Electronic Supplementary Information (ESI)

Sulfur vacancy rich CdS loaded on filter paper derived 3D nitrogen doped mesoporous carbon carrier for photocatalytic VOCs removal

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Experimental section

Material and method

All chemicals were of reagent grade and used without further purification. Structure of **CP** was performed on X-ray single crystal diffractometer at 293 K (AXS SMART APEX II CCD, Bruker). PXRD patterns were recorded on X-ray diffractometer with CuKR radiation (X'Pert Pro Super, Philips). Raman spectroscopy was conducted with an excitation wavelength of 633 nm (LabRAMHR-800, Horiba). The electron paramagnetic resonance spectrum (EPR) was carried out using an Endorspectrometer (JEOL ES-ED3X). The morphology was observed on an ultra plus field emission scanning electron microscope (SEM, ultra plus, Zeiss) and a transmission electron microscopy (TEM, JEOL, JEM-2100F). XPS was performed with MgKα radiation (1253.6 eV) as an excitation source (ESCALab MKII, Thermo Scientific). N_2 sorption analysis was conducted using an ASAP 2020 instrument (Micromeritics, Norcross, GA) at 77 K using BET calculations for the surface area. Diffuse reflectance spectra (DRS) were recorded on a Shimadzu-2501PC spectrometer by using $BaSO_4$ as a standard. Photoluminescence spectra were measured with a FL-2T2 spectrometer (SPEX, USA).

Synthesis of $[Cd(MMTZ)_2]_n$ (CP)

CP was prepared from the mixture of $Cd(OAc)\cdot 2H_2O$ (0.027 g, 0.1 mmol), MMTZ (0.023 g, 0.2 mmol) and 8 mL H_2O. The pH value of this solution was adjusted to 4.0 with NaOH (1 $mol\cdot L^{-1}$). The mixture was stirred for 30 min, then transferred to an 18 mL Teflon-lined stainless steel bomb and kept at 160 ˚C under autogenously pressure for 120 h. The reaction system was cooled to room temperature during 24 h. A large amount of yellow crystals was obtained. Yield: 88 % (based on Cd).

Synthesis of CdS@3D-NPC

After washed with deionized water and ethanol for three times respectively, the filter paper was cut into rectangular slices (4.0 × 2.5 cm^2). Five filter paper slices were immersed in 50 ml **CP** aqueous solution (30 mM) for 24 h at room temperature and dried at 70 ˚C for 8 h in the oven. Finally, the product was calcination under N_2 protection for 4 h to generate **CdS@3D-NPC**. Before application, the photocatalyst was washed with deionized water and ethanol to removed impurities. The obtained composite photocatalysts were denoted as **CdS@3D-NPC(A)**, **CdS@3D-NPC(B)** and **CdS@3D-NPC(C)** respectively with calcination temperature was 400, 500 and 600 ˚C.

Synthesis of CdS@NC

For comparison, direct calcination production of **CP** was obtained as follows: the powders of **CP** were put in a tube furnace and heated at 400 ˚C for 4 h under N_2 protection. The obtained results were collected, washed with deionized water for several times, and then dried in a vacuum oven at 70 ˚C for 24 h. The product was named as **CdS@NC(A)**. The photocatalysts obtained at 500 and 600 ˚C were donated as **CdS@NC(B)** and **CdS@NC(C)** respectively.

Electrochemical measurements

Photoelectrochemical tests were carried out with a conventional three-electrode system in quartz cell filled with 0.1 M Na_2SO_4 electrolyte (40 mL), with the **CdS@3D-NPC** (1.0 × 1.0 cm^2) serving as the working electrode, a Pt plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. A 300 W Xe lamp (Bejing Perfect Co. Ltd., PLS-SXE-300UV) with a cutoff filter ($\lambda \geq 420$ nm) was used as the excitation light source for visible irradiation. Electrochemical impedance spectra (EIS) were recorded in potentiostatic mode. The amplitude of sinusoidal wave was 10 mV, and the frequency of the sinusoidal wave ranged from 100 kHz to 0.05 Hz.

