Supplementary Materials for

Controlling the secondary pollutant on B-doped g-C_3N_4 during photocatalytic NO removal: a combined DRIFTS and DFT investigation

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Characterization

The crystal phases of the samples were analyzed by X-ray diffraction (XRD) with Cu Kαradiation (Model D/max RA, Rigaku Co., Japan). X-ray photoelectron spectroscopy (XPS) with AlKαX-ray radiation (hv = 1486.6 eV) operated at 150 W (Thermo ESCA-LAB 250, USA) was used to investigate the surface properties, Scanning electron microscopy (SEM, Model JSM-6490, Japan) were used to characterize the morphology (TEM, JEM-2010, Japan) were used to characterize the morphology and structure. The UV-vis diffusere flectance spectrometry (UV-vis DRS) spectra were obtained for the dry-pressed disk samples using a scanning UV-vis spectrophotometer (UV2550, Shimadzu, Japan) equipped with an integrating sphere assembly, using 100% $BaSO_4$ as the reflectance sample. Photoluminescence (PL) studies (F-7000, HITACHI, Japan) were conducted to investigate the optical properties of the samples. Nitrogen adsorption-desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, U.S.A.) with all samples degassed at 300℃ for 4h before measurements. Electron spin resonance (ESR) of radicals spin-trapped by 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was recorded on a JES FA200 spectrometer. Samples for ESR measurement were prepares by mixing the samples in 50mM DMPO solution tanks (aqueous dispersion for DMPO-•OH and methanol dispersion for DMPO-$\bullet O_2^-$) and irradiated with visible light. Electron paramagnetic resonance (EPR) measurements were carried out on a Bruker ESP 500 spectrometer.

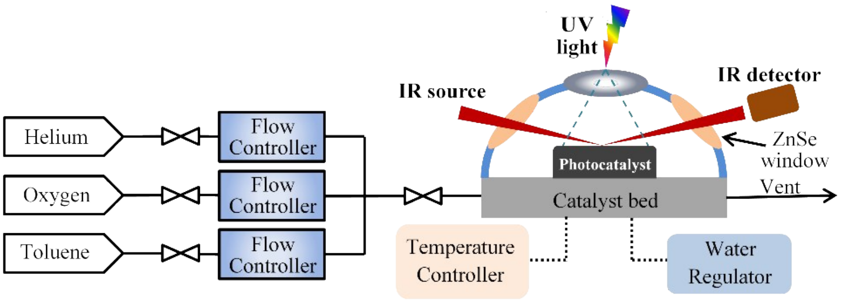
Visible light photocatalytic NO removal

The as-prepared sample (0.20g) was dispersed and coated onto two glass dishes (12.0 cm in diameter) for photocatalytic activity tests. A 150 W commercial tungsten halogen lamp was vertically placed outside and above the reactor and the lamp was turned on when adsorption-desorption equilibrium was achieved. The removal ratio (η) of NO was calculated as $\eta = (1-C/C_0)\times100\%$, where C and C_0 are the concentrations of NO in the outlet steam and the feeding stream, respectively.

In situ DRIFTS study on photocatalytic NO oxidation process

The *in situ* DRIFTS measurements were conducted using the Tensor II FT-IR spectrometer

(Bruker) equipped with an in situ diffuse reflectance cell (Harrick) and shown in Scheme S1. Photocatalysts were put into the reaction cell. First, the He gas (100 mL/min) was used to remove the residual hydrocarbons, H_2O and CO_2 under 300℃. The real-time FT-IR spectrum after ventilation was utilized as background. Then, the reaction mixtures (50mL/min NO, 50mL/min O_2) were introduced into the cell. The NO adsorption on the catalysts was carried out for 20 min. Next, photocatalysts were illuminated by visible light source (MUA-210) for 1 hour. The real-time FT-IR spectra were detected every eight minutes. Meanwhile the gas fluxes keep the same (50mL/min NO, 50mL/min O_2).



Scheme S1 The designed reaction system for the *in situ* DRIFTS signal recording.

