

Electronic Supplementary Material

Synergistic pyridinic N and Fe sites in electrospun carbon nanofibers for economical catalytic synthesis of high-value COS from low-concentration H₂S

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Computational details

All calculations in this work were carried out using the Vienna Ab initio Simulation Package (VASP) based on spin-polarized density functional theory. The exchange–correlation interactions were described by the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA)^[1-3]. To account for the possible van der Waals interactions in the system, Grimme’s DFT-D3 dispersion correction was employed. The projector augmented wave (PAW) method was employed to describe the interactions between core and valence electrons^[4]. For all the calculations, a vacuum layer of 15 Å was applied along the z-direction to avoid potential interaction between periodic surfaces, and the plane-wave cutoff energy was set to 400 eV. Geometry optimizations were performed until the residual force on each atom was

below 0.02 eV Å⁻¹. The electron distribution is analyzed by Bader charge analysis^[5].

Adsorption energies were calculated by

$$E_{\text{ads}} = E_{\text{catalyst/H}_2\text{S}} - E_{\text{catalyst}} - E_{\text{H}_2\text{S}}$$

where $E_{\text{catalyst/H}_2\text{S}}$ and E_{catalyst} are the total energies of the structurally catalyst system with and without adsorbate, respectively. $E_{\text{H}_2\text{S}}$ is the energy of H₂S molecule.

Supporting tables and figures

Table S1 Fe contents determined by ICP analysis

sample	Fe (wt.%)
Fe-CNF-5	1.10
Fe-CNF-10	2.10
Fe-CNF-15	3.07
Fe-CNF-20	3.85

Table S2 N species of Fe-CNF-X

sample	Pyridinic N (atm.%) ^[a]	Fe-Nx (atm.%) ^[a]	Specific surface area (m ² /g) ^[b]
Fe-CNF-5	32.37	15.94	297.9
Fe-CNF-10	36.58	13.10	483.7
Fe-CNF-15	42.77	12.13	724.3
Fe-CNF-20	29.58	15.12	275.2

^[a]Determined by XPS elemental analysis, ^[b]Calculated from N₂-sorption isotherms

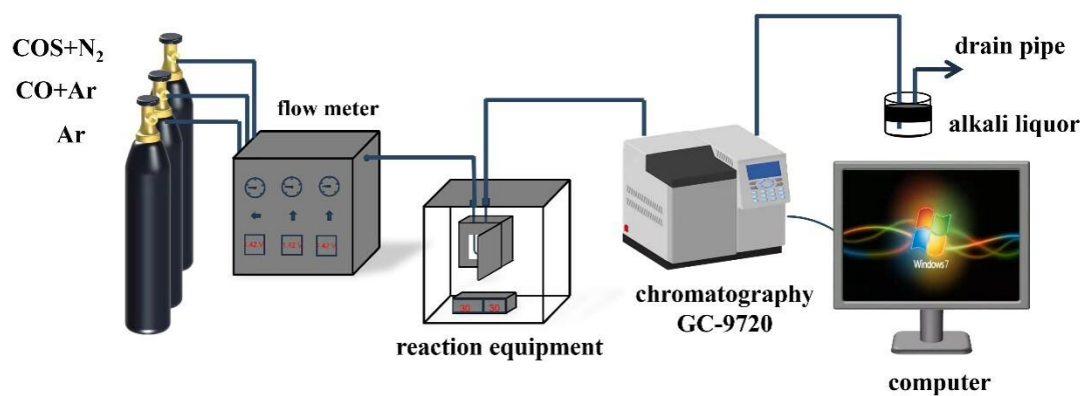


Fig. S1 Schematic diagram of vulcanization reduction performance evaluation device.

