Supplementary Information

Targeted H_2O activation to manipulate the selective photocatalytic reduction of CO_2 to CH_3OH over carbon nitride supported cobalt sulfide

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1 Experiments

1.1 Materials

All used chemicals were analytical-grade reagents without any further purification. Cobalt nitrate hexahydrate and dicyandiamide were purchased from Aladdin Reagent Corp. Anhydrous H_2SO_4 (98%), absolute ethanol (95%), sodium sulfide nonahydrate and silica sand (70-150 mesh) were purchased from Chengdu Kelong Chemical Reagent Corp. 99% ^{13}C enriched $^{13}CO_2$ was provided by Chengdu Keyuan Gas Corp.

1.2 Photoelectrochemical measurements

The photoelectrochemical measurements were conducted by using a CH760E electrochemical workstation (Chenhua Instrument, Shanghai, China) with a three-electrode system. The Ag/AgCl (KCl sat.) was used as the reference electrode, and Pt wire was used as the counter electrode. The working electrode was as-fabricated by a doctor blading technique (Binder: ethylcellulose; Basal: FTO; Active surface area: 1 cm^2), and then it was treated at 90 ^oC for 3 hours. Photocurrent-time and electrochemical impedance measurements of as-prepared samples at open circuit potential (OCP) were performed in 0.5 M Na_2SO_4.

2 Results and Discussion

2.1 The XRD spectra

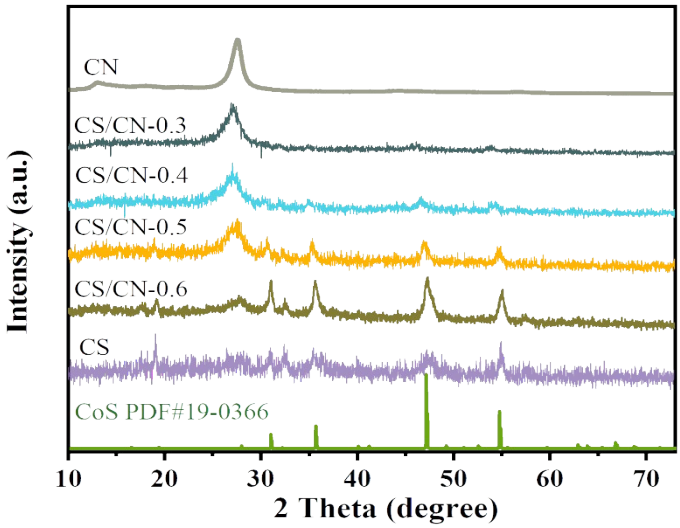

Figure S1. XRD spectra of the as-prepared samples.

2.2 Cycle experiments of photocatalytic reduction CO_2 on CN surface

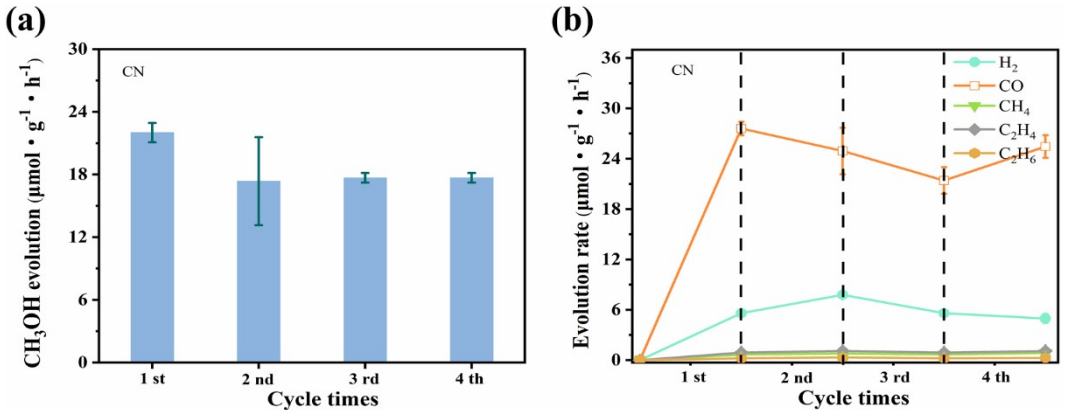

Figure S2. Cycle experiments of photocatalytic reduction CO_2 by CN: (a) CH_3OH production; (b) H_2, CO, C_2H_4, CH_4, and C_3H_6 generation (total: ~16 h).