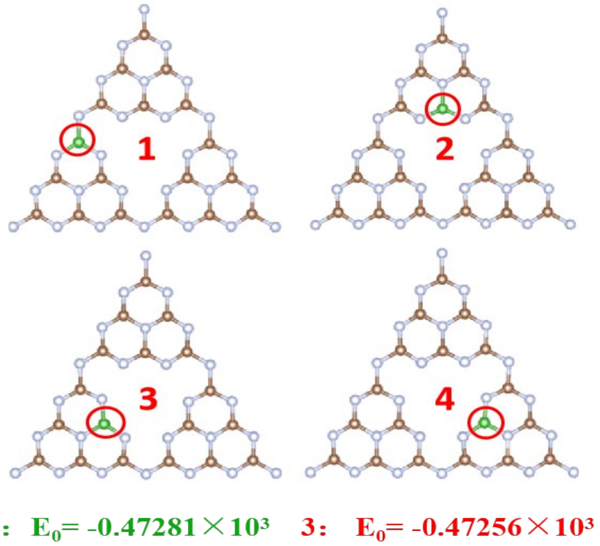


Fig. S1 The optimized local structures of B-doped CN at different in-plane sites. All the energies are given in eV; Gray, brown and green spheres represent N, C and B atoms, respectively; E_0 stands for the doping energy, negative means heat release.

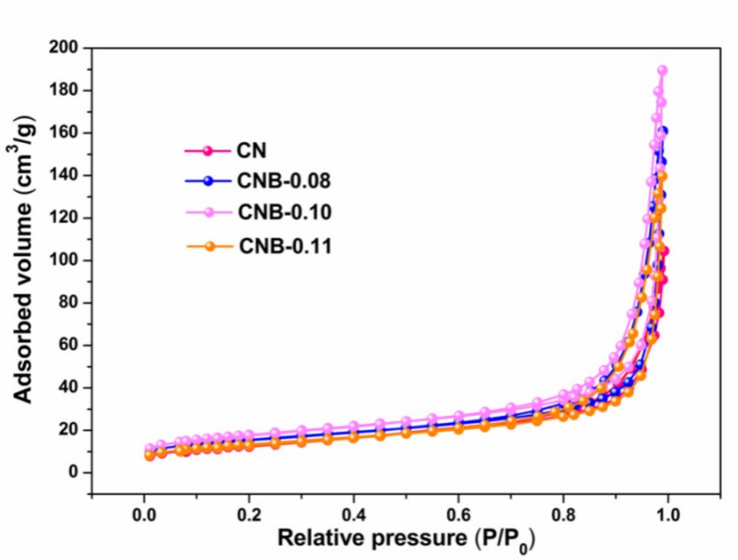


Fig. S2 The N_2 adsorption-desorption isotherms of the CN, CNB-0.08, CNB-0.10 and CNB-0.11.

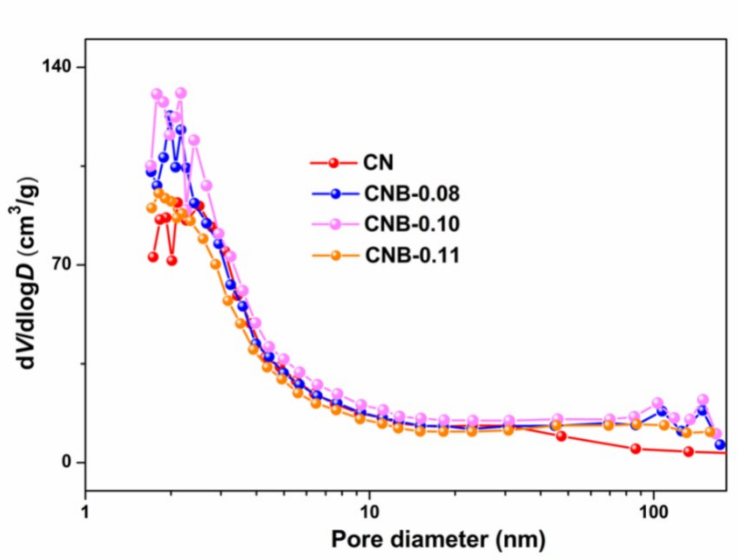


Fig. S3 The corresponding pore size distribution of the CN, CNB-0.08, CNB-0.10 and CNB-0.11.

