Surface Sulfur Doping Induced Enhanced Performance of Cobalt Catalysts in Oxygen Evolution Reactions

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I. Computational and Experimental Details

DFT Calculations

All spin-polarised density-functional theory (DFT) computations are performed using the Vienna ab initio simulation package (VASP) based on the projector augmented wave (PAW) method.[1] Electron-ion interactions are described using standard PAW potentials, with the valence configurations of $2s^22p^63s^23d^7$ for Co, $3s^23p^4$ for S, $2s^22p^4$ for O, and $1s^1$ for H. A plane-wave basis set is employed to expand the smooth part of wave functions with a cut-off kinetic energy of 520 eV. For the electron-electron exchange and correlation interactions, the functional parameterised by Perdew-Burke-Ernzerhhof (PBE),[2] a form of the general gradient approximation (GGA), is used throughout.

To study the mechanistic chemistry of surface reactions, the surface is modeled with four atomic layers separated a sufficiently large vacuum region of 20 Å to ensure the periodic images to be well separated. Based on X-ray diffraction (XRD) patterns and HRTEM images, we concluded that the (111) plane of the Co nanoparticles (NPs) is the most exposed surface to the solution. Thus, the Co (111) surface slab models are used to study the interaction between adsorbates and catalysts. To keep the spin component of Co atoms in the same direction, a relatively large number (32) of electrons in up and down spin component is set for the initial optimisation of geometric and electronic structures to get the corresponding charge density and wave functions. After that, the restricted number of electrons in different spin components will be removed during the optimisation of geometric and structural structures. Based on our calculation, the magnetic moment of each Co atom are 1.62 and 1.68 μB in the bulk and bare Co (111) surface, respectively, which are close to the other theoretical results.[3]

During the geometry optimisations, the bottom two atomic layers are fixed at the bulk position when the surface properties are calculated. In this work, the Brillouin-zone integrations are conducted using Monkhorst-Pack grids of special points. A (6 × 6 × 1) k-point grid is used for the (2 × 2) surface cell. The H_2 and O_2 molecules are calculated in a 20 × 20 × 20 $Å^3$ box. The Brillouin-zone integrations are performed using the Gamma-point only grid. The convergence criterion for the electronic self-consistent loop is set to 10^{-4} eV. And the atomic structures are optimised until the residual forces are below 0.01 eV $Å^{-1}$. The adsorption energy of *O on the surface is calculated according to the broadly used equation:

$$\Delta E_{ad} = E_{tot} - E_{surf} - \frac{1}{2}E_{O2}$$

Where E_{tot} is the total energy of surface with the surface intermediate *O; E_{surf} is the energy of bare surface; and E_{O2} is the energy of an isolated O_2 molecule.

Chemicals

Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$; ACS reagent, ≥98%), n-Hexane (HPLC grade, ≥95%), potassium hydroxide (KOH; ≥99.9%)) and ruthenium (IV) oxide (RuO_2; ≥99.9%) are purchased from Sigma-Aldrich. Sodium oleate ($C_{18}H_{33}O_2Na$ or NaOA) and sodium sulfate (Na_2SO_4; AR grade) are purchased from TCI Co. and Univar respectively. Absolute ethanol is of analytical grade and purchased from Chem-Supply. All chemicals are used as received without any further purification.