2.3 Photocatalytic CO_2 reduction performance

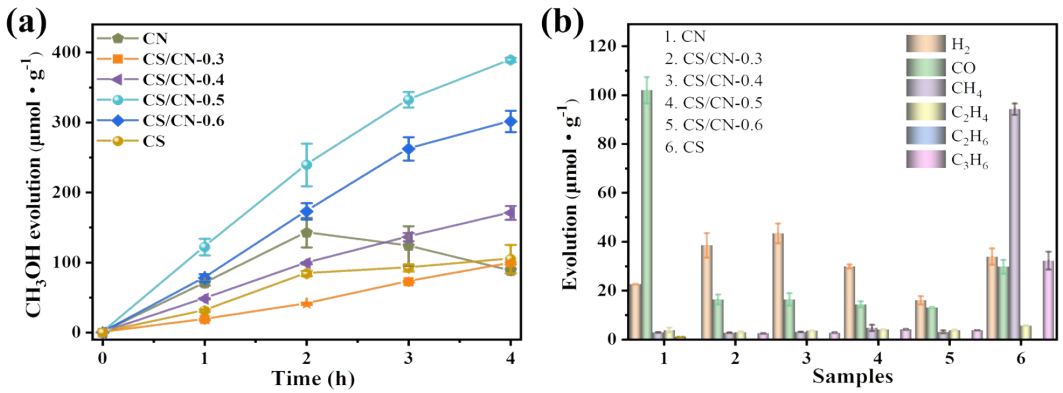

Figure S3. Photocatalytic activity of CO_2 photoreduction with H_2O. (a) CH_3OH production; (b) H_2, CO, CH_4, C_2H_4, C_2H_6, and C_3H_6 prod ucts at 4 hours over the as-prepared photocatalysts.

2.4 Cycle experiments of photocatalytic reduction CO_2 by CS/CN-0.5

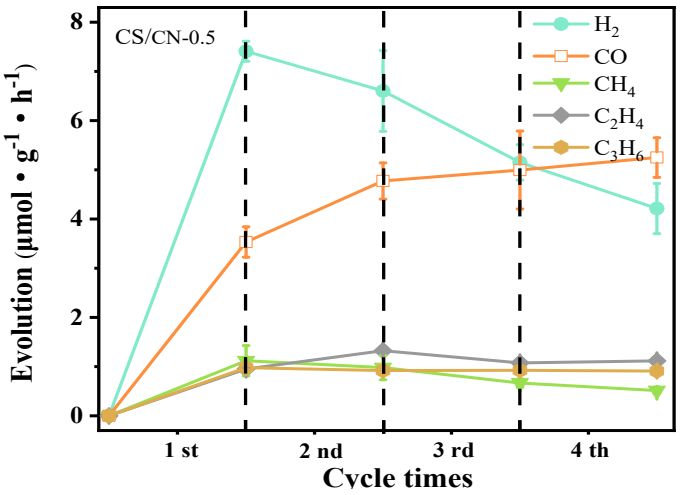

Figure S4. Cycle experiments of CS/CN-0.5 for photoreduction of CO_2: H_2, CO, C_2H_4, CH_4, and C_3H_6 generation rate (total: ~16 h).

