Supplementary Information

Enhancing visible light absorption for efficient CO_2 reduction with black carbon nitride hollow microspheres

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Experimental section

1.1 Materials

The chemical reagents used for the synthesis of 3D black carbon nitrides were commercially available. Melamine, nitric acid, and glycerol were purchased from Aladdin, Shanghai, China. All the chemicals were used as received without further purification.

1.2 Synthesis of 3D-BCN

In a typical synthesis procedure, First, melamine (2g, 99%) was dissolved in glycerol (60ml, 99%) at 100 ^{o}C under stirring (300 rpm) for about 10min to get a clear solution. Then it was cooled to 60 ^{o}C under stirring. 1.4 ml concentrated nitric acid solution (36.0~38.0w%) was added by pipette and stirred for another 2 min. Then, the mixed solution was transferred into a Teflon-lined stainless-steel autoclave (200 mL) and was heated at 150°C for 12h in an oven. After it cooled down, the mixture was filtered to remove the solvent and the precipitate was washed several times with ethanol (95%) and deionized water, followed by drying overnight at 60°C in a vacuum oven. The resulting solid was heated at 500°C for 2h and with a heating rate of 3°C· min^{-1} without protecting gas flow. PCN was also synthesized by directly heating melamine at 500°C for 2h with a heating rate of 3°C·min^{-1}.

1.3 Photocatalytic activity measurements

The photocatalytic CO_2 reduction test was performed using a batch process under visible-light with a 300 W Xenon lamp. In addition, a 420 nm cutoff filter was used to prevent the UV light. In this experiment, the as-prepared photocatalyst (10 mg) was ultrasonically dispersed in 10 mL of deionized water using a 50 mL round-bottom quartz photo-reactor. Then the reactor was tightly closed with a silicone rubber septum and saturates the solution with CO_2 gas for 30 min before the light illumination. After illumination, the gaseous product such as CO was analyzed by gas chromatography.

1.4 Characterization

The field emission scanning electron microscopy (FESEM S-4800, Hitachi, Japan) was used to characterize the morphology characteristics of the sample products. XRD spectra were recorded on a Bruker D8 Advance diffractometer (Cu Ka radiation). The IR spectra were collected with a Thermo Nicolet iS50 FTIR spectrometer, equipped with an attenuated total reflection (ATR) setup. Elemental analysis was performed with a varioMICRO cube from Elementar Analysensysteme GmbH. Diffuse reflectance absorption spectra were recorded on a Varian Cary 4E UV-vis system equipped with a Labsphere diffuse reflectance accessory. Photoluminescence (PL) spectra were acquired on a Fluorescence Spectrophotometer (F-7000, Hitachi, Japan) at an excitation wavelength of 380 nm. X-ray Photoelectron Spectroscopy (XPS) experiments were performed on

Thermo ESCALAB 250 using monochromatized Al Kα at hυ = 1486.6 eV. Bandgap energy (E_g) of the PCN and 3D-BCN samples were calculated according to the formula below:

$$(\alpha h\upsilon)^{1/n} = C(h\upsilon - E_g)$$

where α, υ, and C are the absorption coefficient, light frequency, and a constant, respectively. The parameter n is a pure number corresponding to different electronic transitions (n = 2 or 1/2 for indirect-allowed or direct-allowed transitions, respectively.

1.5 Photoelectrochemical measurements

Ag/AgCl and Pt electrodes were used as the reference and counter electrodes, respectively. 0.5 m Na_2SO_4 aqueous solutions were used as the electrolytes. The working electrode was described below. First, the as-prepared 5 mg catalyst was dispersed in 1 mL ethanol to form solution A. At the same time, 50 μL Nafion was added into 1 mL ethanol to form solution B. Then, 25 μL of each of A and B were mixed and dropped onto a fixed area (≈1 cm^2) of a fluorine-doped tin oxide (FTO) glass. Finally, the FTO glass was naturally dried to obtain the working electrode. The experiment was conducted using a 300 W Xe lamp with a 420 nm cutoff filter (λ ≥ 420 nm) and adjusted illumination intensity of 100×10^{-3} m·cm^{-2} as a light source. Transient photocurrents were measured at 0.6 V (vs Ag/AgCl). EIS measurements were performed at a potential of 0.6 V (vs Ag/AgCl) and an

amplitude of 5 mV. The frequency range was from 100 kHz to 0.1 Hz. Mott–Schottky tests were conducted with different frequencies of 500, 1000, and 2000 Hz.

