a standard three-electrode mode. The working electrode was prepared ITO conductive glass, while the reference electrode and counter-electrode were an Ag/AgCl (saturated KCl solution) electrode and a Pt plate, respectively. The experiment was conducted in a 0.5 M Na_2SO_4 electrolyte at pH 7.1 and 25^{o}C.

Photocatalytic hydrogen evolution tests

In a reactor that was illuminated from the top and sealed from the environment, hydrogen was generated via photocatalytic water-splitting.10 mg of finely ground photocatalyst was dispersed in a solution comprising 10 mL of TEOA and 90 mL of water to initiate the experiment. Then appropriate amount H_2PtCl_6 was added in order to achieve Pt (3 wt%) was loaded on the catalyst by photodeposition. The influence of PImM's mass on HER of PI-CN_x is presented in Fig. S3a and the PI-CN with the optimum mass of PImM in the preparation process shows highest HER. After obtaining the resulting suspension, it was subjected to multiple evacuations to ensure that all the air was completely removed. Finally, the suspension was filled with nitrogen until the atmospheric pressure was reached. Irradiation of the suspension was carried out with a 300 W xenon lamp (PLSSXE300/300UV) through a long-pass filter, which had a cutoff wavelength of 420 nm. The reaction solution was maintained at a temperature of 15^{o}C during the experiment by circulating cooling water. The hydrogen gas was measured using gas chromatography (GC-9790) with a thermal conductivity detector (TCD) and nitrogen as the carrier gas.

Moreover, AQY measurements were performed using band-pass filters with center wavelengths of 400 nm, 420 nm, 450 nm, and 520 nm to determine the wavelength-dependent apparent quantum yield of hydrogen gas evolution.The AQY was calculated utilizing the following formula:

$$\text{AQY (\%)} = \frac{2 \times \text{amount of H2 molecules evolved}}{\text{number of incident photons}} \times 100$$

Supplementary Figures

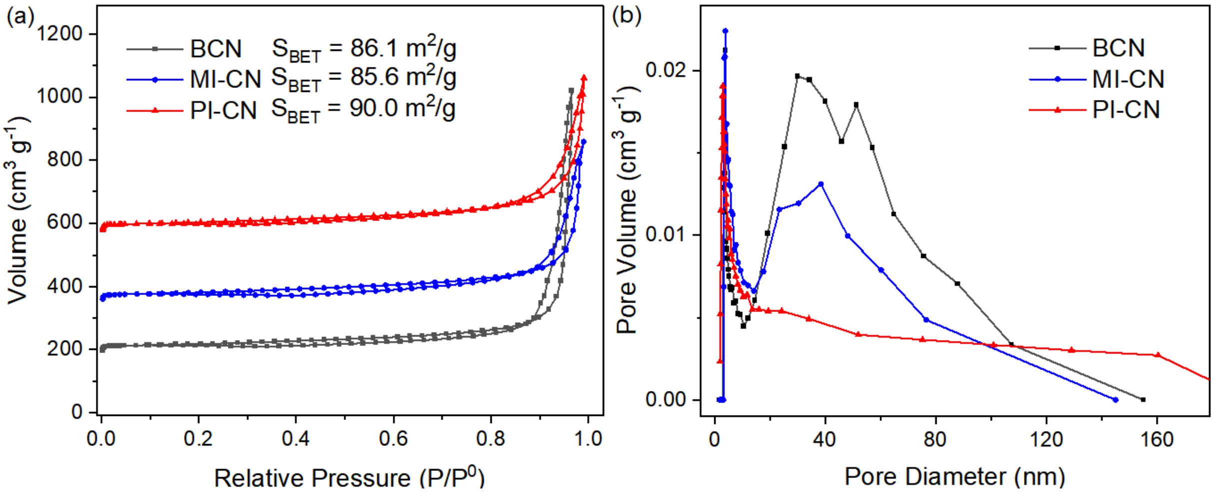

Fig. S1 (a) N_2 adsorption–desorption isotherms and (b) pore size distributions of BCN, MI-CN and PI-CN.