2.5 XAS spectra

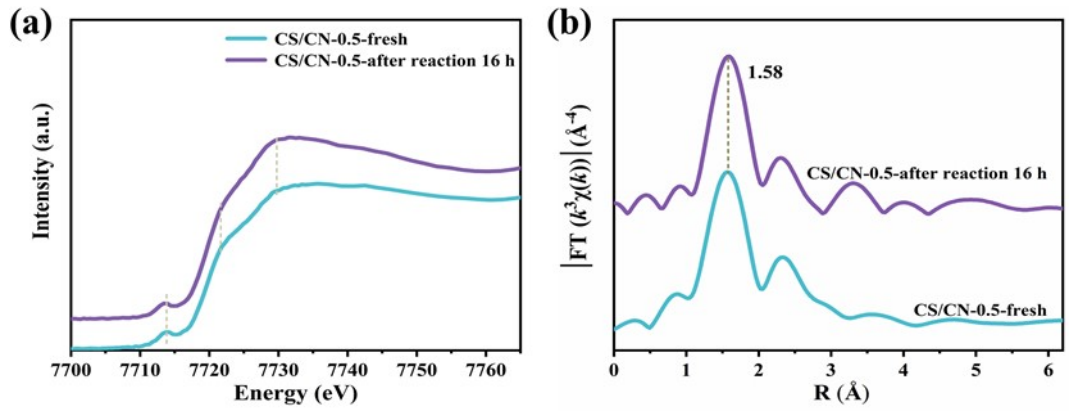

Figure S5. XAS spectra: (a) Co K-edge XANES spectra; (b) FT k^3-weight EXAFS spectra of the CS/CN-0.5-fresh and CS/CN-0.5-after reaction 16 h.

2.6 XPS spectra

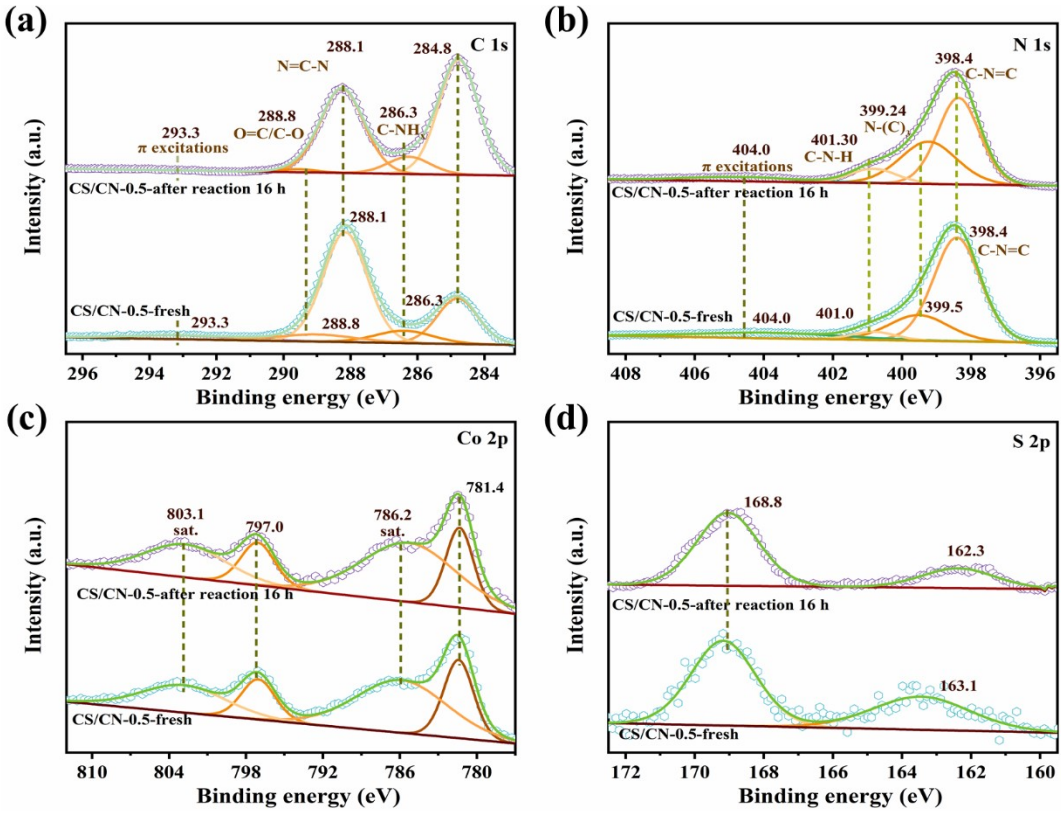

Figure S6. High-resolution C 1s (a), N 1s (b), (c) Co 2p, and (d) S 2p XPS spectra of the CS/CN-0.5-fresh and CS/CN-0.5-after reaction 16 h.