1.6 Calculation of energy bands for PCN and 3D-BCN

Fig. 3d shows the Mott-Schottky plots with Ag/AgCl electrode as the reference electrode. PCN and 3D-BCN both have positive fitting slopes, suggesting they are n-type semiconductors. The flat band potentials of PCN and 3D-BCN are -1.09 and -0.99V (vs Ag/AgCl, pH ≈ 7), respectively, which is equivalent to −0.89 and −0.79 V (vs NHE). It is known that the flat band potential is always more positive by about 0.1 V than the CB potential of n-type semiconductor. Thus, the CB potential of PCN and 3D-BCN could be determined as −0.99 and −0.89 V versus NHE, respectively. The downshift of the CB for 3D-BCN is 0.10 eV compared with PCN, which is mainly due to the formation of defect states caused by nitrogen vacancies. Although the CB potential of the 3D-BCN downshifted, which is still more negative than the reduction potential (-0.51 eV) of CO_2/CO. Accordingly, the VB potential for PCN and 3D-BCN is estimated to be +1.70 and +0.74 V versus NHE, respectively, based on the formula below,

$E_g=E_{VB}−E_{CB}$

Meanwhile, the XPS valence band (VB-XPS) spectra are shown in Figure S3a, and the VB-XPS potentials of PCN and 3D-BCN are estimated to be 1.77 and 0.76 eV, respectively. Furthermore, the valence band positions of PCN and 3D-BCN were further analyzed by UPS (Figure S3b); the Fermi energies (E_{Fermi}) are 1.20 and 1.38 eV, and the

secondary cutoff region energies (E_{cutoff}) are 18.00 and 18.20 eV, respectively. Therefore, according to the equations $\Phi = h\nu - E_{cutoff} + E_{Fermi}$ and $E_{VB} = E_H + \Phi - 4.44$ eV, the E_{VB} values of PCN and 3D-BCN are calculated to be 1.75 and 0.72 eV, respectively. Here, $h\nu = 21.22$ eV (a constant) for the incident photon energy and E_H values are the cutoff energies of VB-XPS for PCN and 3D-BCN (1.77 and 0.76 eV).

Table S1 The mass percentage (wt %) of C, N, H and O elements for the PCN and 3D-BCN samples according to elemental analysis

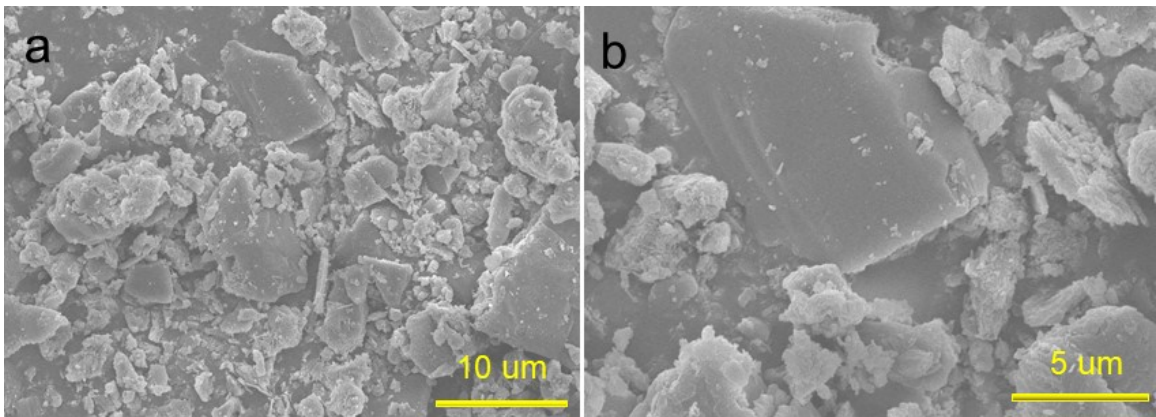| sample	Mass Percentage (wt%)				C/N (atomic molar ratio)
	C	N	H	O	
PCN	34.86	61.89	1.57	1.68	0.66
3D-BCN	37.26	56.69	1.76	4.29	0.81