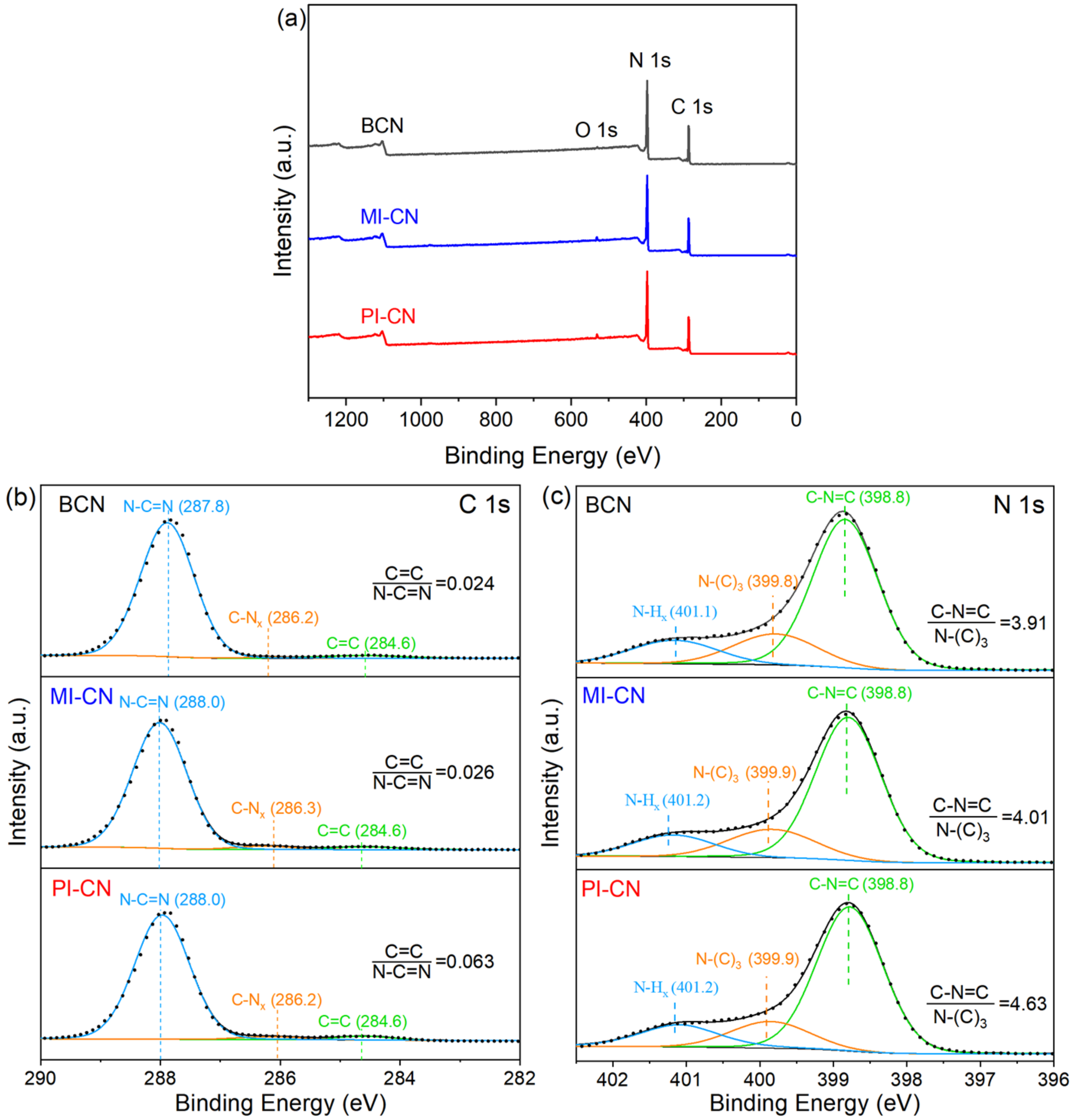

Fig. S2 XPS spectra of BCN, MI-CN and PI-CN: (a) survey, (b) C 1s and (c) N 1s.

