Fullerene as a Probe Molecule for Single-Atom Oxygen Reduction Electrocatalysts

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Experimental Section

1. Chemicals

All chemicals were purchased and used as received without further treatment unless otherwise indicated. C_{60} fullerene (99%) was purchased from Xiamen Funano New Material Technology Co., Ltd. Cobalt(II) meso-tetraphenylporphine (CoP, 98%), nickel(II) meso-tetraphenylporphine (NiP, 97%), iron(III) meso-tetraphenylporphine chloride (FeP, 95%), and (5,10,15,20-tetraphenylporphinato) manganese(III) chloride (MnP, 95%) were bought from Shanghai Aladdin Biochemical Technology Co., LTD. Potassium hydroxide (KOH, ≥85.0%), potassium thiocyanate (KSCN, ≥98.5%), and carbon disulfide (CS_2, 99.9%) were ordered from Sinopharm Chemical Reagent Co., Ltd. Carbon nanotube (CNT, multi-walled, 95%, length of 10–30 μm and diameter of 10–20 nm) was received from Nanjing XFNANO Materials Tech Co., Ltd. Ketjenblack EC-600 JD (KB) was ordered from AkzoNobel. Nafion ionomer solution (5 wt%) was obtained from Sigma Aldrich. Deionized water (18.2 MΩ·cm) was used in all the experiments.

2. Materials Synthesis

Synthesis of CNT-supported metalloporphyrins (MP/CNT)

Taking the synthesis of CoP/CNT as an example, 20 mg of CoP was dissolved in 10 mL of CS_2 to form a homogeneous solution, into which 20 mg of CNT was thoroughly dispersed by ultrasonication for 2 h. The final product was then received by vacuum rotary evaporation at 80 °C and a rotating speed of 400 rpm to remove CS_2. NiP/CNT, FeP/CNT, and MnP/CNT were prepared by simply replacing CoP with the same mass of NiP, FeP, and MnP, respectively.

Synthesis of C_{60}-adsorbed MP/CNT

C_{60}-CoP/CNT was synthesized by dissolving 20 mg of CoP and 22 mg of C_{60} in 10 mL of CS_2 to form a homogeneous solution, into which 20 mg of CNT was thoroughly dispersed by ultrasonication for 2 h. The final product was then received by vacuum rotary evaporation at 80 °C and a rotating speed of 400 rpm to remove CS_2. C_{60}-NiP/CNT was prepared by simply replacing CoP with the same mass of NiP.

3. Material Characterization

Transmission electron microscopy (TEM) was carried out on a JEM-2010F (JEOL) electron microscope at an accelerating voltage of 200 kV. A copper grid coated with a thin carbon film was used

as the specimen holder. Scanning electron microscopy (SEM) was performed on a Nova NanoSEM 450 (FEI) electron microscope at an accelerating voltage of 10 kV.

X-ray powder diffraction (XRD) was performed to obtain the crystallographic information of the samples. The powder diffraction patterns were recorded on a Malvern Panalytical X-ray diffractometer (Empyrean) using Cu Kα radiation source (λ = 1.5406 Å, 45 kV and 40 mA). Scanning angles for all samples were set in the 2θ range of 5−90° with a step size of 0.01313° and time per step of 120 s. Peaks were indexed to the database established by Joint Committee on Powder Diffraction Standards (JCPDS).

Raman spectrum was acquired using a confocal Raman microscope (LabRAM HR800, Horiba JobinYvon) equipped with an optical microscope, a CCD camera, and an argon ion laser source. The laser provided 0.2 mW power at a wavelength of 532 nm for the exciting line. Integration time was 60 s, number of co-addition was 2, and slit aperture size was 50×1000 μm.

X-ray photoelectron spectroscopy (XPS) analysis was performed on the K-Alpha X-ray photoelectron spectrometer system (Thermo Fisher Scientific) utilizing a monochromatic Al Kα source (1486.69 eV). High-resolution spectra were obtained at a pass energy of 50.0 eV, a step size of 0.1 eV, and a dwell time of 250 ms per step. The analysis spot size was 400 μm. All binding energies were calibrated to the graphitic C 1s peak at 284.8 eV. XPS peaks were deconvolved and curve-fitted on the CasaXPS software using the Lorentzian function and Shirley background.