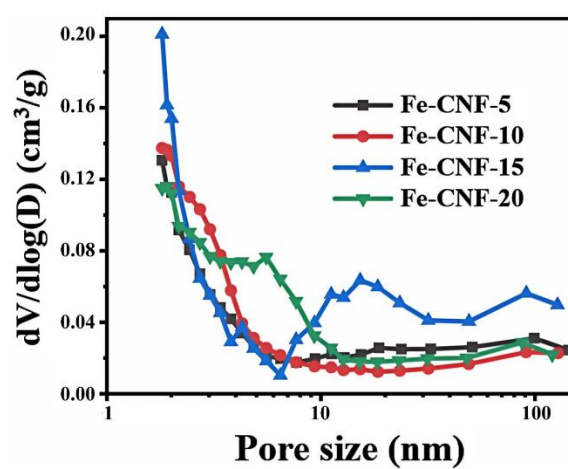


Fig. S2 Pore size analysis of Fe-CNF-X.

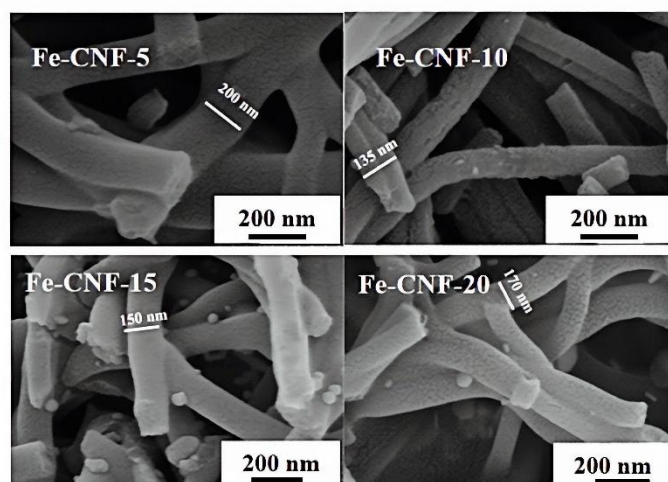


Fig. S3 SEM image of Fe-CNF-5, Fe-CNF-10, Fe-CNF-15, Fe-CNF-20.

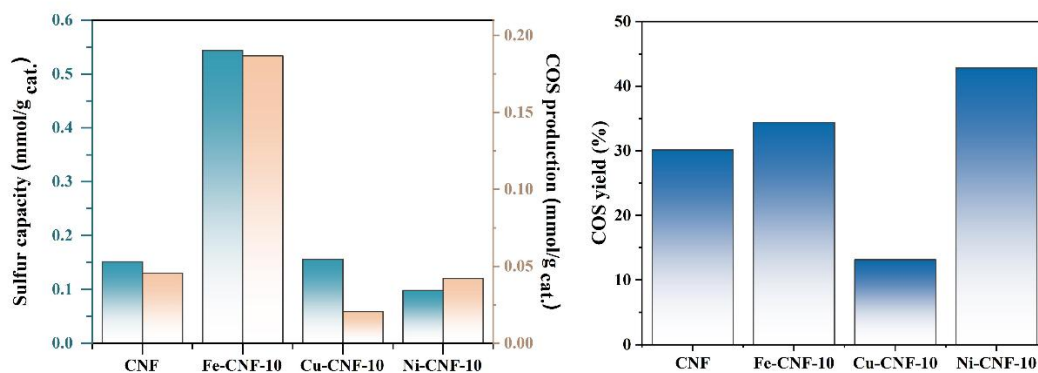


Fig. S4 (a) Sulfur capacity, COS production and (b) COS yield of CNF and M-CNF-10.

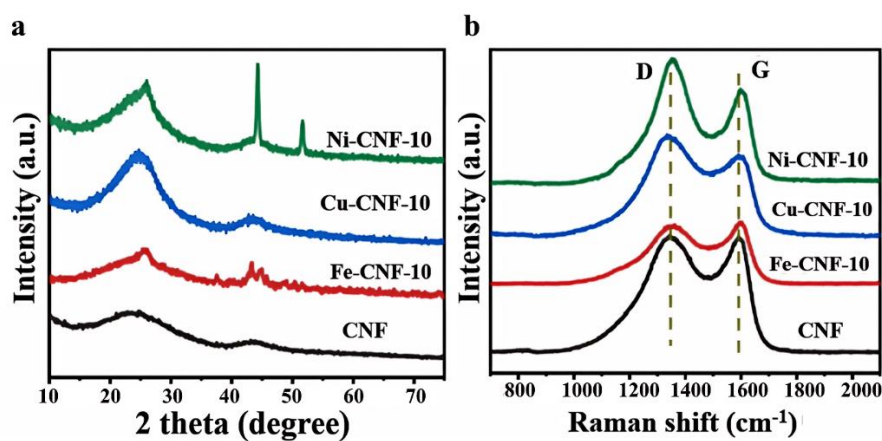


Fig. S5 (a) XRD spectra, (b) Raman spectra of CNF and M-CNF-X.