Photocatalytic degradation of VOCs

Photocatalytic degradation of VOCs was studied in a 2.0 L quartz reactor. The reactor was filled with O_2/N_2 (20 %) at first. Then liquid formaldehyde (or benzene) and water were injected into the reactor and vaporized into gas phase. Finally, photocatalyst (**CdS@3D-NPC**, 2.0 × 2.0 cm^2 or **CdS@NC**, 0.2 g) was fixed in the reactor. Above mentioned light source was used. Before reaction, the sample was kept in dark for 90 min to reach adsorption/desorption equilibrium. The concentrations of VOCs and resulted CO_2 were analyzed by a gas chromatograph (GC7900 equipped with a flame ionization detector and methane reforming furnace). Initial concentration of VOCs was 100 ppm and relative humidity (R. H.) level was kept at 40 %. The degradation rate of VOCs was calculated by the equation of $(1\text{-}c/c_0)$ %, in which c_0 represents initial concentration and c is the concentration at intervals. CO_2 conversion rate was obtained with the equation of (c_{CO2}/c_{total}) %; in which c_{CO2} is the concentration of CO_2 and c_{total} represents theoretic CO_2 concentration produced by VOCs.

To study the kinetic process of this reduction reaction, a set of apparent rate constants (k) were obtained with constant relative humidity (40 %) while varying concentration of VOCs. The concentrations of VOCs were 60, 80, 100, 120, 140 and 160 ppm. Based on above data, the curve of k versus concentration of VOCs was drawn. Langmuir-Hinshelwood model (1) was employed to fit these curve to obtain the adsorption constants of VOCs (K_{VOCs}) and H_2O (K_{water}). In this equation, k represents the surface rate constant; S is the surface area; K_{VOCs} and K_{water} represent adsorption constants of VOCs and H_2O; n and m are the Freundlich exponents.

$$k = k \times S \times K^{n}_{VOCs}(VOCs)^{n-1}(K_{water}[H_2O])^{m}/\{1 + (K_{VOCs}[VOCs])^{n} + (K_{water}[H_2O])^{m}\}^{2} \quad (1)$$

Table S1 Crystal Data and Structure Refinement for **CP**

Empirical formula	$C_6H_8N_6S_2Cd$
Formula weight	340.70
Crystal system	Orthorhombic
Space group	P bcn
a (Å)	13.3099(4)
b (Å)	10.2168(3)
c (Å)	8.0515(3)
V ($Å^3$)	1094.88(6)
Z	4
F (000)	664
Goodness-of-fit on F^2	1.085
R_1 [$I > 2\sigma(I)$]	0.0294
wR_2 [$I > 2\sigma(I)$]	0.0685
R_1 (all data)	0.0352
wR_2 (all data)	0.0743

Table S2 Selected bond lengths and angles of **CP**

Cd(1)-N(1)	2.240	Cd(1)-S(1)	2.498
N(1)-Cd(1)-N(1)	103.35	N(1)-Cd(1)-S(1)	103.94
S(1)-Cd(1)-S(1)	127.95		

