Electronic Supplementary Information

Combining iodic acid and nitric acid to fabricate carbon nitride tubes for enhanced hydrogen evolution under visible light

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Experimental

Synthesis of catalysts

Preparation of Nitric acid-carbon nitride (N-CN): 0.8 g melamine and HNO_3 were dissolved in 80 ml deionized water (the PH value is 1), followed by stirring vigorously for one hour. Then the white mixture was transferred to an autoclave with Teflon liner, heated at 180 °C for 10 hours. The turbid liquid was filtered, washed with deionized water, and dried at 60 °C for 12h. Finally, the powder was calcinated at 500 °C for 4 hours under N_2 flow.

Preparation of Iodic acid-carbon nitride (I-CN): The process is same as above, but replace HNO_3 with 1.5 g HIO_3.

Preparation of I/N-CN: The process is same as above, but use 0.75 g HIO_3 and HNO_3 to adjust PH value.

Preparation of HCN: The process is same as above, however, no acid was introduced.

Materials characterization
Scanning electron microscopy (SEM) images were obtained by using JEOL JSM- 5600LV. X-ray diffraction (XRD) profiles were obtained on an Rigaku Automatic X-ray Diffractometer (D/Max 2400). The XPS spectra were performed on an ESCALAB 250 XPS system with Al Kα X-ray source. Nitrogen adsorption and desorption isotherms were characterized on a Beishide apparatus of model 3H-2000PS1 system at 77 K. Fourier transform infrared (FT-IR) spectra were obtained on Bruker EQUINOX55 infrared spectrometer. The Photoluminescence spectra (PL) were recored on a fluorescence spectrometer (Hitachi F-7000). UV-vis spectra were measured using a UV–Vis spectrometer (JASCO V-550).

Photocatalytic activity measurement

Photocatalytic hydrogen generation reactions of all the samples were carried out in a glass gas circulation system at 15 °C, 10 mg catalyst was added into 100 ml TEOA aqueous solution with a concentration of 10 vol.%. Pt as co-catalyst (3 wt%) was by photodeposition of H_2PtCl_6. Visible irradiation were conducted by a 300W Xenon lamp (PLS-SXE300/300UV, Perfectlight) with a cut-off filter (≥420 nm). The evolved hydrogen was analyed by using gas chromatograph (GC9790, FuLi).

The apparent quantum yield (AQY, %) was measured using 50 mg catalyst in the same system, calculated as follow:

$$AQY (\%)=Ne/Np=2N_{H2}/Np$$

Photoelechemical analysis

The photocurrent responses were carried out on a CHI660E workstation (Chenhua, Shanghai, China) using a conventional three-electrode cell. Pt pole was used as counter electrode, Ag/AgCl electrode as the reference electrode, 0.5 M Na_2SO_4 aqueous solution was used as electrolyte. The working electrodes were prepared as follow: 10 mg of catalyst was suspended in 500 µL terpilenol to form homogeneous suspension that was then dipped and spin-coated onto a 2.0 cm × 2.0 cm indium-tin oxide (ITO) glass.
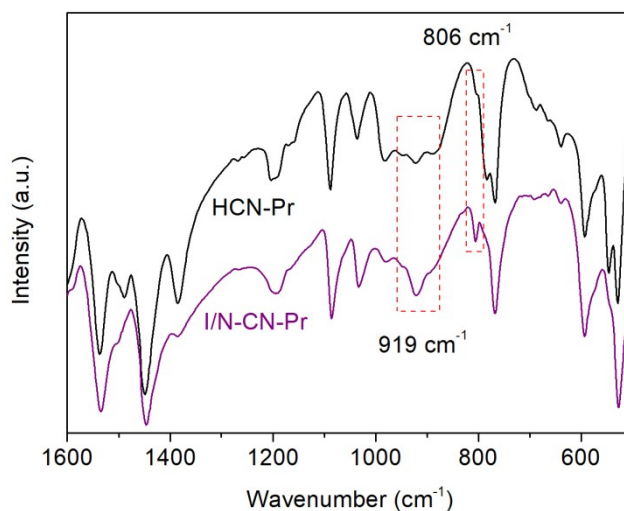

Figure S1 FTIR spectra of HCN precursor, I/N-CN precursor.

To explore the existence of NO_3^- and IO_3^- in the I/N-CN precursor, FTIR spectra was applied (Figure S2). The peak at 919 cm^{-1} is assigned to NO_3^-,[1] the peak in 806 cm^{-1} is ascribed to IO_3^-.[2] These attest to the existence of nitric acid and iodic acid in the supramolecular aggragates.

Table S1

XPS analysis of the samples.

Samples	N (%)	N_{2C} (%)	N_{3C} (%)	C (%)	C-C (%)	C-NH$_X$ (%)	N-C=N (%)
HCN	33.0	82.1	8.6	58.2	47.0	8.1	44.9
N-CN	41.9	64.7	23.4	52.9	34.6	11.5	53.9
I-CN	47.3	69.1	16.3	48.7	34.7	3.4	61.9
I/N-CN	45.2	68.4	20.5	47.8	26.9	12.7	60.6

Table S2

Textural properties of the catalysts.

Samples	S_{BET}[a] ($m^2\ g^{-1}$)	V_{total}[b] ($cm^3\ g^{-1}$)
HCN	13.6	0.14
N-CN	19.9	0.17
I-CN	15.2	0.19
I/N-CN	18.4	0.24

a The total surface area (S_{total}) was obtained from multipoint Brunauer–Emmett–Teller (BET) plots and V–t plots, respectively. b The total pore volume (V_{total}) was determined at P/P0 = 0.99, and the micropore volume (V_{micro}) was calculated from the H-K plot.
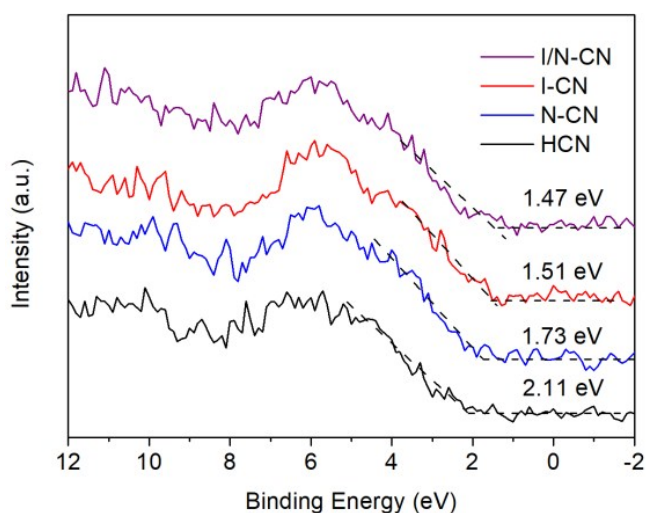

Figure S2 XPS valence band spectra.

1   M. Rivallan, G. Ricchiardi, S. Bordiga and A. Zecchina, *J. Catal.*, 2009, **264**, 104–116
2   G. Pracht and H. D. Lutz, *Thermochim. Acta*, 2000, **354**, 153-160