



Cite this: *Mater. Adv.*, 2021,  
2, 7054

Received 29th June 2021,  
Accepted 30th August 2021

DOI: 10.1039/d1ma00566a

rsc.li/materials-advances

## Enriching surface oxygen vacancies of spinel $\text{Co}_3\text{O}_4$ to boost $\text{H}_2\text{O}$ adsorption for HER in alkaline media†

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Oxygen-defective  $\text{Co}_3\text{O}_{2.64}\text{S}_{0.33}$  (namely  $\text{CoO}_{0.88}\text{S}_{0.11}$ ) particulate spheres (PS) were prepared *via* the solid-state sulfurization of spinel  $\text{Co}_3\text{O}_4$  at 300 °C in an Ar atmosphere. The introduction of sulfur (S) atoms was found to enrich the surface oxygen vacancies ( $V_{\text{so}}$ ) remarkably in the as-derived  $\text{CoO}_{0.88}\text{S}_{0.11}$  PS relative to pristine  $\text{Co}_3\text{O}_4$  and  $\text{CoS}_2$ , thus offering more active sites for catalytic reactions. Theoretical calculations were also performed to justify that the enrichment of  $V_{\text{so}}$  is favorable to boost the adsorption of  $\text{H}_2\text{O}$  molecules. As a result, these  $\text{CoO}_{0.88}\text{S}_{0.11}$  PS with exposed (111) facets demonstrated enhanced electrocatalytic performance in  $\text{H}_2$  evolution reaction (HER) with a low overpotential (OP) of 83 mV to realize a current density of  $10 \text{ mA cm}^{-2}$ , and a high turnover frequency (TOF) of  $1.589 \text{ H}_2 \text{ s}^{-1}$  was obtained in 1 M KOH aqueous electrolyte.

### 1. Introduction

Cobalt oxides and sulfides, such as  $\text{Co}_3\text{O}_4$ ,  $\text{CoO}$ ,  $\text{CoS}$ ,  $\text{Co}_3\text{S}_4$ ,  $\text{Co}_9\text{S}_8$ , and  $\text{CoS}_2$ , have been widely explored in photo/electrochemical energy storage and conversion because of their intrinsic merits of low cost, high availability, and excellent chemical stability.<sup>1,2</sup> For example,  $\text{Co}_3\text{O}_4$  has been intensively employed as an anode material in lithium ion batteries due to its high theoretical capacity and high reversibility.<sup>3–5</sup> As a typical p-type semiconductor,  $\text{CoO}$  is one of the most studied photocatalysts, which can utilize solar energy for water splitting by engineering the band edges.<sup>6,7</sup> Compared to their oxide counterparts, cobalt sulfides usually exhibit higher electroactivity and better electric conductivity, making them more promising in metal ion batteries,<sup>8–10</sup> supercapacitors,<sup>11–13</sup> and electrocatalysis.<sup>14–16</sup> Nano engineering and structural design are considered effective strategies to optimize the physical and chemical properties of cobalt oxides/sulfides,<sup>17</sup> because the specific surface area, porous texture, electron transport, and chemical stability of the functional materials can be readily tuned and manipulated, so as to realize high specific capacities, prolonged cycle life, or excellent catalytic rates.<sup>18</sup> However, the intrinsic properties of the respective cobalt oxides/sulfides are still not fully explored due to the poor understanding of the

mechanisms for charge distribution and transfer in the electrochemical/catalytic process.

The electrocatalytic performance of particulate catalysts is highly related to atomic defects, such as oxygen vacancies.<sup>19,20</sup> For example,  $V_{\text{so}}$  are reported to influence the adsorption of zinc ions on the material surface, whereby the calculated Gibbs free energy of  $\text{Zn}^{2+}$  can be altered.<sup>21</sup> A recent work has shown that  $V_{\text{so}}$  played a complicated role in the PEC process, where  $V_{\text{so}}$  can increase the carrier concentration to enhance charge transfer and suppress bulk recombination.<sup>22</sup> Engineering of  $V_{\text{so}}$  in cobalt oxides has been attractive for electrocatalysis. Wang *et al.* demonstrated that the presence of  $V_{\text{so}}$  in  $\text{Co}_3\text{O}_4$  has led to the formation of more  $\text{Co}^{2+}$  active centers on the  $\text{Co}_3\text{O}_4$  surface, which is significant to improve the catalytic performance.<sup>23</sup> In a later work by the same group, they found that  $V_{\text{so}}$  are favorable to promote the reconstruction/deprotonation of intermediate  $\text{Co-OOH}^*$ , providing a strong evidence for the role of  $V_{\text{so}}$  in electrocatalytic oxygen evolution reaction (OER).<sup>24</sup> Ma *et al.* prepared defective  $\text{Co}_3\text{O}_{4-x}$  by calcining SBA-15 to downshift the conduction bands of the Co 3d orbitals, thus improving the electron transfer for electrocatalytic OER.<sup>25</sup> It has been reported that the substitution of chalcogen elements can be used to generate oxygen vacancies in a recent research,<sup>26</sup> and the enrichment of oxygen vacancies could be attributed to the extrusion of O by S atoms with a larger atomic radius. By surface engineering of  $\text{Co}_3\text{O}_4$ ,  $V_{\text{so}}$  were generated by a deoxygenation process to optimize the band edges and electronic structures, which can facilitate charge transfer during the catalytic process. Though various strategies for  $V_{\text{so}}$  have been developed and many exciting results have been reported,

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1ma00566a

controllable enrichment of  $V_{so}$  in spinel  $Co_3O_4$  by partial S substitution has been rarely performed so far.