Fig. S1. SEM images of PCN.
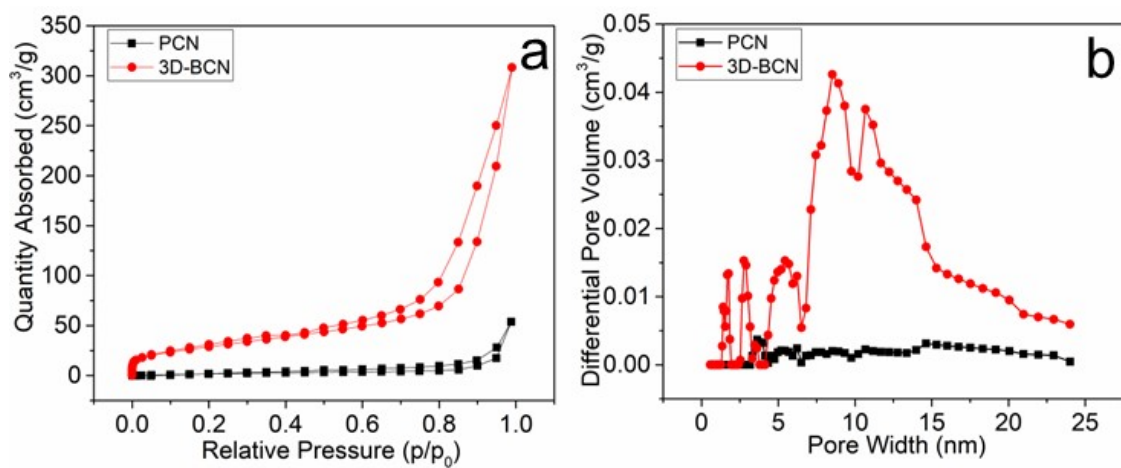
Fig. S2. (a) N_2 adsorption/desorption isotherm and (b) BJH pore size distribution of PCN and 3D-BCN.
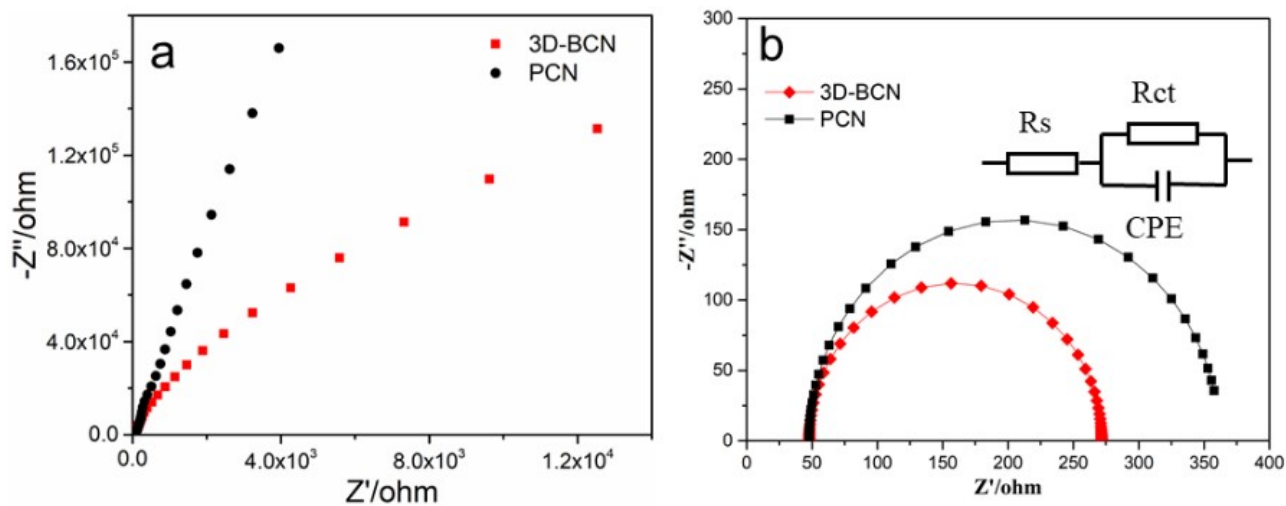
Fig. S3. (a) Electrochemical impedance spectroscopy and (b) Nyquist plots of 3D-BCN; The inset is the equivalent circuit.
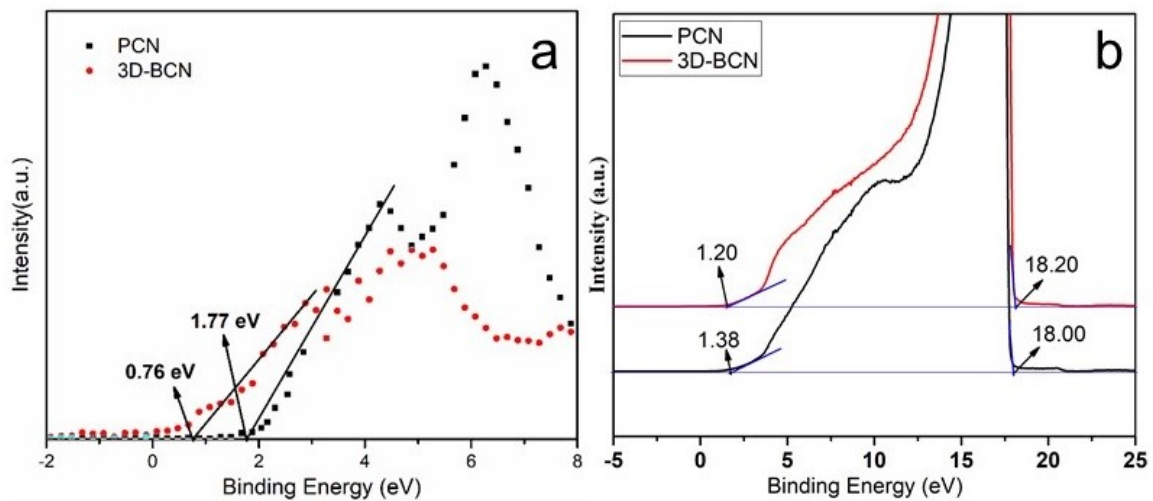
Fig. S4. XPS spectra and the derived valence bands (a) and UPS spectra (b) of PCN and

3D-BCN.