

Electronic Supplementary Information for

OH/Na co-functionalized carbon nitride: directional charge transfer and enhanced photocatalytic oxidation ability

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Characterization

The crystal phases of the samples were analyzed by X-ray diffraction (XRD) with CuK α radiation (Model D/max RA, Rigaku Co., Japan). X-ray photoelectron spectroscopy (XPS) with AlK α X-ray radiation ($h\nu = 1486.6$ eV) operated at 150 W (Thermo ESCALAB 250, USA) was used to investigate the surface properties. Scanning electron microscopy (SEM, Model JSM-6490, Japan) and transmission electron microscopy (TEM, JEM-2010, Japan) were used to characterize the morphology and structure. Nitrogen adsorption-desorption isotherms were obtained on a nitrogen adsorption apparatus (ASAP 2020, USA) with all samples degassed at 300 °C for 4 h 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 prepared by mixing the samples in 50 mm DMPO solution tanks (aqueous dispersion for DMPO- \bullet 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. Photoluminescence (PL) studies (F-7000, HITACHI, Japan) and UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained for the dry-pressed disk samples using a scanning UV-vis spectrophotometer (UV-vis DRS, UV-2450, Shimadzu, Japan) equipped with an integrating sphere assembly to investigate the optical properties of the samples.

Continuous reactor for photocatalytic NO removal

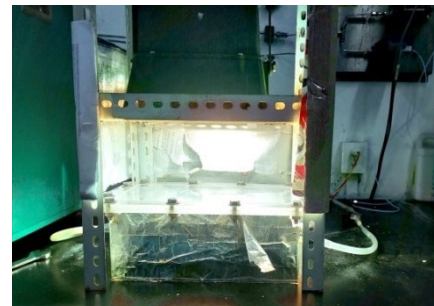
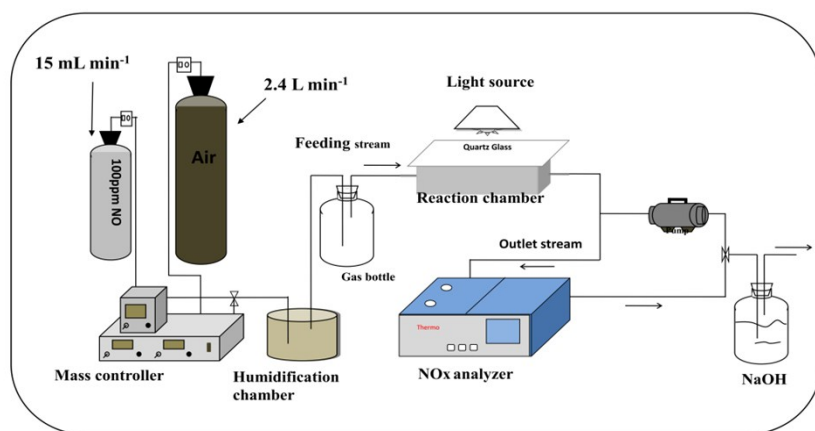
The photocatalytic NO purification ratio was investigated by the continuous-flow reactor at ppb level (500 ppb) (Scheme 1). A commercial tungsten halogen lamp (150 W, 0.16 W/cm 2) was placed vertically outside and above the reactor (rectangular reactor, 30 \times 15 \times 10 cm). A UV cutoff filter (420 nm) was adopted to remove UV light during the photocatalytic testing process. Preparation 0.2 g samples was evenly coated onto two glass plates with 10 mL distilled water and dried in an oven at 60 °C.

Then the dry glass plates were put into the reactor. The lamp was turned on when the adsorption–desorption equilibrium was reached. A NO_x analyzer (Thermo Scientific, 42i-TL, USA) was applied to monitor the concentration of NO, NO₂ and NO_x (NO + NO₂) every minute. The purification ratio (η) of NO was calculated using $\eta = (1 - C/C_0) \times 100\%$, where C and C₀ respectively represent the concentration of NO before and after turning on the lamp.