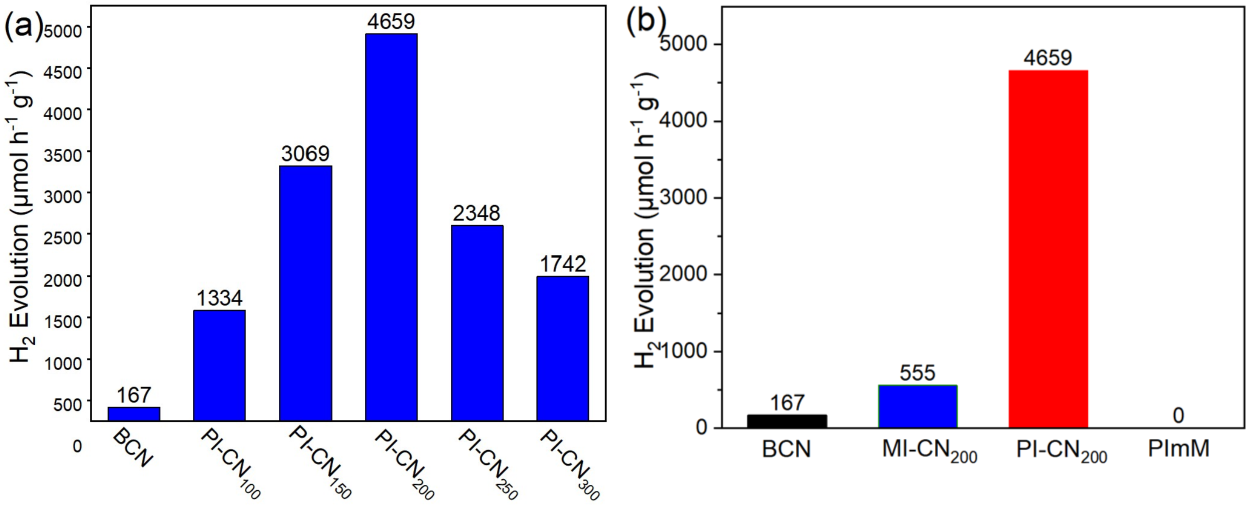

Fig. S3 (a) Influence of PImM mass on HER of PI-CN$_x$, (b) The HER of BCN, MI-CN$_{200}$, PI-CN$_{200}$, and PImM.