In this work,  $CoO_{0.88}S_{0.11}$  PS with enriched  $V_{so}$  were prepared *via* the solid-state sulfurization of spinel  $Co_3O_4$  PS at 300 °C in the presence of sulfur (S) powder in Ar gas. Specifically, the generation and preservation of  $V_{so}$  were realized by the introduction of appropriate S species in addition to deoxygenation in Ar gas. As a result, the as-synthesized  $CoO_{0.88}S_{0.11}$  PS with exposed (111) facets exhibited enriched  $V_{so}$ , improved electronic conductivity, and a higher ECSA, relative to pristine  $Co_3O_4$  and  $CoS_2$  that was derived from complete sulfurization. When used as electrocatalysts for HER, these  $CoO_{0.88}S_{0.11}$  PS demonstrated a low OP of 83 mV to realize a current density of 10 mA cm<sup>-2</sup> with a small Tafel slope of 80 mV dec<sup>-1</sup> (in 1 M KOH aqueous solution), which are much better than those of pristine  $Co_3O_4$  (168 mV, 196 mV dec<sup>-1</sup>) or  $CoS_2$  (96 mV, 119 mV dec<sup>-1</sup>). In addition,  $CoO_{0.88}S_{0.11}$  PS can yield a high TOF of 1.589 H<sub>2</sub> s<sup>-1</sup>, suggesting a great potential for practical electrocatalytic application. Density-functional theory (DFT) was also employed to calculate the adsorption energies of H<sub>2</sub>O molecules at the (111) facets for all the samples to verify the experimental results.  $CoO_{0.88}S_{0.11}$  with enriched  $V_{so}$  exhibited the largest H<sub>2</sub>O adsorption energy of 0.4 eV (absolute value) among all the samples. This work has provided a new path of  $V_{so}$  engineering for metal oxide electrocatalysts to enhance HER.

## 2. Experimental section

### 2.1 Synthesis of the $Co_3O_4$ particulate spheres (PS)

The cobalt based precursor (CBP) PS were synthesized *via* a solvothermal method in an isopropanol (IPA) solution. In a typical synthesis procedure, 2 mmol  $Co(NO_3)_2 \cdot 6H_2O$  was firstly dissolved in 30 mL of IPA by magnetic stirring for 10 min. Next, 1 mL of ethylene glycol (EG) was added to the above solution and the mixture was stirred for another 10 mins. Finally, 3 mg of polyvinyl pyrrolidone (PVP, average molecular mass  $\sim 10\,000$  g mol<sup>-1</sup>) was dissolved into the mixture by magnetic stirring for another 10 min. The obtained transparent lavender solution was transferred into a Teflon lined sealed stainless-steel autoclave and heated at 180 °C for 6 h. The light purple product was washed by a rinse-centrifugation process with ethanol several times. The collected CBP powder was dried in an air-flow oven at 60 °C for 24 h.  $Co_3O_4$  PS were obtained by annealing the as-obtained CBP PS at 200 °C in a muffle furnace at a heating rate of 1 °C min<sup>-1</sup> for 2 h.

### 2.2 Synthesis of $CoO_{0.88}S_{0.11}$ PS

The collected  $Co_3O_4$  powder (100 mg) was placed at the downstream side of a tube furnace, and sulfur powder (200 mg) was placed at the upstream side of the tube furnace. Then,  $Co_3O_4$  was heated to 300 °C (heating rate of 3 °C min<sup>-1</sup>) and reacted for 5 h under an argon (Ar) atmosphere. After the reaction, the tube furnace was allowed to cool down naturally to ambient temperature to collect the  $CoO_{0.88}S_{0.11}$  PS product. In the control experiments, cobalt sulfide ( $CoS_2$ ) PS were obtained

using the same sulfurization process of  $Co_3O_4$  powder but at a higher temperature of 400 °C. Partial sulfurization was also performed at 200, 250, and 350 °C using the same procedure to produce the  $Co_3O_4$ -200, 250, and 300 samples, respectively, which were specifically subjected to ESR measurements.

### 2.3 Materials characterization

All the samples were characterized by scanning electron microscopy (SEM, Quanta FEG 250) equipped with energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM, Titan G2 60-300) equipped with an elemental mapping system, X-ray diffraction (XRD, Rigaku D/Max 2500,  $CuK_{\alpha} = 1.5406$  Å), and X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi). Room-temperature electronic spin resonance (ESR) spectra were measured using an ESR spectrometer (Bruker A300) at 300 K. The frequency of microwave used is 9.853 GHz with a power of 10.8 mW. The magnetic center field is 3510 G with a sweep width of 100 G. The module amplitude is 1 G with a time constant of 1.25 mS and a sweep time of 19.456 s.