2.7 XRD patterns

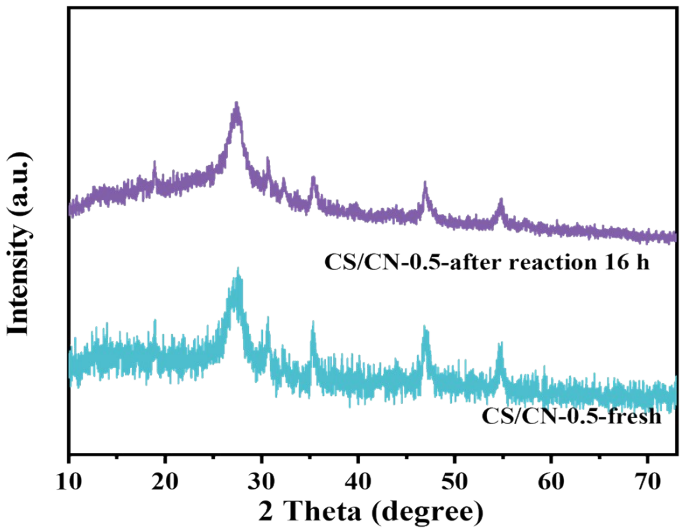

Figure S7. XRD patterns of the CS/CN-0.5-fresh and CS/CN-0.5-after reaction 16 h.

2.8 TG spectra

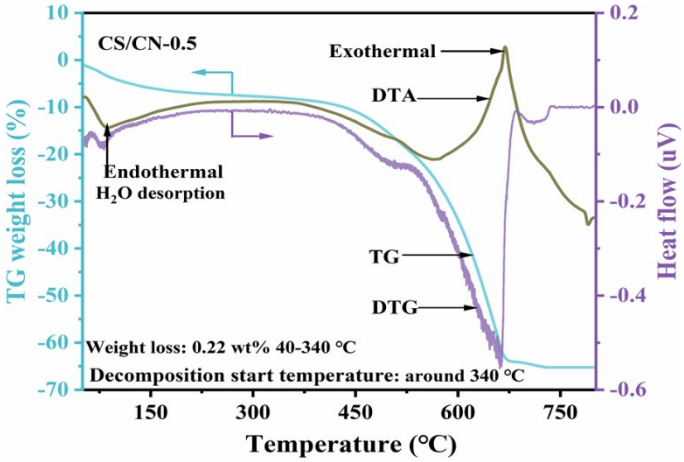

Figure S8. TG, DTA, and DTG curves of CS/CN-0.5.

2.9 Isotope experiment

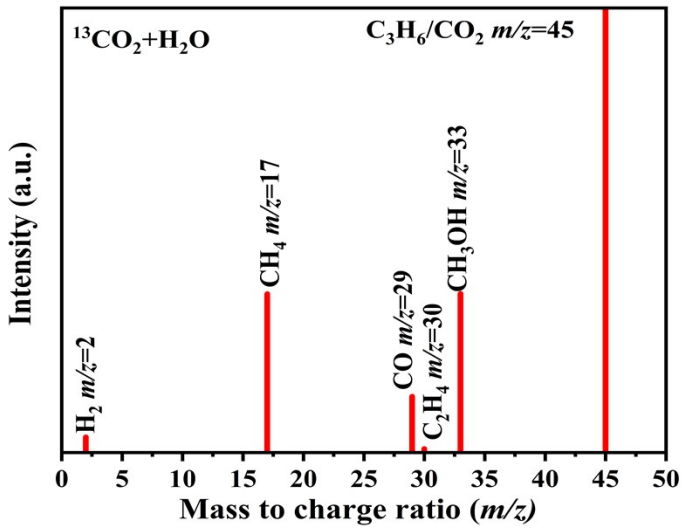

Figure S9. Mass spectra obtained during the photocatalytic conversion of $^{13}CO_2$ over CS/CN-0.5.