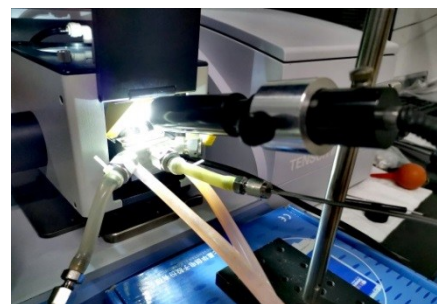
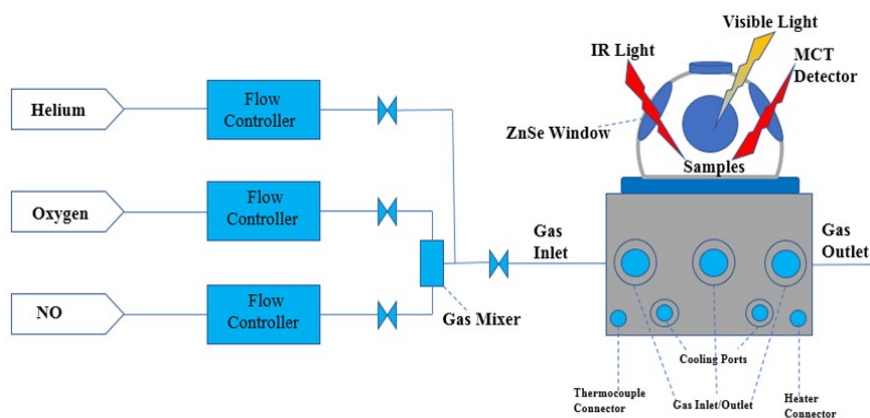
In situ DRIFTS study on photocatalytic NO oxidation process

Photocatalysts were put into the reaction cell. First, the He gas (100 ml/min) was used to remove the residual hydrocarbons, H₂O and CO₂ under 110 °C. The real-time FT-IR spectrum after ventilation was utilized as background. Then, the reaction mixtures (50 ml/min NO, 50 ml/min O₂) 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 h. The real-time FT-IR spectra were detected every eight minutes. Meanwhile the gas fluxes keep the same (50 ml/min NO, 50 mL/min O₂). Finally, FT-IR spectra were recorded every two minutes with the same gas fluxes after turning off the light. The IR scanning range was 4000–600 cm⁻¹. The intervals 2999-2400 cm⁻¹ and 2249-750 cm⁻¹ were analyzed to present the photocatalytic oxidation process on the catalysts.

Figures



Scheme S1 Schematic diagram of continuous photocatalytic reactor and the photo of the system



Scheme S2 The designed reaction system for the *in situ* DRIFTS signal recording and the picture