### 2.4 Electrochemical measurements.

(1) Alkaline electrolyte: all the electrocatalytic measurements were carried out using an IVIUM V38120 electrochemical workstation in a three-electrode cell with a 1 M of potassium hydroxide (KOH) aqueous solution as the electrolyte. The saturated calomel electrode (SCE) and graphite rod served as the reference and counter electrodes, respectively. The working electrodes were prepared as follows: 18 mg of catalyst powder, 2 mg of polyvinylidene fluoride (PVDF), and 0.2 mL of *N*-methyl-2-pyrrolidinone (NMP) were mixed together and then ground for 10 minutes to obtain a homogeneous slurry. The slurry was then pasted homogeneously onto a piece of nickel foam (1 cm × 2 cm, coating area  $\sim 1$  cm<sup>2</sup>, mass loading  $\sim 4$  mg). Then the as-prepared working electrode was dried in a vacuum oven at 60 °C for 12 h.

(2) Acidic electrolyte: the electrochemical experiments were tested in standard three electrode system using an IVIUM V38120 electrochemical workstation, and the electrolyte was an aqueous solution of 0.5 M sulfuric acid ( $H_2SO_4$ ). The saturated calomel electrode (SCE) and graphite rod served as the reference and counter electrodes, respectively. The working electrodes were prepared as follows: 4 mg of catalyst and 30 μm of Nafion solution were added to 1 mL of water-ethanol mixture solution (volume ratio of 3 : 1), and the solution was ultrasonicated for 1 h to form a homogeneous ink. Then 5 μL of the ink was dropped onto a glassy carbon electrode (GCE) with a 3 mm diameter.

Linear sweep voltammetry (LSV) was performed at a scan rate of 5 mV s<sup>-1</sup> in a potential window of 0 to -0.5 V *versus* reversible hydrogen electrode (RHE). Electrochemical impedance spectroscopy (EIS) was performed at the frequency from 0.1 MHz to 0.01 Hz with an amplitude of 5 mV. The current variation with time (*i*-*t* curve) under constant voltage was measured for 12 h. To simplify the evaluation, a current density of 10 mA cm<sup>-2</sup> was used to compare the OPs for all the samples. Electrochemical surface area (ECSA) measurements



were performed within a non-faradaic voltage window ranging from  $-0.1$  to  $0$  V (vs. SCE). The lattice parameters of all the samples were obtained from PXRD to calculate the unit lattice volumes. The TOFs were then estimated based on the lattice volume, ECSA, and exchange current density using the following equation:<sup>27</sup>

$$\text{TOF} = \frac{\text{total hydrogen turnovers} \times |\text{current density}|}{\text{active sites} \times \text{ECSA}}$$

where the total hydrogen turnovers can be calculated from the current density collected from the LSV curves, the absolute value of current density is the value at zero overpotential, and active site density is the number of active sites per real surface area calculated from unit lattice volume.

## 2.5 Theoretical calculations

The calculations were conducted using density functional theory (DFT) with the Perdew–Burke–Ernzerhof (PBE) form of generalized gradient approximation functional (GGA).<sup>2</sup> The Vienna *ab initio* simulation package (VASP)<sup>28,29</sup> was used to calculate the exchange–correlation interaction of Co ( $3d^7 4s^2$ ), O ( $2s^2 2p^4$ ), S ( $3s^2 3p^4$ ), and H ( $1s^1$ ) valence electrons with the plane wave energy cutoff at 400 eV. The gamma-centered *K*-point meshes were set as  $3 \times 3 \times 3$  for  $\text{Co}_3\text{O}_4$  and  $\text{CoS}_2$  bulk, and  $2 \times 2 \times 1$  for  $\text{Co}_3\text{O}_4(111)$  surface,  $\text{CoO}_{0.88}\text{S}_{0.11}(111)$  surface, and  $\text{CoS}_2(111)$  surface. The energy (converged to  $1.0 \times 10^{-6}$  eV per atom) and force (converged to  $10^{-3}$  eV  $\text{\AA}^{-1}$ ) were set as the convergence criteria for geometry optimization.