2.10 The UV-vis spectra

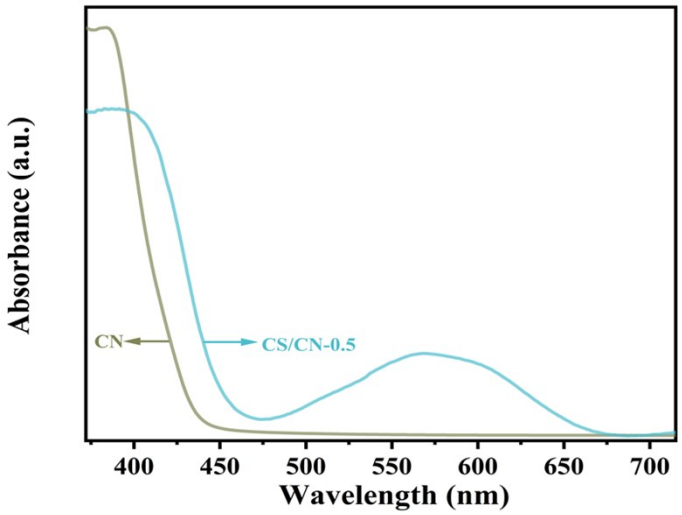

Figure S10. UV-vis diffuse reflectance spectra of CN and CS/CN-0.5.

2.11 High-resolution Co 2p and S 2p XPS spectra

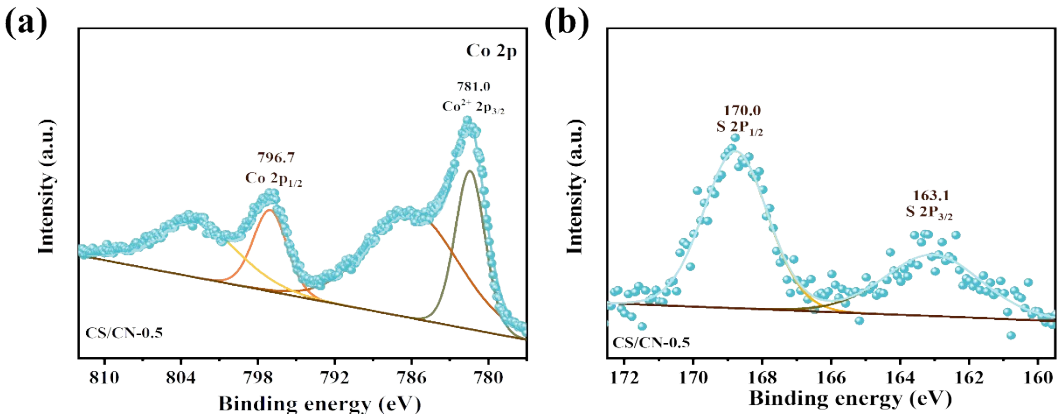

Figure S11. High-resolution Co 2p and S 2p XPS spectra of CS/CN-0.5.

2.12 FT of Co K-edge EXAFS spectra of CS/CN-0.5

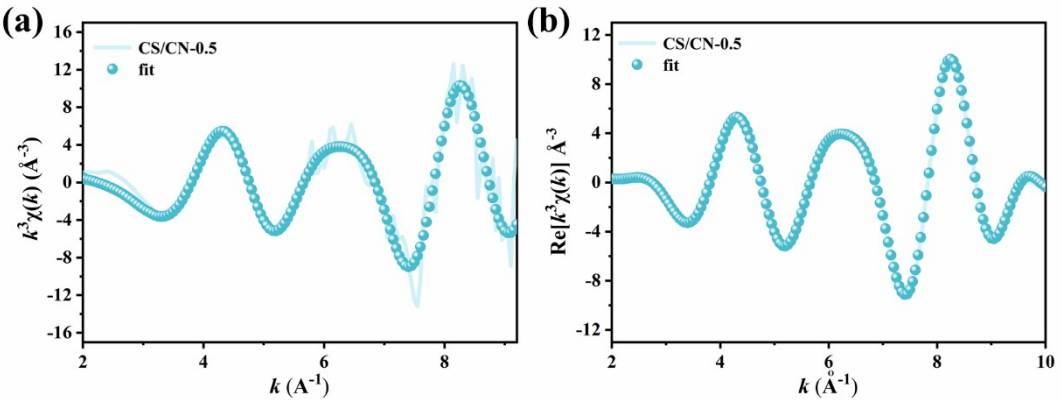

Figure S12. Fourier transform of Co K-edge EXAFS spectra in *k* (a) and *q* (b) space for the CS/CN-0.5.