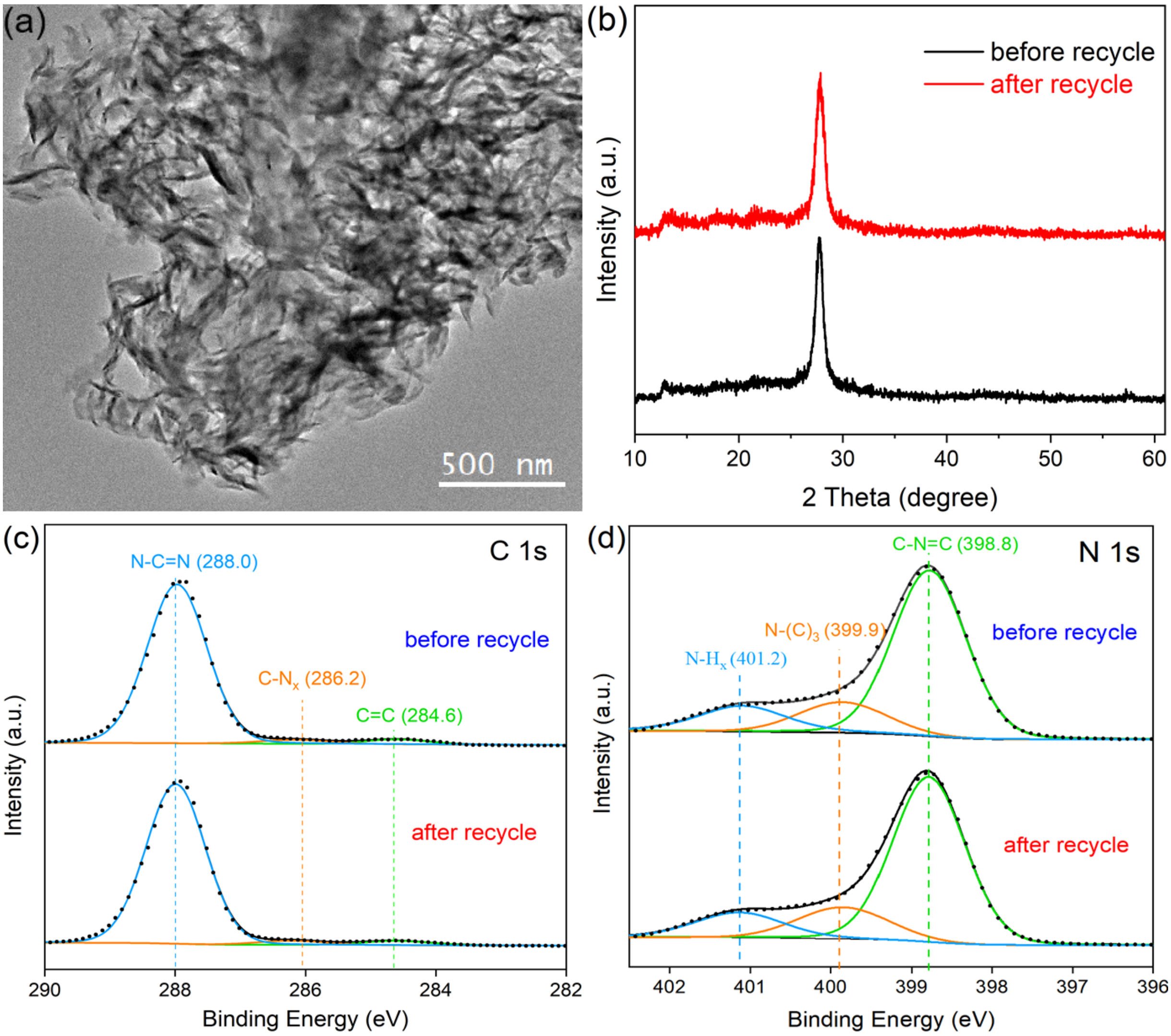

Fig. S4 (a) TEM of PI-CN after recycle, (b) XRD, (c) C 1s , and (d) N 1s XPS spectra of PI-CN before and after recycle.

Supplementary Tables

Table S1. Elemental analysis of the BCN, MI-CN, and PI-CN.

Sample	XPS				OEA		
	C (At%)	N (At%)	C/N_{XPS}	Cl (At%)	C (At%)	N (At%)	C/N_{OEA}
BCN	41.63	57.48	0.72	-	34.19	50.47	0.68
MI-CN	41.79	56.25	0.74	0.04	35.39	50.30	0.70
PI-CN	42.16	55.96	0.75	0.04	35.3	50.13	0.70

Table S2. Recently published C-doped CN materials towards photocatalytic hydrogen generation.

catalysts	Conditions	HER (μmol h^{-1} g^{-1})	AQY (420 nm)	Reference
PI-CN	**photocatalyst (10 mg)** **TEOA (10 vol%), Pt (3 wt%)**	**4659**	**10.1%**	**(this work)**
g-C_3N_4-MF	photocatalyst (50 mg) TEOA (10 vol%), Pt (3 wt%)	3613	8.6%	2
BD-CN	photocatalyst (50 mg) TEOA (10 vol%), Pt (3 wt%)	3160	5.4%	3
CNB NS	photocatalyst (100 mg) TEOA (10 vol%), Pt (3 wt%)	1323	7.4%	4
C2GCN	photocatalyst (30 mg) TEOA (10 vol%), Pt (3 wt%)	2421	2.0%	5
SCN-BTH	photocatalyst (50 mg) TEOA (10 vol%), Pt (1 wt%)	3950	-	6
g-C_3N_4/CDs	photocatalyst (100 mg) TEOA (10 vol%), Pt (1.5 wt%)	1924	-	7
ABT-C_3N_4	photocatalyst (20 mg) TEOA (10 vol%), Pt (2 wt%)	3638	0.2%	8
CCTs	photocatalyst (50 mg) methanol(10 vol%), Pt (3 wt%)	3538	10.9%	9

Light source: 300 W xenon lamp (λ> 420nm).

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