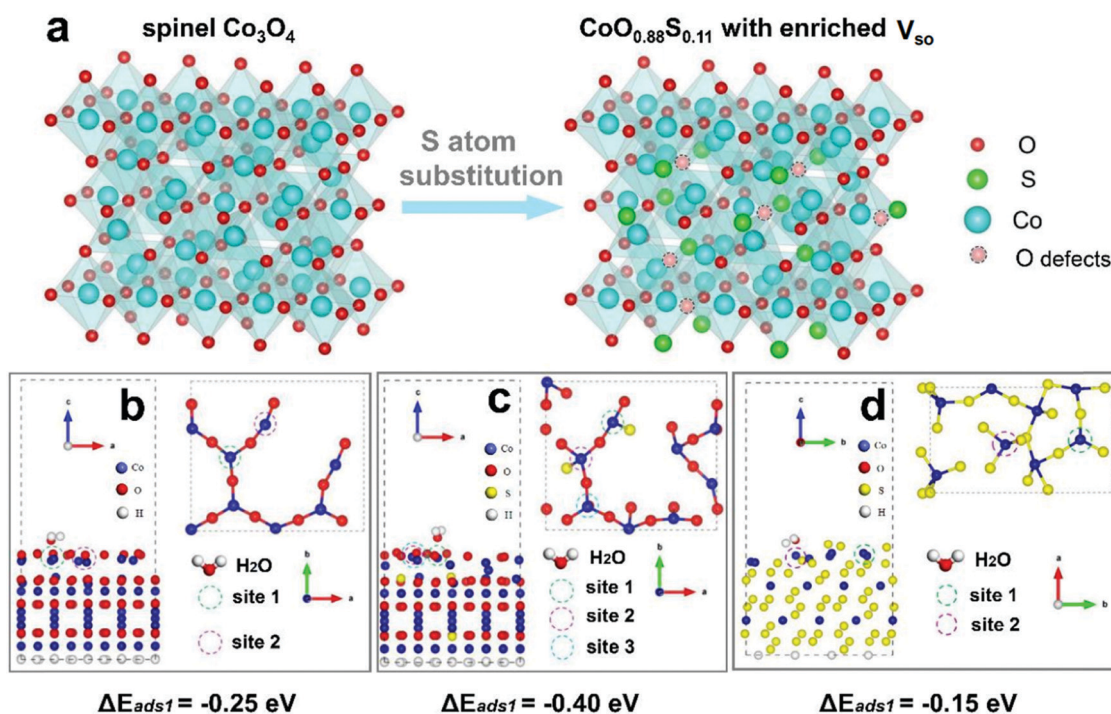
We have obtained the XRD results of  $\text{Co}_3\text{O}_4$  (JCPDS no. 74-2120:  $a = b = c = 0.8400$  nm, space group  $Fd\bar{3}m$ ), and  $\text{CoS}_2$  (JCPDS no. 89-1492:  $a = b = c = 0.5506$  nm, space group  $PA\bar{3}$ ), and thus the basic crystal models of  $\text{Co}_3\text{O}_4$ ,  $\text{CoO}_{0.88}\text{S}_{0.11}$ , and  $\text{CoS}_2$  can be illustrated. The (111) facets of all the samples were identified from the XRD and HRTEM images. In all the optimization for structural calculations, the atoms of the bottom layers were fixed, while the positions of the other atoms were allowed to relax. A vacuum layer as large as 15  $\text{\AA}$  was used along the *c* direction normal to the surface to avoid periodic interactions. Oxygen vacancies are formed by deleting oxygen atoms. In the  $\text{Co}_3\text{O}_4(111)$  surface model, there are 40 Co atoms, 48 O atoms, and 16 H atoms (for the bottom passivation). If one oxygen atom is deleted, there is one oxygen vacancy, and the percentage of oxygen vacancy is  $100 \times (1/48)\%$ . If two oxygen atoms are deleted, there are two oxygen vacancies, and the percentage is  $100 \times (1/24)\%$ . For the defective  $\text{CoS}_2(111)$ , one of the surface S atom was removed to simulate the S vacancy.

The chemisorption energies of  $\text{H}_2\text{O}$  on the (111) facets are described as follows:

$$E_{\text{ads}} = E_{\text{H}_2\text{O}/\text{catalytic}(111)} - E_{\text{H}_2\text{O}} - E_{\text{catalytic}(111)}$$

where  $E_{\text{H}_2\text{O}/\text{catalytic}(111)}$  is the total energy of  $\text{H}_2\text{O}$  on the (111) surface;  $E_{\text{H}_2\text{O}}$  is the total energy of free  $\text{H}_2\text{O}$  and  $E_{\text{catalytic}(111)}$  is the total energy of the (111) surface.  $E_{\text{H}_2\text{O}/\text{catalytic}(111)}$  and  $E_{\text{catalytic}(111)}$  were calculated with the same parameters.  $E_{\text{H}_2\text{O}}$  was calculated by setting the isolated adsorbate in a box of  $10 \text{ \AA} \times 10 \text{ \AA} \times 10 \text{ \AA}$ .

Based on the crystalline structures, the calculations of adsorption energies were carried out for the (111) facets with



**Fig. 1** Schematic crystalline structures of spinel  $\text{Co}_3\text{O}_4$  and the derived  $\text{CoO}_{0.88}\text{S}_{0.11}$  with enriched surface oxygen vacancies by S substitution (a), and diagrams of  $\text{H}_2\text{O}$  adsorption sites (b–d) for  $\text{Co}_3\text{O}_4(111)$  with one unit of O vacancy (b),  $\text{CoO}_{0.88}\text{S}_{0.11}(111)$  with two units of O vacancies (c), and  $\text{CoS}_2(111)$  with one unit of S vacancy (d).





Co–O or Co–S terminals. Adsorption sites for perfect surfaces, one, and two units of O or S vacancies were built to simulate the surfaces with no defect or enriched defects.

### 3. Results and discussion

A schematic of the transformation from spinel  $\text{Co}_3\text{O}_4$  to  $\text{CoO}_{0.88}\text{S}_{0.11}$  with enriched  $V_{\text{so}}$  by S atom substitution *via* solid-state sulfurization is displayed in Fig. 1a. At an elevated temperature, sublimation of sulfur powder takes place and the S species enter the spinel structure of  $\text{Co}_3\text{O}_4$ , and then replace partial O atoms at the solid–gas interface. As a result, more O ( $R = 0.074$  nm) atoms are squeezed out of the crystalline structure due to the much larger atomic radius of S ( $R = 0.102$  nm), thus forming  $\text{CoO}_{0.88}\text{S}_{0.11}$  with enriched oxygen vacancies at the surface. It should be noted that the crystalline structure is not altered after introduction of S species because a slight surface sulfurization is employed herein (recall experimental details).