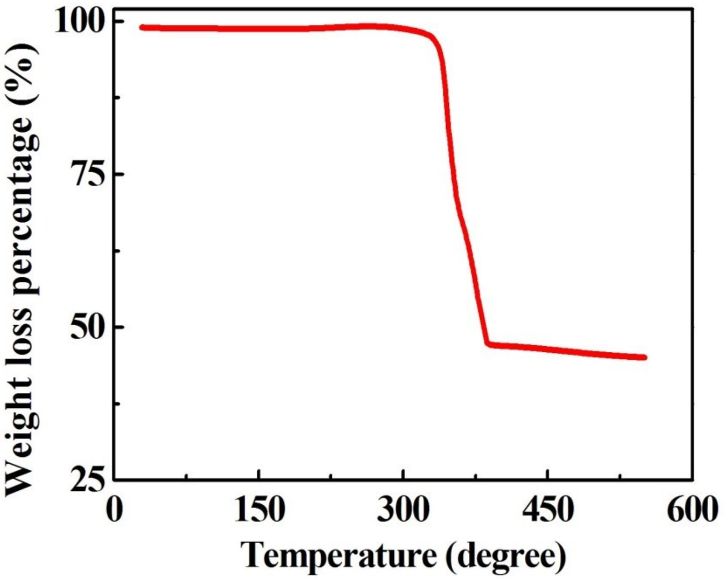

Fig. S1 TGA of **CP**

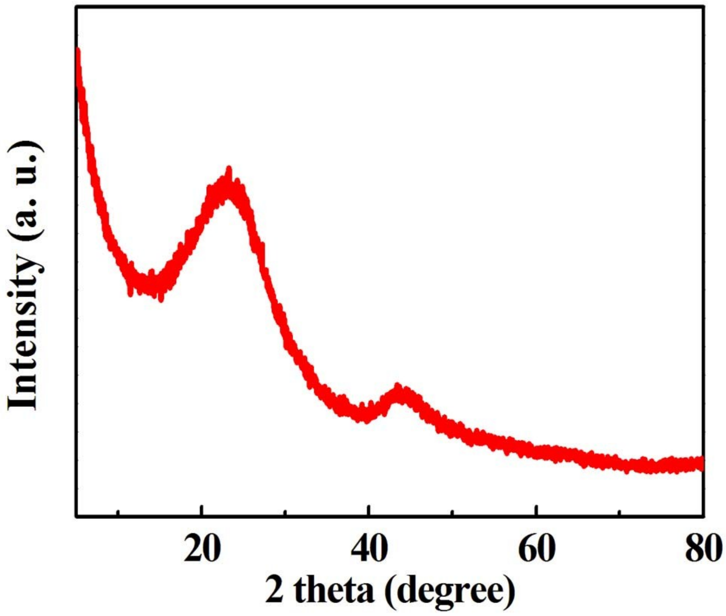

Fig. S2 PXRD of **3D-NPC**

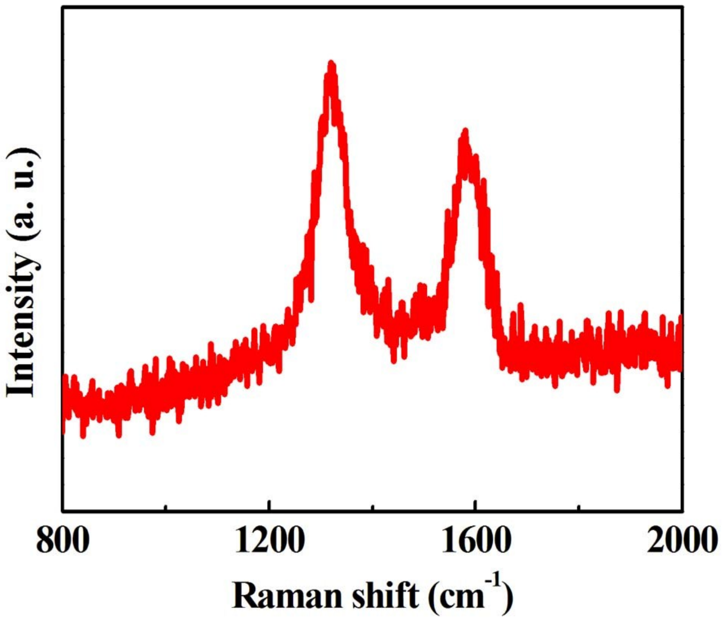

Fig. S3 PXRD of **3D-NPC**