4. Electrochemical Measurements

Electrochemical measurements were conducted on a CHI760E electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd., China) and a MSR rotator (Pine Instrument Company, USA) in a standard three-electrode cell at room temperature (25 °C). A glassy carbon rotating disk electrode (RDE, diameter of 5 mm), an Ag/AgCl in saturated KCl electrode, and a platinum foil were used as the working, reference, and counter electrodes, respectively. All potentials were calibrated to the reversible hydrogen electrode (RHE) according to the Nernst equation $E_{vs\ RHE} = E_{vs\ Ag/AgCl} + 0.198 + 0.0592 \times pH$. 0.1 M KOH aqueous solution with a pH value of 13 was used as the electrolyte.

The working electrode was fabricated via the following procedures: 5 mg of the as-prepared catalyst was dispersed in a mixture of 960 μL of ethanol and 40 μL of 5 wt % Nafion solution. The mixture was ultrasonically dispersed for at least 0.5 h to obtain a homogeneous suspension. Then 20 μL of the

suspension was taken by a microsyringe and drop-casted onto a clean RDE with an overall loading of 0.25 mg cm^{-2}. The modified RDE was dried naturally in air. Prior to the tests, the electrochemical cell was saturated by purging N_2 or O_2 for at least 30 min. The linear sweep voltammetry (LSV) scan potential was set from 1.2 to 0 V, the scan rate was 10 mV s^{-1}, and the rotational speeds were 400–1600 rpm. In the SCN^- poisoning experiment, the working electrode with CoP/CNT was immersed in 0.01 M KSCN solution for 2 h. The immersed electrode was then immediately tested by LSV in O_2-saturated 0.1 M KOH to avoid the slow reaction between SCN^- and KOH.

The rotating ring-disk electrode (RRDE) measurements were conducted in O_2-saturated 0.1 M KOH at 1600 rpm and a scan rate of 10 mV s^{-1}. The ring potential was set as 1.3 V. The *n* value and peroxide yield (HO_2^-) were calculated by the following equations:

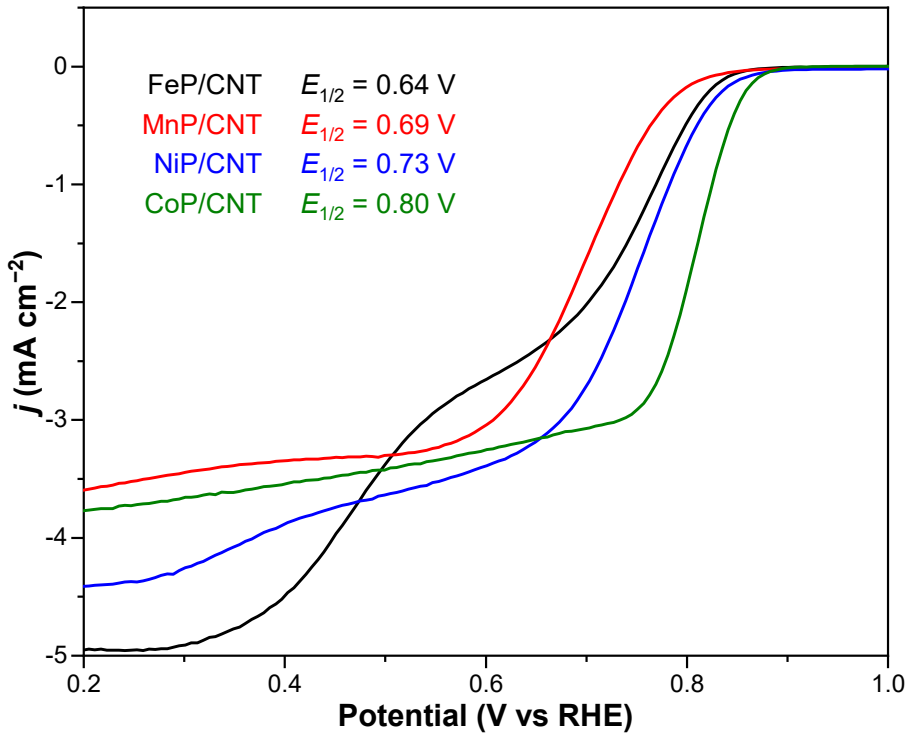
$$HO_2^-(\%) = 200 \times \frac{I_r/N}{I_d + I_r/N} \#(1)$$

$$n = 4 \times \frac{I_d}{I_d + I_r/N} \#(2)$$

where I_r and I_d are the ring and disk currents, respectively, and N is the current collection efficiency of RRDE (0.37).