It has been reported that the presence of surface defects is important to promote the intrinsic properties of catalysts. As for electrocatalytic water splitting, adsorption of  $\text{H}_2\text{O}$  molecules at the catalyst surface is the dominant step in the HER process. Thus, DFT calculations were then performed to compare the  $\text{H}_2\text{O}$  adsorption energies of the (111) facets (will be discussed in XRD and HR-TEM later) for all the three samples. The detailed calculation parameters are described in the experimental part, and corresponding simulation models are presented in Fig. S1 (ESI†). Fig. 1b–d show the diagrams of the adsorption sites (ads) of  $\text{Co}_3\text{O}_4$  (111) with Co–O terminals,

$\text{CoO}_{0.88}\text{S}_{0.11}$  (111) with Co–O terminals, and  $\text{CoS}_2$  (111) with Co–S terminals, respectively. Specifically, each Co atom at site 1 of  $\text{Co}_3\text{O}_4$  (111) is bonded with four O atoms, and contains one unit of O vacancy, as shown in Fig. 1b. Similarly, each Co atom at site 1 of  $\text{CoO}_{0.88}\text{S}_{0.11}$  (111) in Fig. 1c is bonded with two O and one S atoms, and contains two units of O vacancies (denoting enriched  $V_{\text{so}}$ ). Meanwhile for  $\text{CoS}_2$  (111), each Co atom at site 1 is bonded with three S atoms, and contains one unit of S vacancy. The calculation results have revealed that the adsorption energies ( $\Delta E_{\text{ads}}$ ) at sites 1 for  $\text{Co}_3\text{O}_4$ ,  $\text{CoO}_{0.88}\text{S}_{0.11}$ , and  $\text{CoS}_2$  are  $-0.25$ ,  $-0.40$ , and  $-0.15$  eV, respectively. Significantly,  $\text{CoO}_{0.88}\text{S}_{0.11}$  (111) with one unit of O vacancy also shows a larger  $\Delta E_{\text{ads}}$  of  $-0.39$  eV, compared to its  $\text{Co}_3\text{O}_4$  and  $\text{CoS}_2$  counterparts (more calculations shown later). A larger absolute number of  $\Delta E_{\text{ads}}$  suggests a more stable adsorption of  $\text{H}_2\text{O}$  molecules at the catalyst surface, which is favorable to expedite the HER process. These calculations have preliminarily implied the importance of surface sulfurization with enriched  $V_{\text{so}}$  for improving electrocatalytic performance.

Following our theoretical and experimental methods, cobalt based materials were then synthesized and characterized. Cobalt based precursor (CBP) PS were prepared using a solvo-thermal process (SEM images shown in Fig. S2, ESI†). Next, the as-synthesized CBP PS were transformed to  $\text{Co}_3\text{O}_4$  through a heat treatment at  $200^\circ\text{C}$  in air, which were subsequently used for partial or complete sulfurization. As the typical sample of this work,  $\text{CoO}_{0.88}\text{S}_{0.11}$  PS were examined by SEM and EDX, as shown in Fig. 2. From the SEM results, monodispersed spheres with uniform particle size ( $\sim 2\ \mu\text{m}$ ) can be observed (Fig. 2a and b). A magnified SEM image in Fig. 2c reveals that a particle is composed of nanosheets with a porous texture. The overall