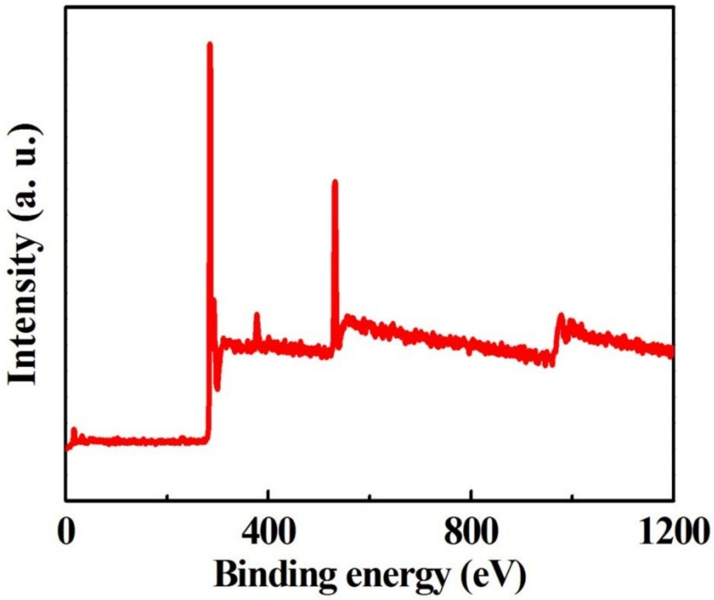

Fig. S4 XPS survey of **3D-NPC**

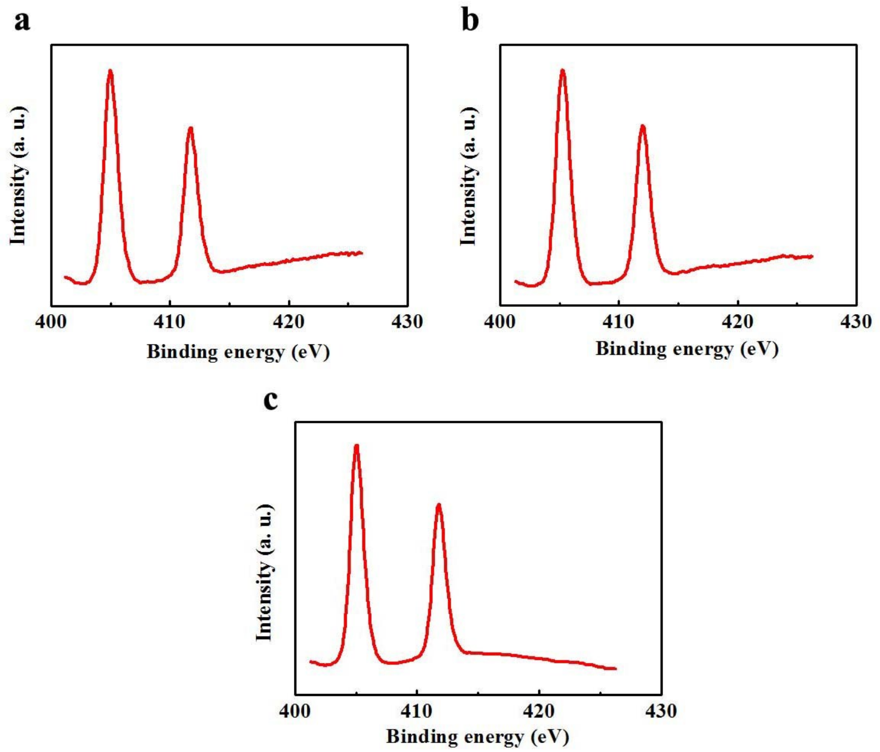

Fig. S5 XPS spectra of Cd 3d, (a) **CdS@3D-NPC(A)**; (b) **CdS@3D-NPC(B);** (c) **CdS@3D-NPC(C)**.