2.13 The N_2 isothermal adsorption/desorption measurements

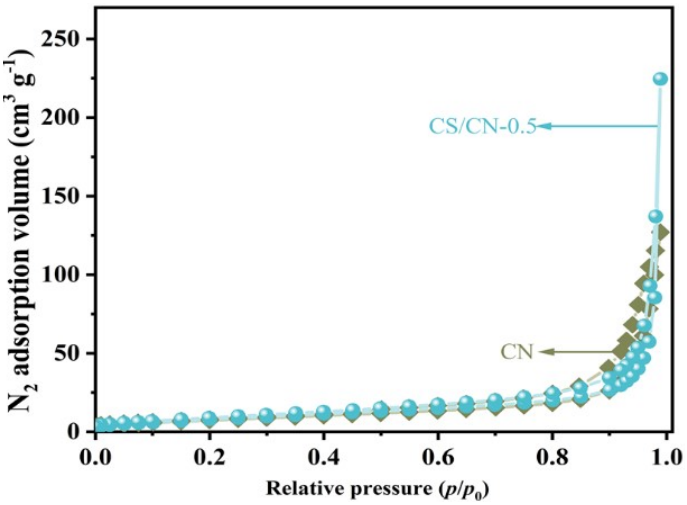

Figure S13. The N_2 isothermal adsorption/desorption measurements over CN and C/CN-0.5.

2.14 Tauc plots and band structure

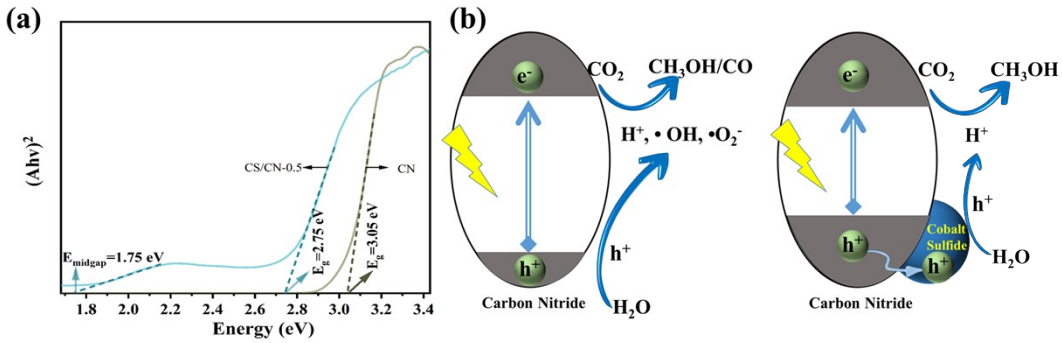

Figure S14. (a) Tauc plots of CS/CN-0.5 and CN; (b) Band structure of CS/CN-0.5 and CN.