Preparation of S-Co/CNS and Co/CNS Catalysts

In a typical synthesis method, 3.0 mmol of $Co(NO_3)_2 \cdot 6H_2O$ is dissolved in 20 mL of Milli-Q water (18 Ω), then 6 mmol of NaOA is added to the mixture; 30 mL n-hexane and 20 mL ethanol are further added to the above mixture. The resulting suspension mixture is refluxed at 70 °C for 30 min with continuous stirring. After 30 min, 6 mmol of KOH is added and further refluxing is continued for another 3 h at 70 °C. Then, the suspension is allowed to cool down at room temperature and poured into a separatory funnel. The bottom aqueous layer containing unreacted metal ions and oleate (OA) is drained off; and the light organic top layer containing $Co(OH)_2$/OA is collected in a beaker. This solid mixture is dried at 80 °C to prepare the final precursor which mainly contains $Co(OH)_2$ (**Fig. S1**) and OA (**Fig. S2**). The obtained greenish colored solid is mixed with Na_2SO_4 maintaining the weight ratio of 1: 20 and finely grounded. This finely grounded powder is calcinated at 500 °C at a heating rate of 10 °C min^{-1} under continuous Ar flow and hold for 3 h in a tubular furnace. After that, the material is allowed to cool down at room temperature and washed with copious water by centrifugation at 12000 rpm for at least five times followed by absolute ethanol. At the final step, the black powder is dried at 60 °C for 24 h and named as S-Co/CNS. Pure cobalt nanoparticles (NPs) supported on carbon nanosheet (Co/CNS) is also prepared using the similar procedure without any sulfur source (Na_2SO_4).

Characterisations

Scanning electron microscope (SEM, JSM-7001F), transmission electron microscope (TEM, Philips F20), and X-ray diffraction (XRD, Bruker D8 Advance diffractometer, equipped with a graphite monochromator) techniques are employed for characterising the sample crystal structures. The chemical compositions of the samples are analysed by X-ray photoelectron spectroscopy (XPS, Kratos Axis ULTRA incorporating a 165 mm hemispherical electron energy analyzer). Raman spectra are collected with a Renishaw 100 system Raman spectrometer using 632.8 nm He-Ne laser. The real-time gases (H_2O, CO, H_2S and CO_2) produced during the calcination is monitored by an online mass spectrometer (MS, OmniStar GSD 320) connected with a tubular furnace. The total amount of Co contents (wt%) in both S-Co/CNS and Co/CNS samples are estimated to be 38.9 and 39.1% by inductively coupled plasma emission spectroscopic (ICP-OES, Agilent 710) technique. Fourier transform infrared spectroscopy (FTIR) analysis of the samples are carried out using Perkin Elmer spectrum 1000 FTIR spectrometer with KBr as reference matrix.

To examine the OER catalytic performance, a homogeneous ink is first prepared by adding 4.0 mg of catalyst in 1000 µL of solvent mixture of Nafion (5%), absolute ethanol and Mili-Q water maintaining the volume ratio of 1:1:8 followed by continuous ultra-sonication for at least 1 h. Then 12.0 µL (loading of 0.24 mg cm^{-2}) of catalyst ink is drop casted on the clean rotating disk electrode (RDE) and dried in air at room temperature. The OER activities are measured in a standard three electrodes system, where the catalyst loaded RDE, an Hg/HgO (1.0 M NaOH) electrode and platinum mesh act as working, reference and counter electrode respectively. The electrochemical responses are recorded using a computer-controlled potentiostat (CHI 760D, CH Instrument, USA) and the current density is normalised to the geometric surface area of RDE (0.196 cm^2). All potentials displayed in this work are converted to the reversible hydrogen electrode (RHE) scale using the equation $E_{RHE} = E_{Hg/HgO} + 0.059 \times pH + 0.098$, where pH = 14 in 1.0 M KOH electrolyte. The polarisation curves are corrected with 95% iR-compensation. AC impedance measurements are carried out under the same experimental configuration at overpotential of 340 mV from the frequencies ranging from 10^5 to 10^{-1} Hz with the applied potential amplitude of 5 mV. The chronopotentiometric (CP) and chronoamperometric (CA) stability are tested at the current density of 10 mA cm^{-2} and 1.56 V (vs. RHE) respectively for 12 h.