5. Theoretical Calculation Details

All the density functional theory (DFT) calculations were conducted with the projector-augmented wave method implemented in the Vienna *ab initio* Simulation Package (VASP).[S1,2] The implicit solvent model was included by VASPsol.[S3] Atomic models, including C_{60} on the same side and opposite sides of a CoP molecule that is pre-stabilized on intact graphene were built for corresponding investigations. A 8×4×1 sized supercell consisting of 128 carbon atoms was used as the graphene-based matrix. Periodic boundary conditions and a supercell with a separation of about 14 Å were used to ensure that the interactions between adjacent supercells were negligible. Meanwhile, a vacuum of 15 Å was imposed in the Z direction. The Perdew-Burke-Ernzerhof (PBE) within the generalized gradient approximation (GGA) was employed as an exchange-correlation functional.[S4] A plane-wave cutoff energy of 450 eV was chosen for all the computations to describe all atoms' valence electrons. The convergence criterion of energy and force was set to 10^{-4} eV and 0.02 eV $Å^{-1}$, respectively. The van der Waals (vdW) interactions were described by the Grimme's scheme (DFT-D3) correction method.[S5]



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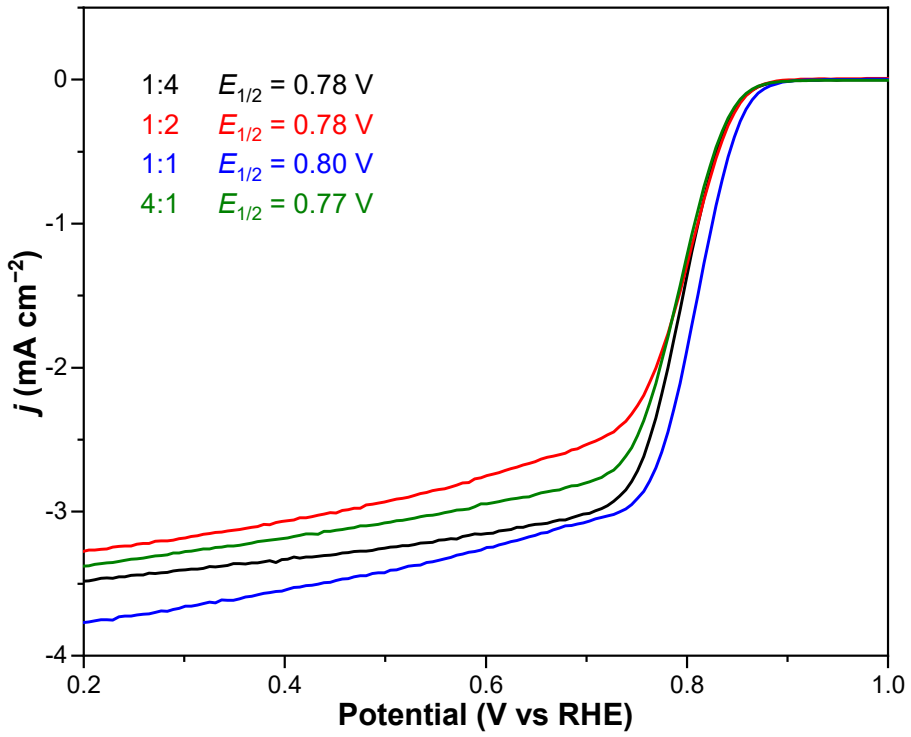