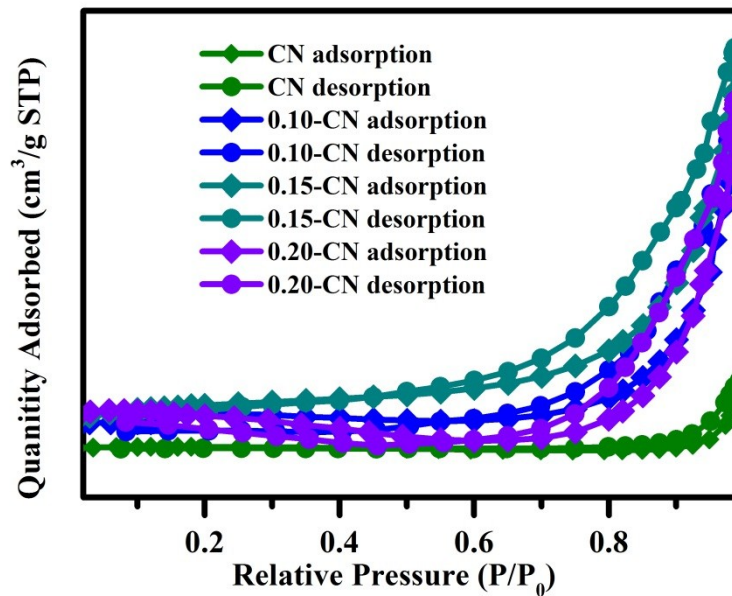


Fig. S1 N_2 adsorption-desorption isotherm

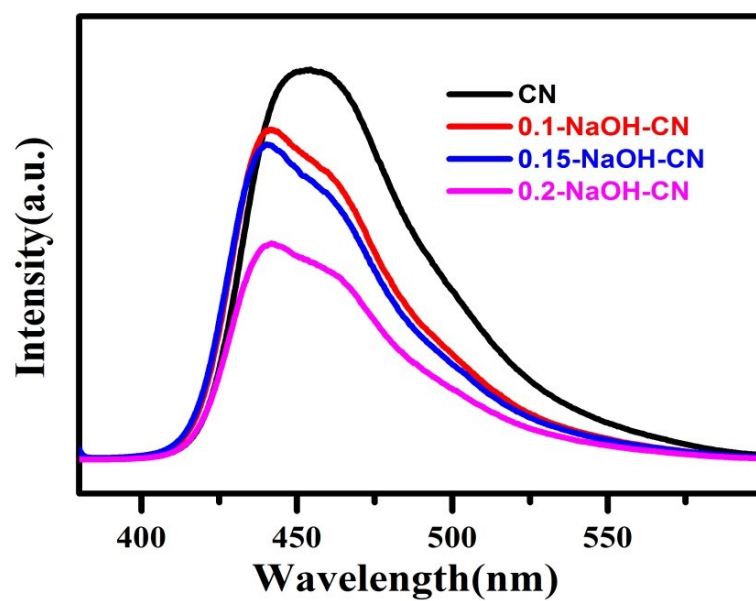


Fig. S2 Photoluminescence spectra of the as-obtained samples

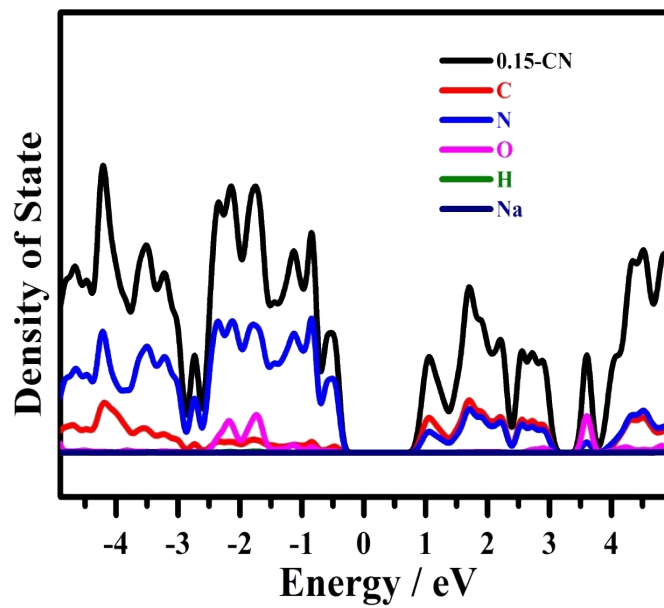


Fig. S3 The 0.15-CN of density of states (total and each element)

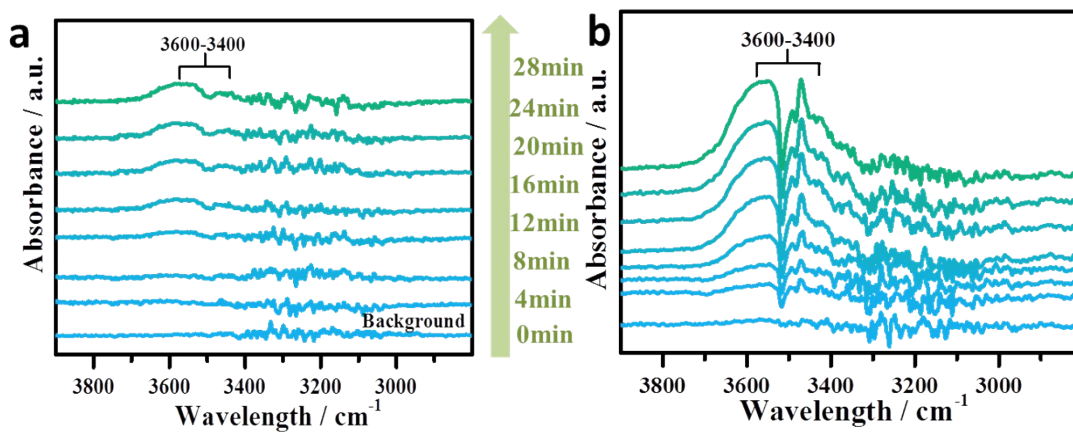


Fig. S4 In the gas component of $\text{NO}+\text{O}_2$, photocatalytic adsorption process for CN (a) and 0.15-CN (b)

Table

Table S1 The BET surface area (S_{BET})

Sample	CN	0.10-CN	0.15-CN	0.20-CN
S_{BET} , m ² /g	4.8774	65.0354	39.5300	51.1141

Table S2 Assignments of the IR bands observed during NO adsorption over CN

Wavenumbers (cm ⁻¹)	Assignment	References
801	NO ₂ ⁻	1
859/883	chelated nitrites	1,2,3
915	N ₂ O ₄	4
1044/1049/1100	NOH/NO ⁻	5,6,7
1363	monodentate nitrates	8
1463	bidentate nitrates	9
1600-1700	NO and free nitrate	7
2188	NO ⁺	10,11
2772/2882	bridged nitrates	12
3400-3600	O-H	5,12

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