II. Supporting Figures

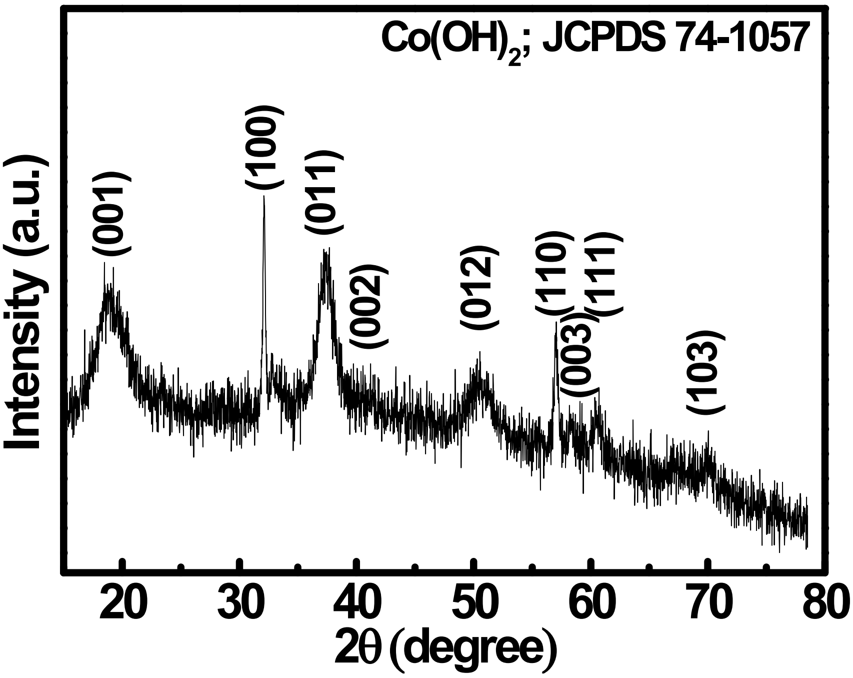

Fig. S1 XRD pattern of as synthesised precursor as $Co(OH)_2$/OA used for the preparation of Co/CNS and S-Co/CNS catalysts.

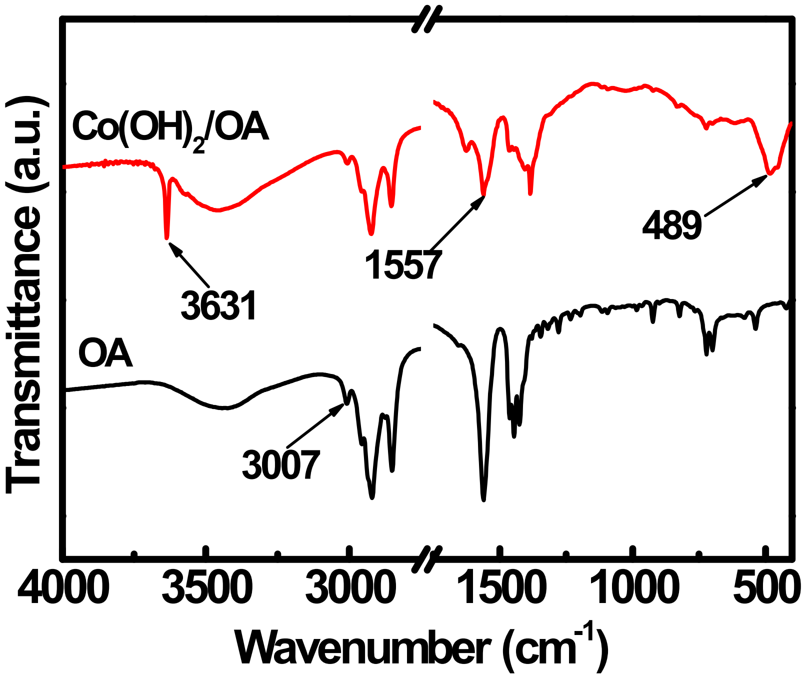

Fig. S2 FTIR spectra of Co(OH)$_2$/OA precursor. Pure sodium oleate (OA) is taken into account for comparison purpose.

In the FTIR spectra of Co(OH)$_2$/OA, the peak located at 3631 and 489 cm^{-1} can be assigned as the characteristic non-hydrogen bonds (O-H) stretching vibration and Co-O bending vibrations in Co(OH)$_2$.[4] On the other hand, the peak intensity drops at the position 1557 cm^{-1} compared to pure OA indicates the formation of cobalt-oleate complex.[5] Also, the peak at 3007 cm^{-1} related to vinyl C-H stretching further confirms the successful preparation of Co(OH)$_2$/OA precursor.