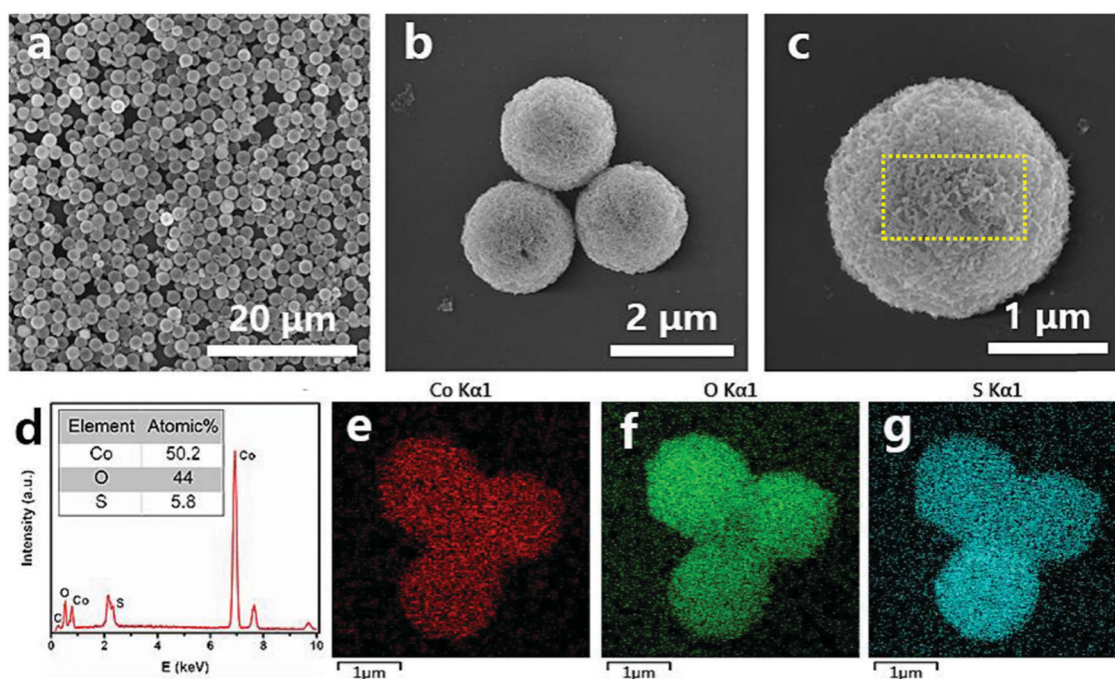


Fig. 2 SEM images (a–c), EDX (d), and elemental mappings (e–g) of the as-prepared  $\text{CoO}_{0.88}\text{S}_{0.11}$  PS.



morphology of the PS is well retained after partial sulfurization, compared to SEM results of  $\text{Co}_3\text{O}_4$  PS (Fig. S3a–c, ESI†). A complete sulfurization from  $\text{Co}_3\text{O}_4$  to  $\text{CoS}_2$  has led the conversion of nanosheets to aggregated particles, as shown in Fig. S3d–f (ESI†). Then, the EDX information of the typical sample in Fig. 2d was captured from the area indicated by the yellow rectangle in Fig. 2c, which confirms the presence of Co, O, and S elements (atomic ratio is roughly at 1:0.88:0.11, hence denoted as  $\text{CoO}_{0.88}\text{S}_{0.11}$ ) in the PS. In addition, elemental mappings were performed to find out the distributions of Co, O, and S, as shown in Fig. 2e–g. It can be seen that Co and O signals are almost overlapped, while S shows a slightly larger area than Co and O, suggesting a partial surface sulfurization of the pristine  $\text{Co}_3\text{O}_4$  particles.

The detailed structural, compositional, and electronic features were further investigated by TEM and ESR. Fig. 3a displays an individual  $\text{CoO}_{0.88}\text{S}_{0.11}$  PS, in which a hollow interior can be clearly observed. The magnified TEM image in Fig. 3b indicates that PS are composed of porous nanosheet structures, suggesting a high surface area of the material. Fig. 3c shows the HRTEM image which was taken from the area indicated by a yellow oval in Fig. 3b. The lattice spacings of 0.57 and 0.28 nm can correspond to  $\text{Co}_3\text{O}_4$  (111) and (220), respectively.<sup>30</sup> Notably, the spacing of (111) was enlarged from the usual  $\sim 0.46$  nm to 0.57 nm, which should be caused by the substitution of O by S with a larger atomic radius. In addition, a lattice distortion of  $\sim 17^\circ$  is observed for the (111) planes, demonstrating that the introduction of S heteroatoms may have deformed the periodic crystalline structure of  $\text{Co}_3\text{O}_4$ . The TEM and HR-TEM images were also obtained and presented for pristine  $\text{Co}_3\text{O}_4$  and  $\text{CoS}_2$  (Fig. S4, ESI†), which clearly reveal the high exposure of  $\text{Co}_3\text{O}_4$  (111) and  $\text{CoS}_2$  (111).

To confirm the existence of  $\text{V}_{\text{so}}$ , ESR tests were carried out for pristine  $\text{Co}_3\text{O}_4$ ,  $\text{CoS}_2$ , and the partially sulfurized  $\text{Co}_3\text{O}_4$  samples at different temperatures, respectively. The ESR spectra in Fig. 3d clearly show that  $\text{CoO}_{0.88}\text{S}_{0.11}$  ( $\text{Co}_3\text{O}_4$ -300) delivers a much higher signal than  $\text{Co}_3\text{O}_4$  or  $\text{CoS}_2$  at  $g = 2.004$ , which indicates the appearance of oxygen vacancies.<sup>31</sup> Unexpectedly,  $\text{CoS}_2$  exhibited only a bit higher signal than pristine  $\text{Co}_3\text{O}_4$ , which suggests that complete substitution of O with S may have changed the crystalline structure, thus causing the oxygen vacancies to vanish. In addition, it is interesting to find that lower sulfurization temperatures ( $\text{Co}_3\text{O}_4$ -200 and 250) failed to generate a large number of  $\text{V}_{\text{so}}$ , whereas higher temperature ( $\text{Co}_3\text{O}_4$ -350) was not favorable to preserve the O vacancies.

