An *In situ* Vapour Phase Hydrothermal Surface Doping Approach for Fabrication of High Performance Co₃O₄ Electrocatalyst with Exceptionally High S-doped Active Surface

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A facile *in situ* vapour phase hydrothermal (VPH) surface doping approach has been developed for fabrication of high performance S-doped Co₃O₄ electrocatalyst with an unprecedentedly high surface S content (>47%). The demonstrated VPH doping approach could be useful for enrichment of surface active sites for other metal oxide electrocatalysts.

Electrocatalyst plays a critical role in energy conversion technologies such as solar and fuel cells. To date, high performance electrocatalysts used for these applications are mainly fabricated by noble metals that are precious and scarce, hindering their widespread use. Extensive efforts have therefore been made to develop non-precious-metal-based electrocatalysts using transition metal alloys, oxides, chalcogenides, nitrides, phosphides, carbides and metal/organic composites.¹

For developing non-precious-metal-based high performance electrocatalysts, a central task is the pursuit of effective and efficient means to introduce rich catalytic active sites into the materials. Various active site creation/enrichment strategies have been reported such as morphological control, surface engineering and anchoring onto porous supports.² Among them, introducing exterior elements into existing material structures (doping) has been proven to be an effective approach.³ Furthermore, available evidences suggest that the richness of active sites in the resultant electrocatalyst closely depends on the dopant content.⁴ However, introducing a high dopant content via the majority of the reported bulk doping approaches is highly challenging because high dopant contents are destructive to the original crystal structures.⁵ This is particularly true for anions doped electrocatalysts where the maximum dopant contents are generally less than 10%.³a,⁶

It is well known that the activity of an electrocatalyst is determined by its surface active sites rather than those bulk ones.⁷ Therefore, developing new doping approaches to realise selective surface high-content doping and non-destructive to the bulk material structures is highly desirable.

In this work, we venture to extend the VPH methods⁸ for selective doping high content of exterior anion elements on the surface of metal oxides. Sulphur and spinel-type cobalt oxide (Co₃O₄) are respectively used as the anion dopant and bulk metal oxide to demonstrate the effectiveness of the proposed doping approach. An unprecedented 47% doped S content on the surface of Co₃O₄ nanosheets can be achieved, leading to a dramatically enhanced electrocatalytic performance. Although versatile applications of Co₃O₄ in catalysis have been reported,⁹ the anion-doped Co₃O₄ catalysts have rarely been investigated.⁶b,¹⁰

**Fig. 1** (a) XRD patterns, (b) Raman spectra of CNS and S-CNS samples; (c) Cross-sectional SEM, (d) TEM and (f) HRTEM image of S-CNS sample.

The Co₃O₄ nanosheets coated FTO (denoted as “CNS”) was firstly prepared via electrodeposition followed by sintering. Fig. S1 schematically illustrates the *in situ* VPH doping approach. Briefly, the synthesised CNS as the doping substrate is suspended in a VPH reactor containing Al₂S₃ and a small quantity of water as the doping reactants. The VPH doping is...
carried out at a low temperature of 90°C for 6 h to obtain the S-doped Co₃O₄ nanosheets (denoted as “S-CNS”). An initial heating will generate water vapour, triggering a slow hydrolysis reaction of Al₂S₃ to produce H₂S gas that acts as the S doping source.

X-ray diffraction (XRD) data of the samples before and after VPH doping treatment show similar diffraction patterns (Fig. 1a) that can be assigned to spinel Co₃O₄ crystal structure (cubic, a = 8.056 Å, space group Fd-3m, JCPDS: PDF-74-1656, ICSD: 27497). However, the S-CNS sample shows diffraction peaks being slightly shifted (Δ2θ = 0.15°) towards lower angle due to the increased lattice constants resulting from S doping. These results confirm that there is no significant change in the bulk crystal structures of S-CNS sample. The room-temperature Raman spectra of both samples reveal 5 distinctive peaks ascribable to spinel Co₃O₄ crystals (Fig. 1b). Notably, compared to CNS, all peaks observed from S-CNS appear at lower frequencies, indicating an increase in structural disorder and decreased bond strength of S-doped Co₃O₄.