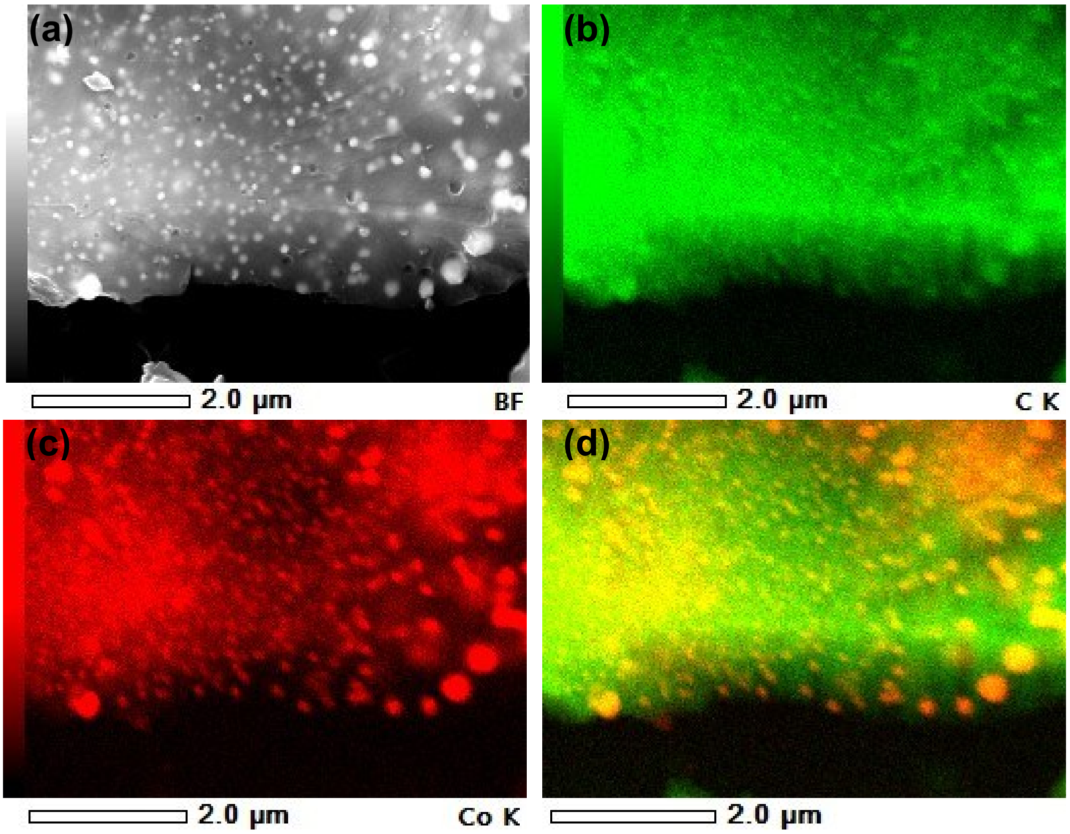

Fig. S3 (a) Dark-field SEM, (b) carbon, (c) cobalt and (d) overlay elemental mapping image of Co/CNS sample.