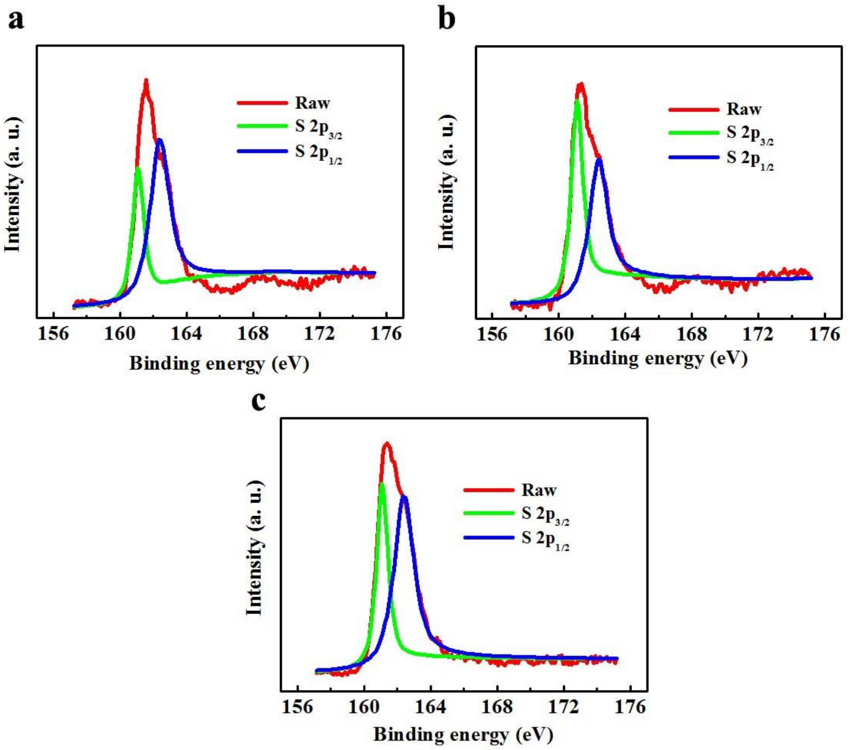

Fig. S6 XPS spectra of S 2p, (a) **CdS@3D-NPC(A)**; (b) **CdS@3D-NPC(B)**; (c) **CdS@3D-NPC(C)**.

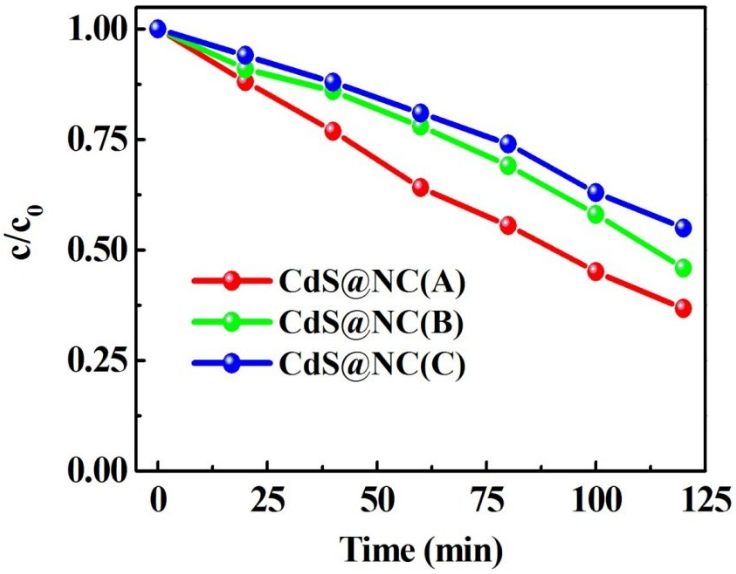

Fig. S7 Time courses of photocatalytic formaldehyde degradation by **CdS@NC**.