The high-resolution Co 2p₃/2 spectra (Fig. 2b) can be fitted due to the increased lattice constants resulting from S doping. The Co 2p₃/2 peak (centred at 779.9 eV) of CNS shifts to 779.3 eV, close to that of Co₃S₄ (779.0 eV). For the O 1s spectra (Fig. 2c), the peak centred at 529.6 eV observed from CNS can be assigned to the lattice oxygen (Olat, Co-O) and the rest of the peaks are attributed to absorbed non-stoichiometric oxygen. Notably, the Osurf peak of S-CNS vanishes while others shift towards higher binding energies. Importantly, the surface O replacement by S can be confirmed from the observed main S 2p₂/₃ peak centred at 162.4 eV (assigned to Co-S) and the minor peak centred at 163.5 eV (related to S₆²⁻ species) from S-CNS (Fig. 2d).

Scanning electron microscopic (SEM) observations of the samples before (Fig. S2) and after (Fig. 1c) S doping confirm that CNS and S-CNS samples are composed of a 200 nm layer of uniformly coated nanosheets (~6 nm in thickness) and the VPH doping process has no noticeable effect on the nanosheet structure. The transmission electron microscope (TEM) image reveals that the nanosheets are formed by multiple closely-packed single crystals (Fig. 1d). The high resolution TEM (HRTEM) image shows that these nanosheets are mainly bounded with Co₃O₄ {111} facets (Fig. 1e), further confirming the well-maintained bulk Co₃O₄ crystals after VPH doping.

Fig. 2 XPS data: (a) survey spectra, (b) Co 2p and (c) O 1s spectra of CNS and S-CNS samples; (d) S 2p spectrum of S-CNS sample.

The electrocatalytic activity of S-CNS electrode was evaluated for the most commonly employed I-/I₃⁻ electrolyte system in dye-sensitised solar cells (DSSCs). The cyclic voltammogram (CV) of CNS electrode in I-/I₃⁻ solution shows ill-defined I-/I₃⁻ redox responses, indicating a poor reversibility and electrocatalytic activity (Fig. 3a). In strong contrast, the CV of S-CNS electrode obtained under the same conditions reveals two pairs of well-defined redox peaks, representing the distinctive characteristic of I-/I₃⁻ redox processes, confirming the superior electrocatalytic activity of S-CNS (Fig. 3a). Comparing to Pt (Fig. 3a) and metal sulphide electrodes (e.g., NiS₂, MoS₂, Co₃S₄ and Ni₃S₈), S-CNS electrode exhibits a noticeable anodically shifted cathodic peak potential and significantly reduced redox peak separation (Eap2-Ecp2) corresponding to I-/I₃⁻ redox processes, further confirming the superiority of S-CNS. The excellent electrochemical stability of S-CNS electrode is demonstrated by the almost identical CV responses obtained from 100 consecutive cycles (Fig. S3).

The electrocatalytic activity of S-CNS as a counter electrode in DSSC was also evaluated (Fig. 3b). The key performance parameters are summarised in Table S1. The DSSC assembled with the S-CNS counter electrode shows a conversion efficiency of 7.79%, almost identical to that of the DSSC assembled with a benchmark Pt counter electrode.
adsorbed 0.33 and -1.20 eV. The XPS results (Fig. 2) suggest that the high performance electrocatalyst for I\textsuperscript{3-} reduction reaction functional theory (DFT). Previous studies have shown that a doping should be the main form of surface active sites. The calculated ∆E\textsubscript{ad} of I on such optimised surface is -0.57 eV, close to ∆E\textsubscript{ad} values obtained from Pt (-0.52 eV) and CoS (-0.59 eV) surfaces. This indicates that the surface Co-S bonds resulted from VPH doping should be the main form of surface active sites.

In summary, the effectiveness of VPH approach has been validated for in situ selective doping of exceptionally high S contents onto the surface of Co\textsubscript{3}O\textsubscript{4} crystal without destruction to the bulk structures. The obtained electrocatalyst exhibits superior electrocatalytic activity for I\textsuperscript{-} reduction, almost identical to that of the benchmark commercial Pt catalyst. The VPH surface doping approach demonstrated in this work is simple, effective and directly applicable to a wide spectrum of metal oxides-based electrocatalysts for other applications such as hydrogen and oxygen evolution reactions.

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Notes and references

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