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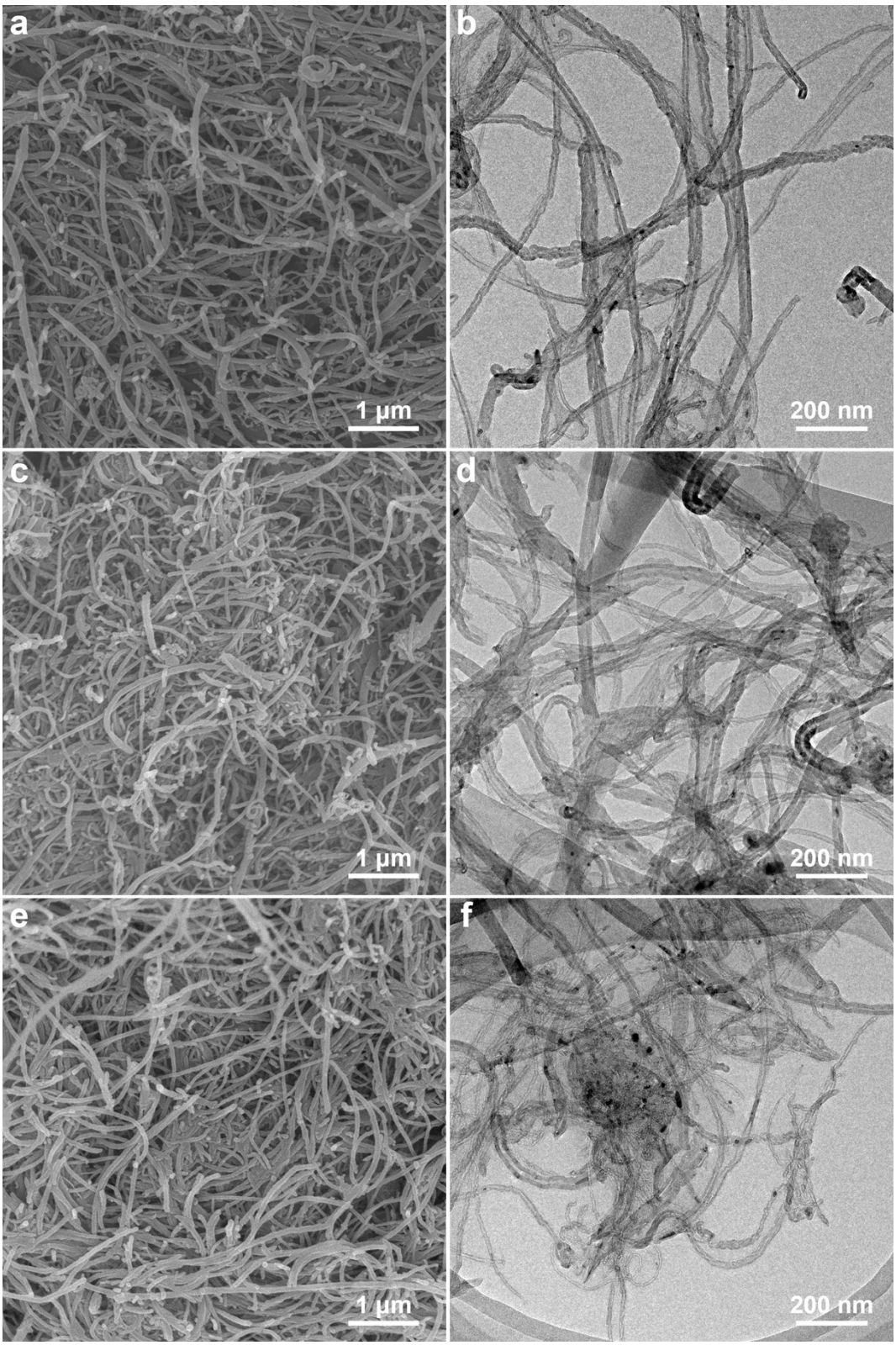