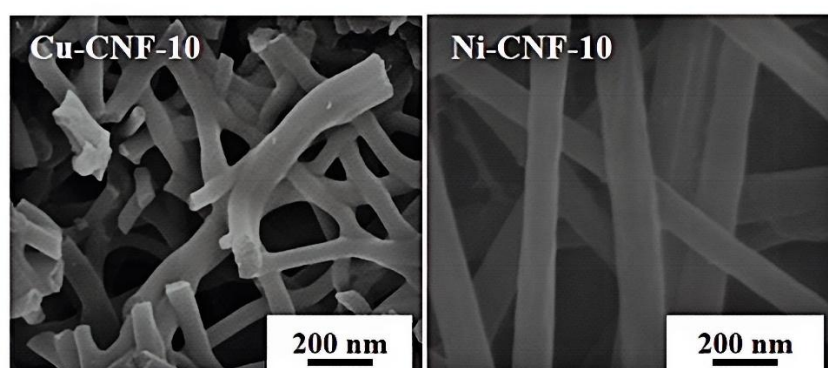


Fig. S6 SEM image of Cu-CNF-10 and Ni-CNF-10.

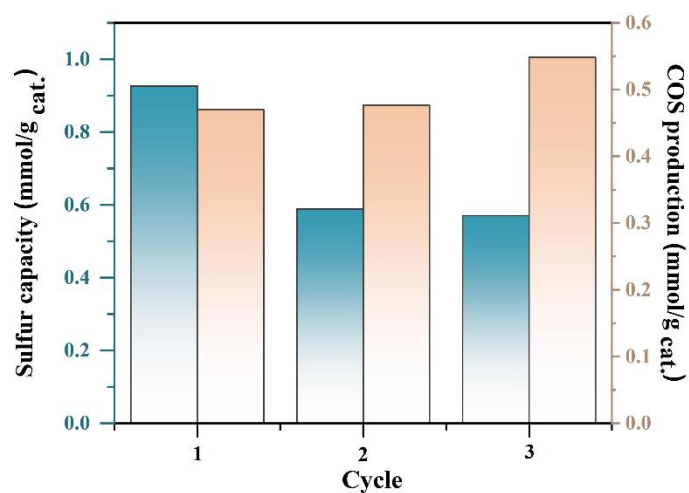


Fig. S7 Sulfur capacity and COS production of Fe-CNF-15.

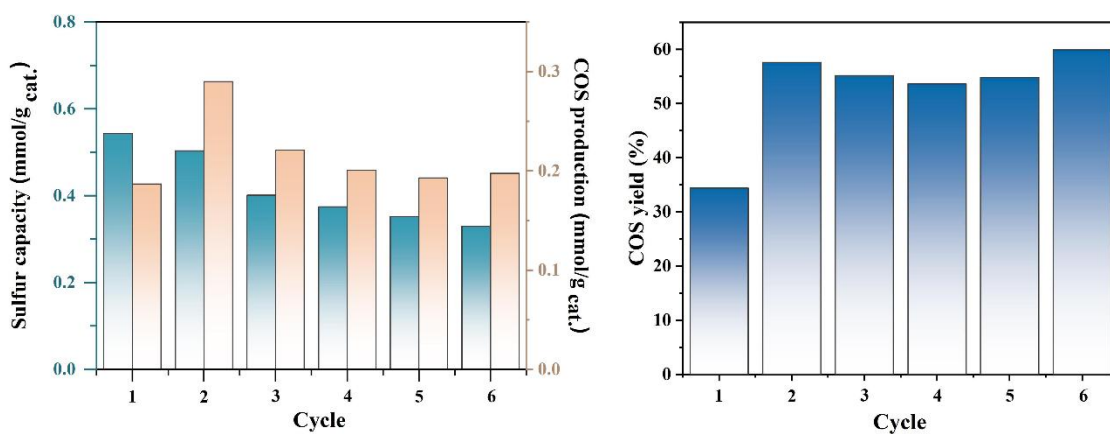


Fig. S8 (a) Sulfur capacity and COS production of Fe-CNF-10. (b) COS yield during six consecutive sulfidation–reduction cycles.