The XRD patterns of all the three samples are displayed in Fig. S5 (ESI†). All the peaks recorded from  $10$ – $80^\circ$  (Fig. S5a, ESI†) for  $\text{Co}_3\text{O}_4$  can be assigned to spinel  $\text{Co}_3\text{O}_4$  (JCPDS no. 74-2120),<sup>32</sup> while all the identified peaks for  $\text{CoS}_2$  should be assigned to cubic  $\text{CoS}_2$  (JCPDS no. 89-1492).<sup>33</sup> For  $\text{CoO}_{0.88}\text{S}_{0.11}$ , only peaks of  $\text{Co}_3\text{O}_4$  can be matched, indicating that the crystalline phase is not altered under such a slight sulfurization. However, slight shifts can still be distinguished in the diffraction peaks for all the XRD peaks of  $\text{CoO}_{0.88}\text{S}_{0.11}$ . For example, as shown in the magnified region in Fig. S5b (ESI†), the peak of  $\text{Co}_3\text{O}_4$  (311) was shifted from  $36.86^\circ$  to  $36.78^\circ$  after partial sulfurization, which should be caused by the replacement of the O positions by S atoms. In addition, it can be calculated that the unit cell parameter of  $\text{CoO}_{0.88}\text{S}_{0.11}$  is 0.8098 nm, which has been reduced compared to that of  $\text{Co}_3\text{O}_4$ . To further examine the chemical composition and status of the typical sample  $\text{CoO}_{0.88}\text{S}_{0.11}$ , XPS was carried out and the results are shown in Fig. 4. The survey spectrum in Fig. 4a confirms again the presence of Co, O, and S. The paired peaks of 779.7 and 795.7 eV shown in Fig. 4b can be attributed to  $\text{Co } 2p_{3/2}$  and  $\text{Co } 2p_{1/2}$ , respectively, corresponding to the characteristic spin orbitals of  $\text{Co}^{3+}$ .<sup>34</sup>  $\text{Co}^{3+}$  has shifted toward lower binding energies after partial sulfurization compared to pristine  $\text{Co}_3\text{O}_4$  (781.1 and 796.4 eV, respectively, Fig. S6a, ESI†), which is consistent with a previous work that demonstrates oxygen defects in  $\text{Co}_3\text{O}_4$ .<sup>35</sup> In addition, the presence of two satellite peaks centered at around 786 and 803 eV, respectively, should be attributed to the  $\text{Co}^{2+}$  oxidation state, which indicates that part of  $\text{Co}^{3+}$  has been reduced to  $\text{Co}^{2+}$  during the formation of  $\text{V}_{\text{so}}$ .<sup>36</sup> There are two binding energies for O 1s (Fig. 4c), which can be assigned to  $\text{Co-O}$  (529.3 eV),<sup>37</sup> and  $\text{O}^-$  (531.2 eV) related to oxygen vacancies,<sup>38</sup> respectively. Both  $\text{Co-O}$  and  $\text{O}^-$  shifted to lower binding energies compared to those of pristine  $\text{Co}_3\text{O}_4$  (530.7 and 532 eV, respectively, Fig. S6b, ESI†). The XPS peaks located at 162.3 and 164 eV (Fig. 4d) should be ascribed to  $\text{S } 2p_{3/2}$  and  $\text{S } 2p_{1/2}$ , respectively.<sup>39</sup> The broad peak at 168.6 eV can be assigned to  $\text{S-O}$  bond associated with  $\text{SO}_x$ .<sup>40</sup> Fig. S7 (ESI†) shows the XPS results of the  $\text{CoS}_2$  sample, in which strong peaks of  $\text{S-O}$  bonds (oxidized S, 168–170 eV) can be distinguished. Combining the results of TEM, XRD, and XPS analyses, we have demonstrated that S species were introduced into the lattice of  $\text{Co}_3\text{O}_4$  without altering the crystalline phase. However, S atoms may

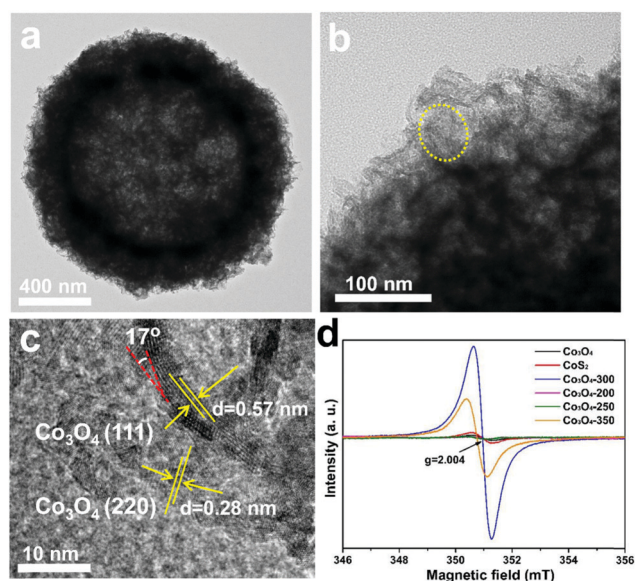


Fig. 3 TEM (a and b) and HRTEM (c) images of  $\text{CoO}_{0.88}\text{S}_{0.11}$  PS, and the ESR results (d) of pristine  $\text{Co}_3\text{O}_4$ ,  $\text{CoS}_2$ , and the partially sulfurized  $\text{Co}_3\text{O}_4$  at different temperatures ( $\text{Co}_3\text{O}_4$ -300 is  $\text{CoO}_{0.88}\text{S}_{0.11}$ ); the signal at  $g = 2.004$  corresponds to the O vacancies.