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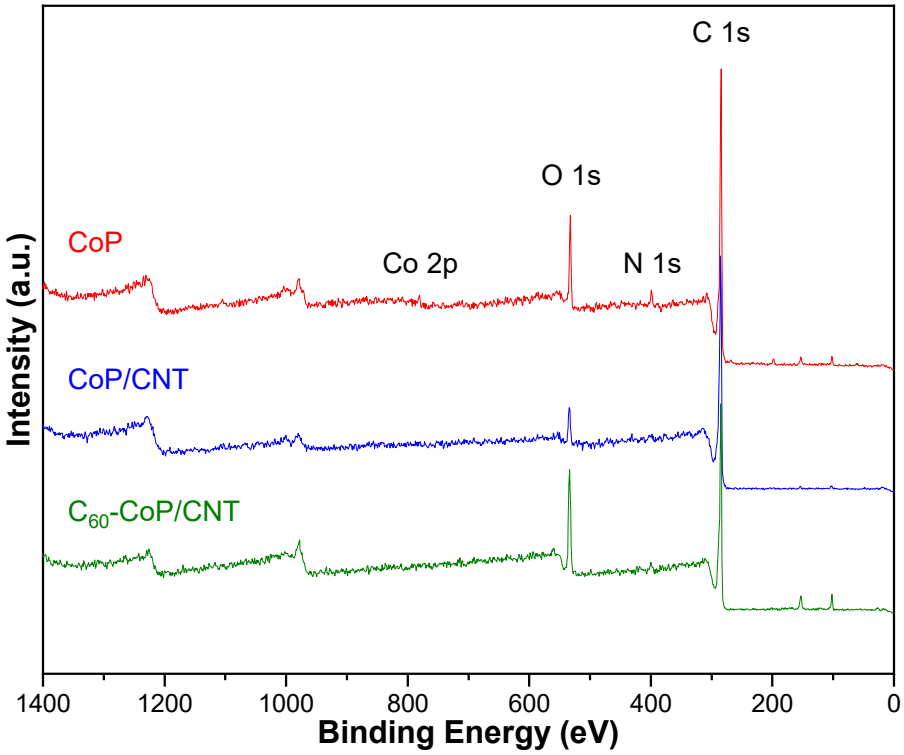

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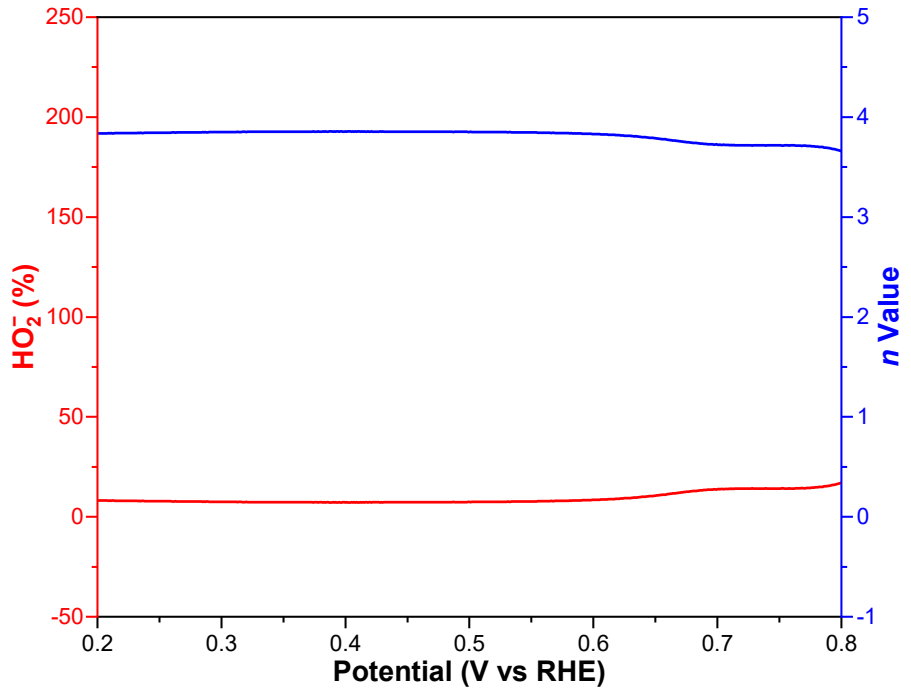