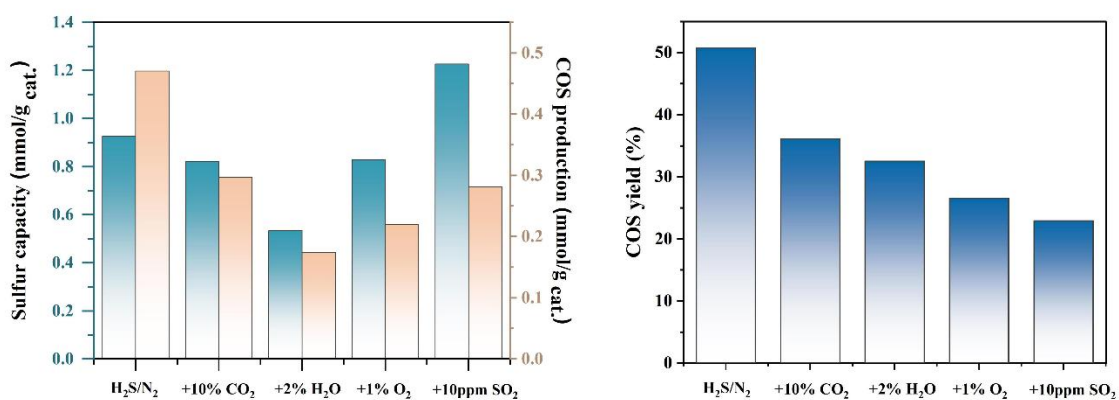


Fig. S9 (a) Sulfur capacity and COS production of Fe-CNF-15 under different sulfidation atmospheres. (b) COS yield after subsequent reduction under identical 5% CO/Ar atmosphere.

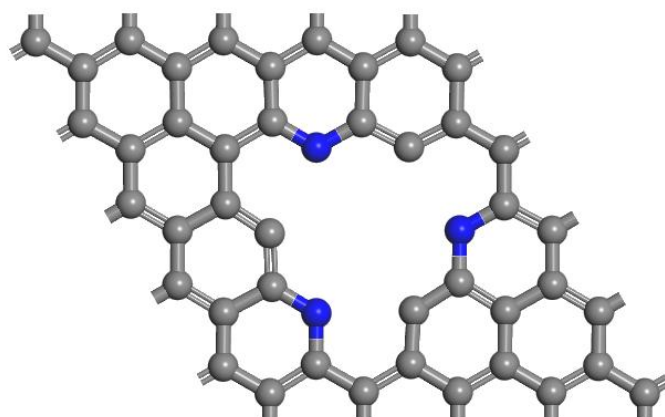


Fig. S10 Schematic illustration of the optimized nitrogen-doped carbon (NC) model.
Gray: C atoms; Blue: N atoms.

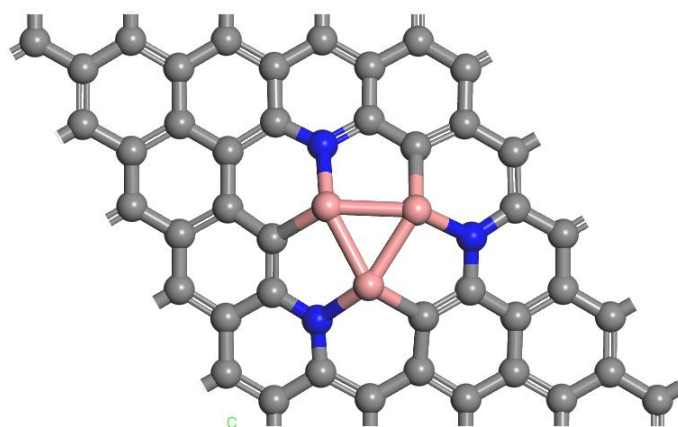


Fig. S11 Schematic illustration of the optimized Fe_3NC model, showing three Fe atoms embedded in the N-doped carbon framework. Gray: C atoms; Blue: N atoms; Pink: Fe atoms.