2.15 Radical-trapping experiment

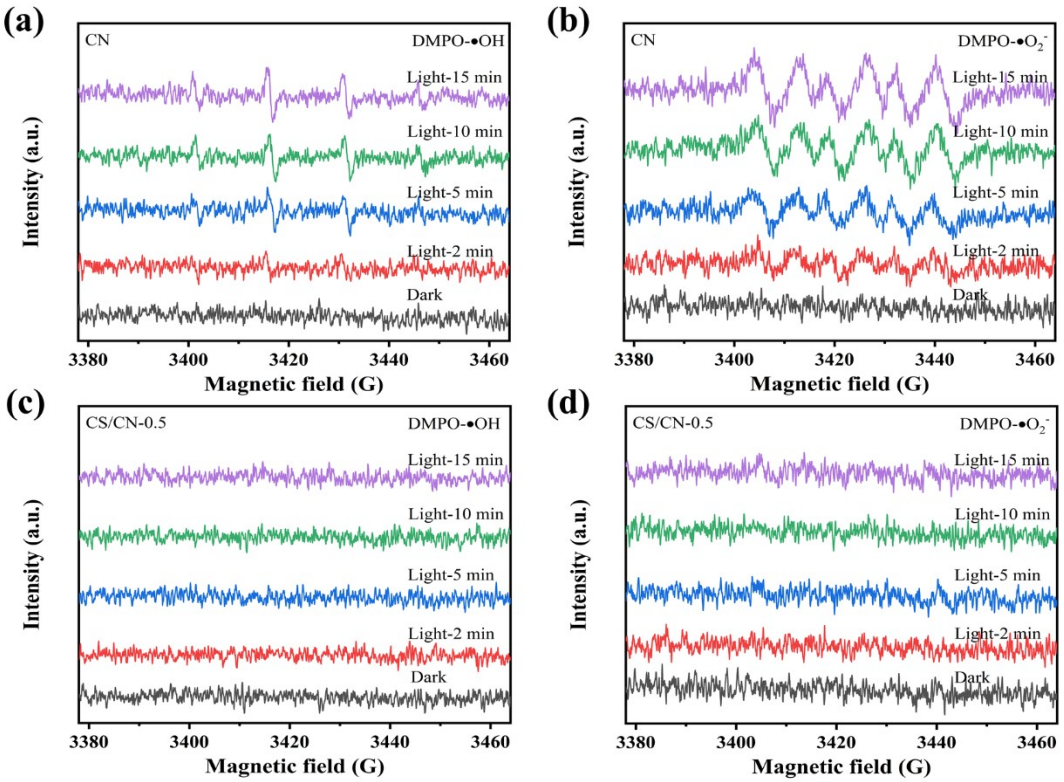

Figure S15. DMPO spin-trapping ESR spectra recorded for (a, c) •OH and (b, d) $•O_2^-$ over CN and CS/CN-0.5.