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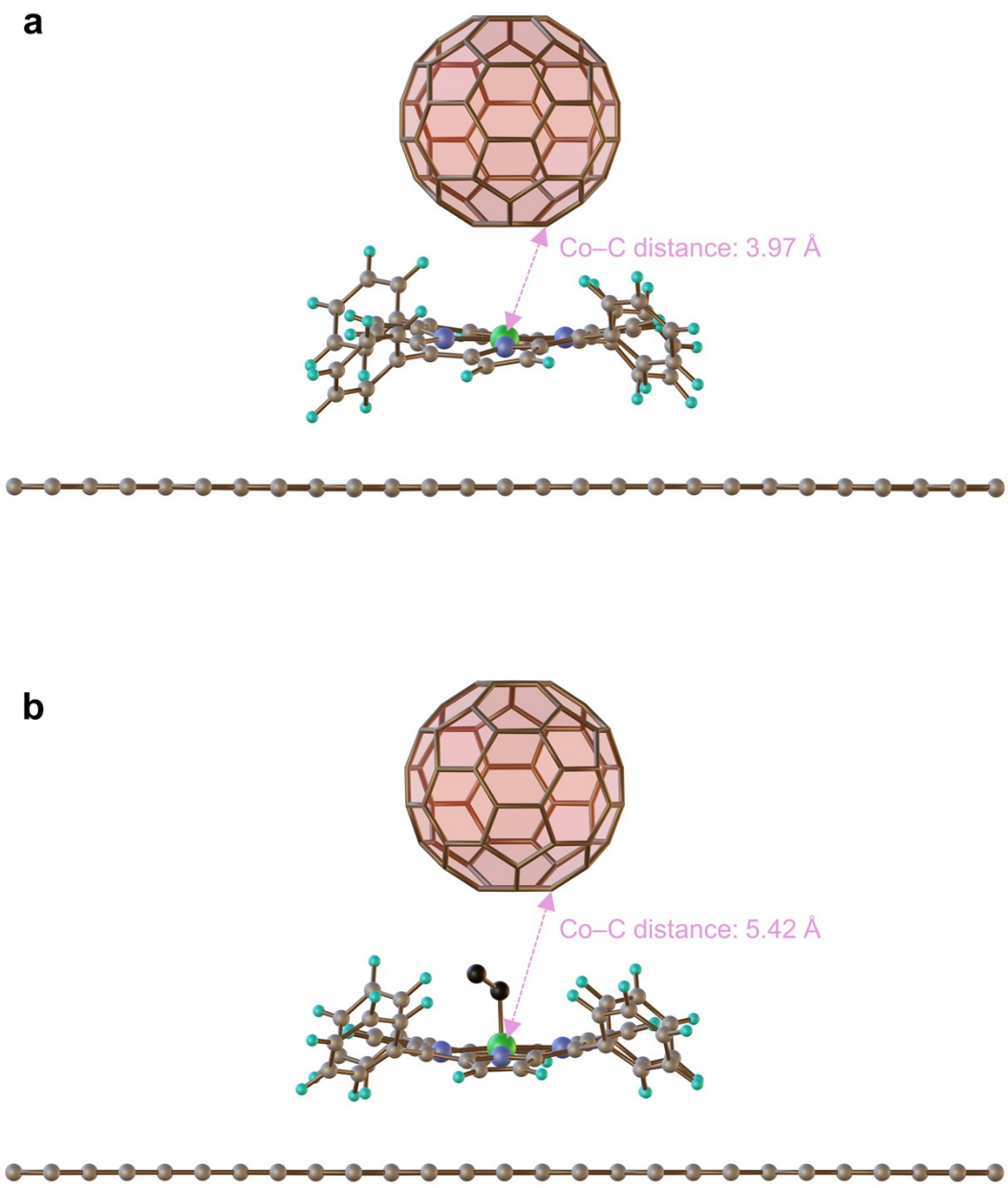

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The extended spatial distance between Co atom and C_{60} molecule after O_2 adsorption indicates that steric hindrance is created after C_{60} adsorption such that O_2 molecules will have to overcome the considerable interactions between C_{60} and CoP to be able to approach the central Co atom.

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