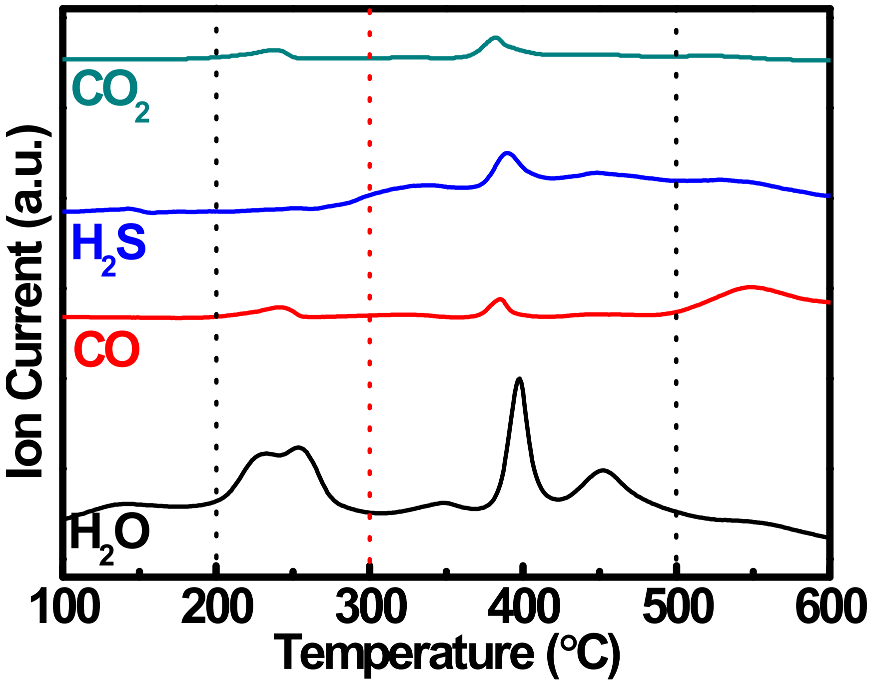

Fig. S4 MS responses during the calcination of $Co(OH)_2$/OA precursor from 100 to 600 °C under Ar protection. The production of various gases (H_2O, CO, H_2S and CO_2) is monitored by an online MS spectrometer.

Based on the detected gas during calcination, the formation of S-Co/CNS can be proposed through the following reactions which are merely consistent with the literature elsewhere.[6]

$\text{Na-OA} + Co(NO_3)_2{\cdot}6H_2O \rightarrow Co(OA)_2 + NaNO_3 + H_2O$ (1)

$Co(OA)_2 + KOH \rightarrow Co(OH)_2/OA$ (2)

$Co(OH)_2/OA \rightarrow CoO + H_2O + C$ (3)

$C + Na_2SO_4 \rightarrow Na_2S + CO + CO_2$ (4)

$Na_2S + H_2O \rightarrow H_2S + NaOH$ (5)

$CoO + C + H_2S \rightarrow \text{S-Co/CNS} + H_2O$ (6)

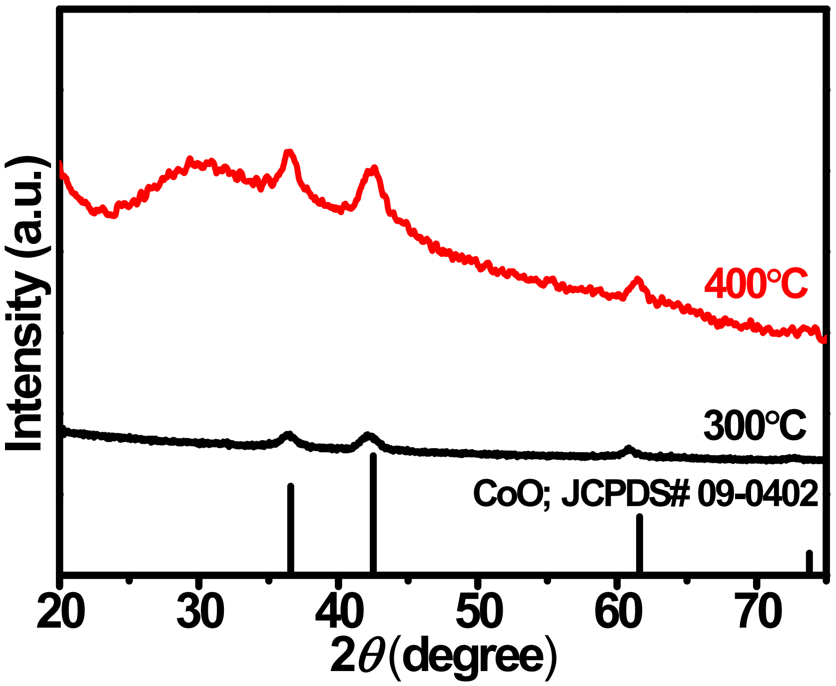

Fig. S5 XRD patterns of the samples prepared at 300 and 400 °C.