Table S1 Assignments of the IR bands observed during the NO adsorption over CN and CNB-0.10.

Wave number (cm^{-1})	Band assignment	References
1095, 1891,2001	NO	45,47
2084,2089	NO_2	45,48
2223	N_2O	46
1024	Monodentate nitrates	49
857,1102,1158,1170,13	Chelated nitrites	47,48,52
1324,1340	NO_2^-	53
917, 918	N_2O_4	46
981, 1218	Bidentade nitrates	48,54, 55

Table S2 Assignments of the IR bands observed during the NO oxidation over CN and CNB-0.10.

Wave number (cm^{-1})	Band assignment	References
1881,2001	NO	45,46
2086, 2096	NO_2	45,56
2223	N_2O	46
1027	Monodentate nitrates	49
860,1101,1163	Chelatednitrites	6,47,48
1340	NO_2^-	53
918	N_2O_4	46
1220,928,978	Bidentade nitrates	54, 55

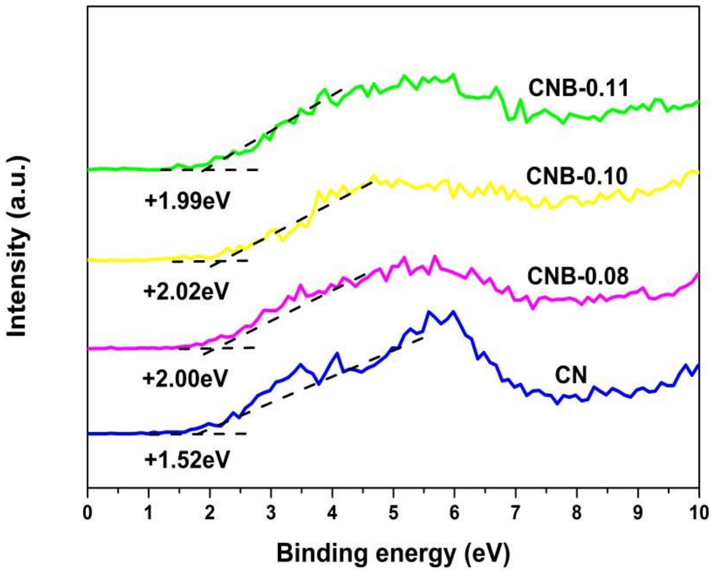


Fig. S4 Determination of the valence band maximum edges (E_{VB}) of CN, CNB-0.08, CNB-0.10, CNB-0.11 by VB XPS technique.

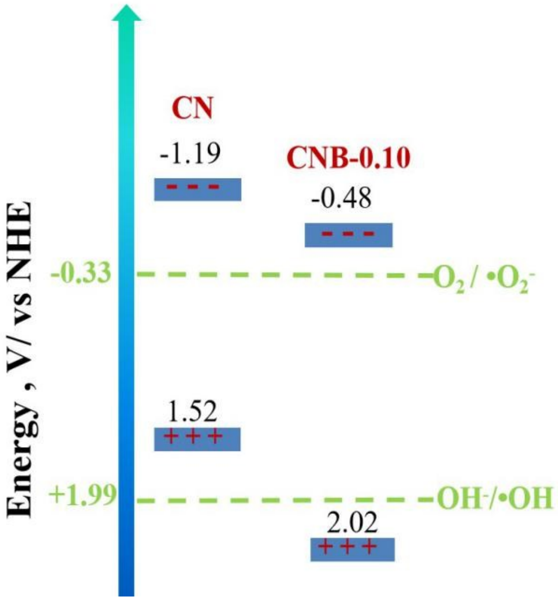


Fig. S5 Proposed band structures for the CN and CNB-0.10.