2.16 *In situ* DRIFTS experiments

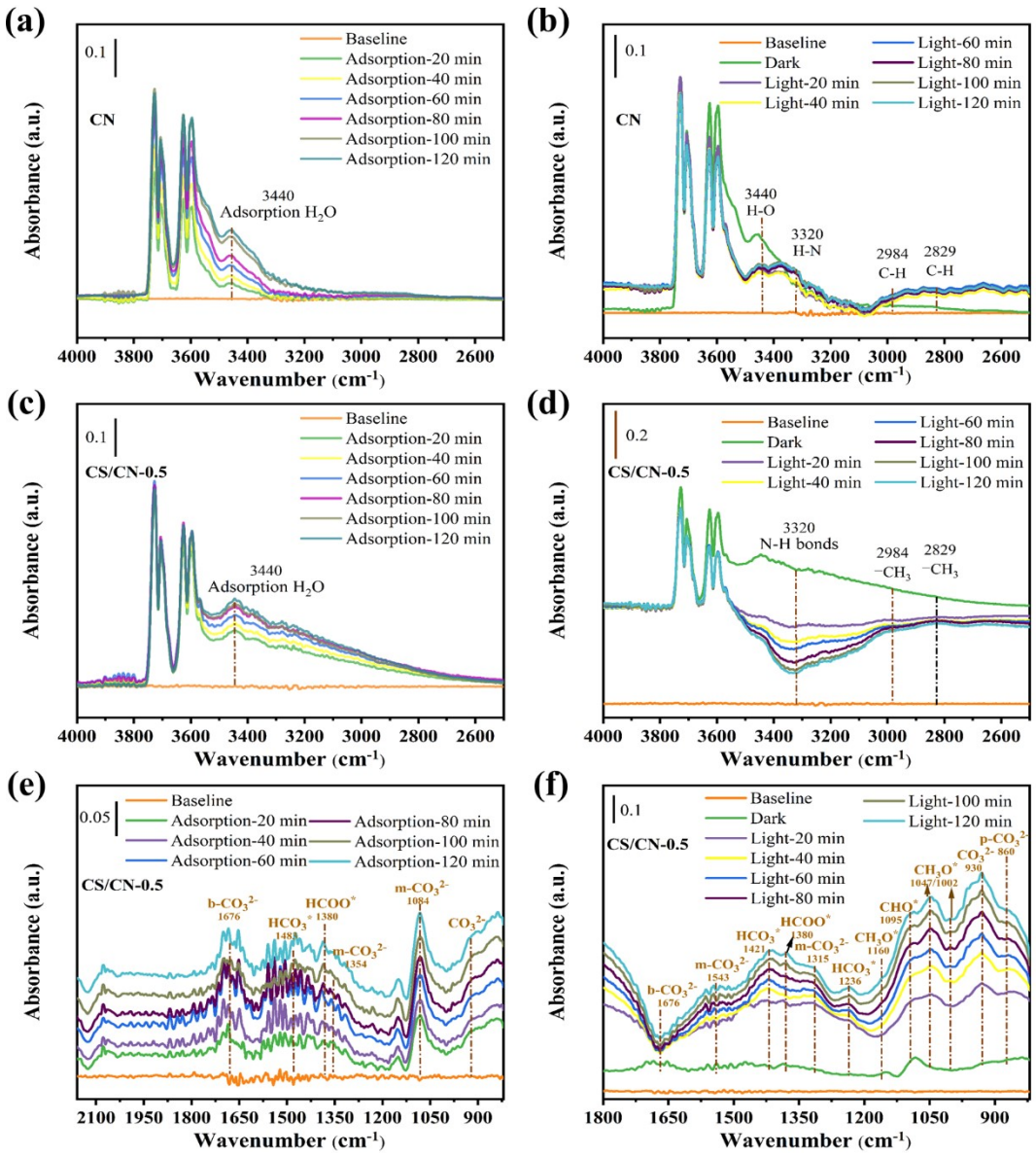

Figure S16. In situ DRIFTS spectra of photoreduction CO_2 with H_2O process over CN and CS/CN-0.5. (a, c) H_2O adsoprtion under dark, (b, d) H_2O reduction process under light irradiation; (e) CO_2 adsoprtion under dark, (f) CO_2 reduction process under light irradiation.

2.17 In situ DRIFTS experiments

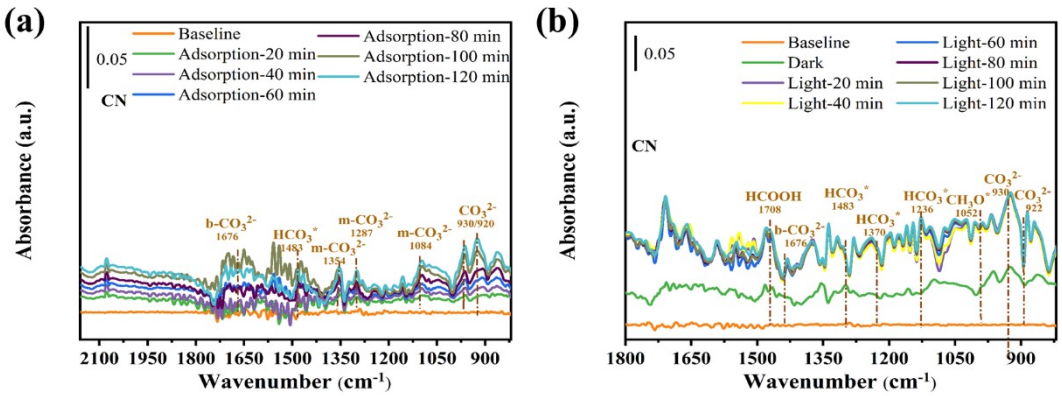

Figure S17. *In situ* DRIFTS spectra of CO_2 photoreduction process over CN (a) CO_2 adsoprtion under dark; and (b) CO_2 reduction process under light irradiation.

2.18 The Co K-edge EXAFS fitting parameters

Table S1. Structural parameters obtained from the Co K-edge EXAFS fits.

Samples	**bonds**	**CN**	**R (Å)**	**σ^2(10^{-3} Å^2)**	**△E (eV)**	**χ_v^2 / R factor**
CS/CN-0.5	Co-C/N	2.5	0.028	5.0	2.87	21/0.0025
	Co-S	0.9	0.028	14.0		
	Co-Co	3.1	0.21	6.7		