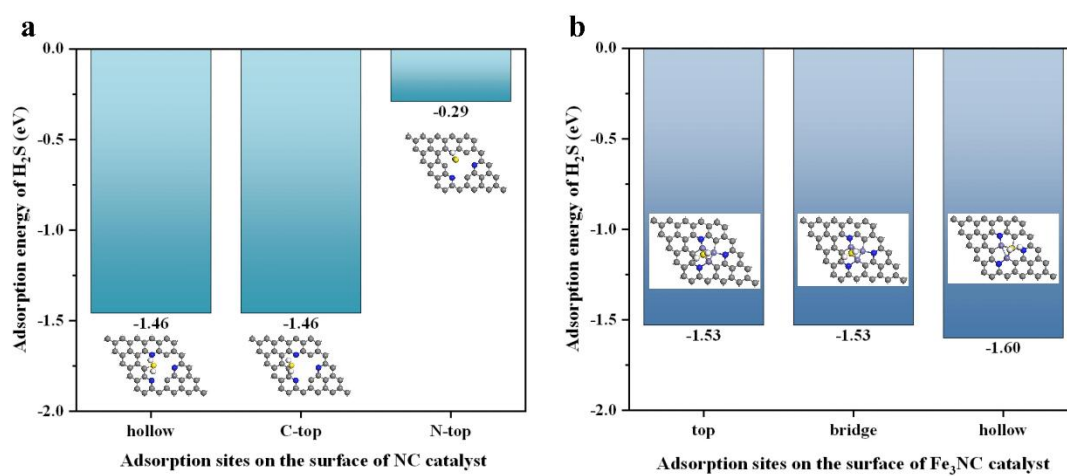


Fig. S12 Optimized adsorption configurations and adsorption energies of H_2S on different sites of NC (a) and Fe_3NC (b) surfaces.

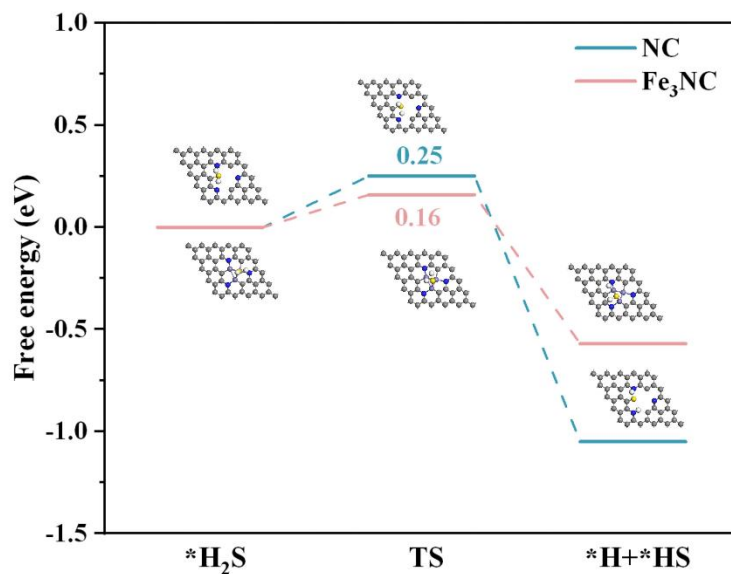


Fig. S13 Energy profiles for H₂S activation on NC and Fe₃NC surfaces.

We further evaluated the activation energy for H₂S dissociation. On the Fe₃NC surface, the cleavage of the H-S bond requires overcoming a barrier of only 0.16 eV, which is significantly lower than that on the NC surface (0.25 eV). This result indicates that H₂S is more readily activated on Fe₃NC.