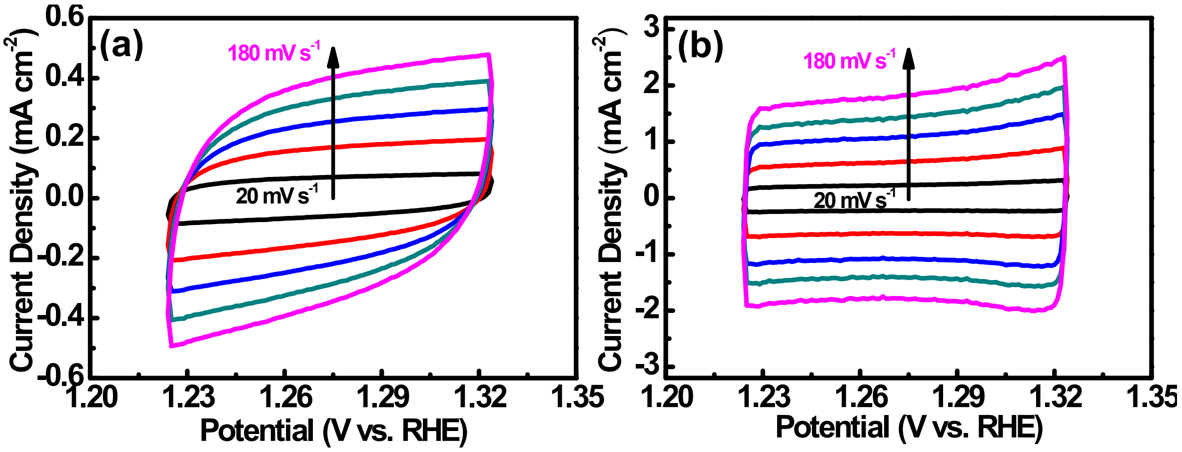

Fig. S6 Cyclic voltammograms of (a) Co/CNS and (b) RuO_2 at different scan rates (20, 60, 100, 140 and 180 mV s^{-1}) in a potential window (1.224-1.324 V vs. RHE) where no Faradic processes occur.

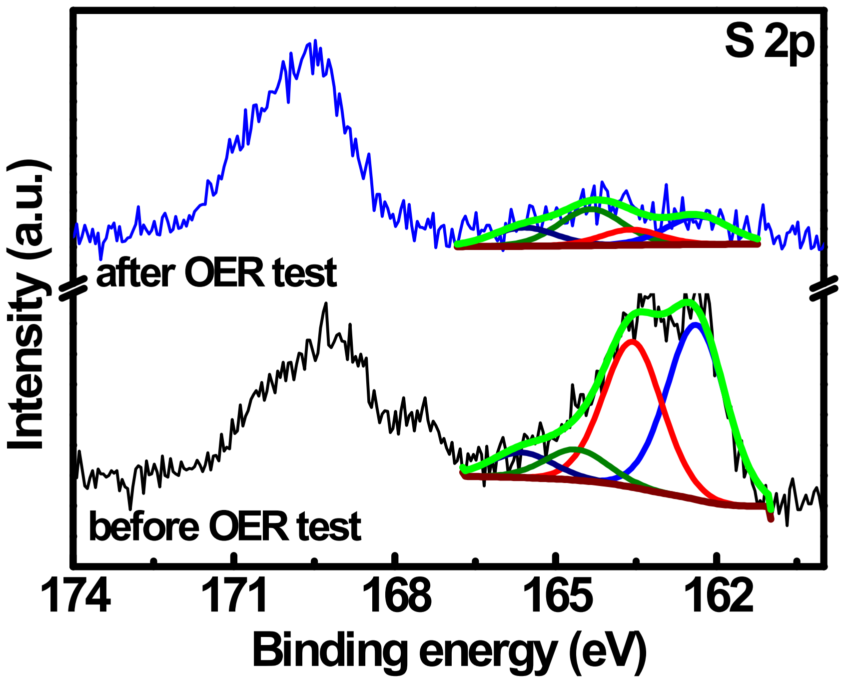

Fig. S7 Comparison of high resolution S 2p XPS spectra of S-Co/CNS before and after 12 h OER test.

As shown in Fig. S7, after 12 hour OER test, the S^{2-} states bonded with the Co surface still exist, which indicates that the good stability of S-Co/CNS catalysts.

Supporting References

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