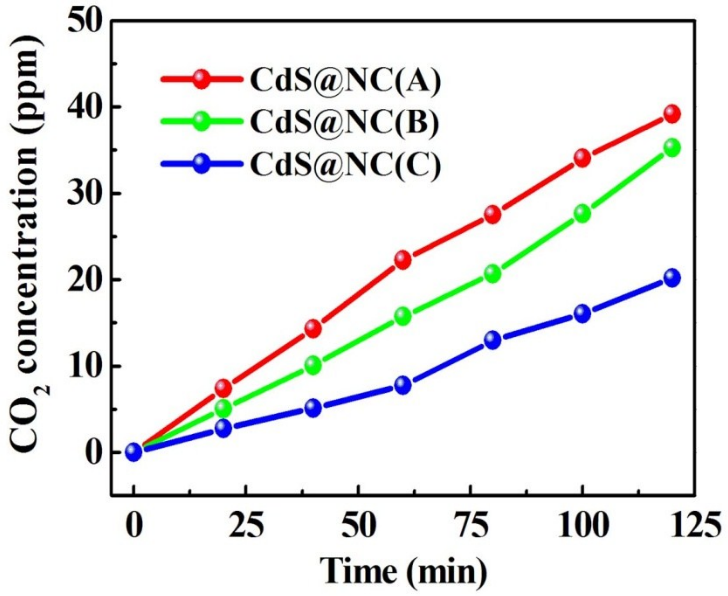

Fig. S8 The rate of CO_2 production by **CdS@NC**.

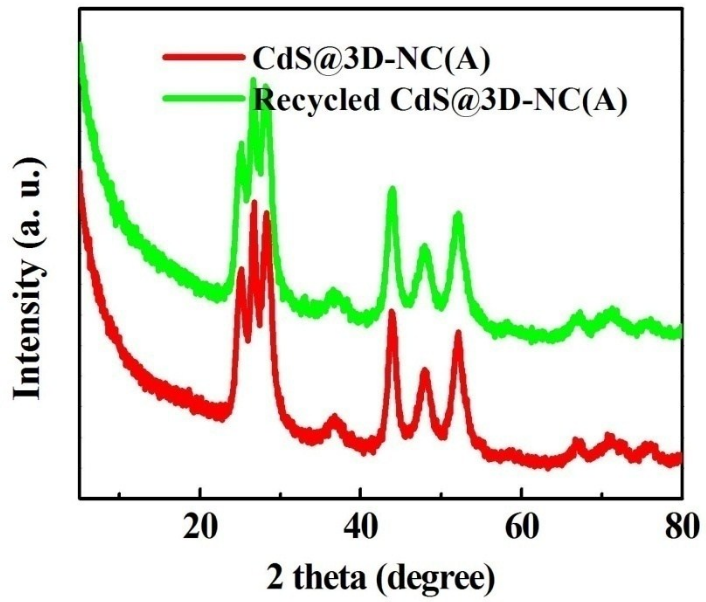

Fig. S9 Repeated PXRD of **CdS@3D-NPC(A)** after formaldehyde degradation.

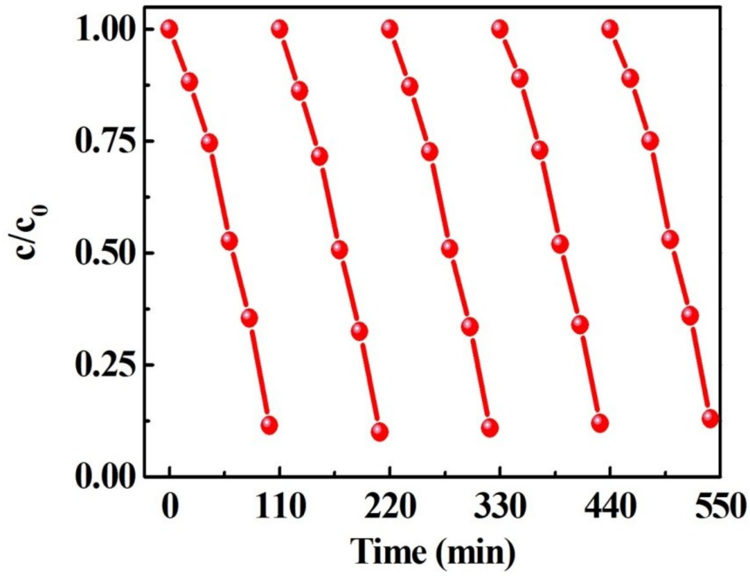

Fig. S10 Repeated time courses of benzene degradation by **CdS@3D-NPC(A)**.