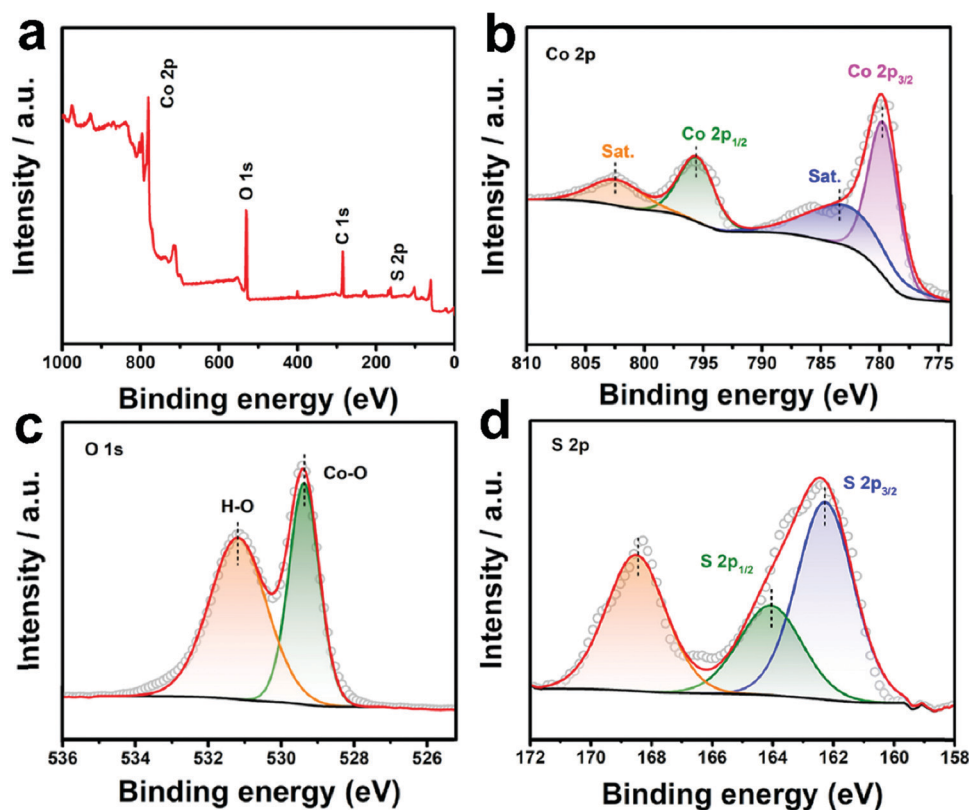
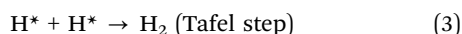
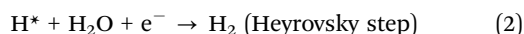
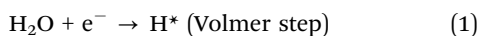


Fig. 4 XPS survey spectrum (a), Co 2p (b), O 1s (c), and S 2p (d) of the as-prepared  $\text{CoO}_{0.88}\text{S}_{0.11}$  PS.

replace O positions in the  $\text{Co}_3\text{O}_4$  crystal structure, and thus induce the generation of  $V_{\text{so}}$  with lattice distortion, which is essential to increase the intrinsic catalytic activity.

The HER properties were evaluated for all the samples using a standard three-electrode configuration in 1 M KOH. In an alkaline electrolyte, the HER process can proceed as the following Volmer–Heyrovsky and Volmer–Tafel reactions (1)–(3):<sup>41</sup>



The reactions start with the adsorption of  $\text{H}_2\text{O}$  molecules on the catalyst surface to generate  $\text{H}^*$  via the Volmer-step reduction process. Next,  $\text{H}_2$  molecules will be formed by the electrochemical bonding of  $\text{H}_2\text{O}$  with  $\text{H}^*$  (Heyrovsky step), or through the chemical combination of two  $\text{H}^*$  (Tafel step). By increasing the adsorption energy and reducing the dissociation energy barrier, the HER process can be efficiently facilitated in the presence of  $V_{\text{so}}$ .<sup>42</sup> In this work,  $\text{H}_2\text{O}$  adsorption energies in the presence of O vacancies in different samples have been studied using DFT calculations (more results and discussion later).

Fig. 5a shows the LSV curves of all the samples. The OPs at a current density of  $10 \text{ mA cm}^{-2}$  for  $\text{Co}_3\text{O}_4$ ,  $\text{CoS}_2$ ,  $\text{CoO}_{0.88}\text{S}_{0.11}$ , and Pt/C are recorded as 168, 96, 83, and 23 mV, respectively.

Additionally, an OP of 329 mV is required for  $\text{CoO}_{0.88}\text{S}_{0.11}$  to realize a current density of  $100 \text{ mA cm}^{-2}$ , which is the best performance among all the three samples (all the data are  $iR$  corrected). Tafel slopes are used to describe the catalytic kinetics of electrocatalysts, and a smaller Tafel slope usually represents faster kinetics. Tafel slopes of 196, 119, 80, and  $32 \text{ mV dec}^{-1}$  were calculated for samples  $\text{Co}_3\text{O}_4$ ,  $\text{CoS}_2$ ,  $\text{CoO}_{0.88}\text{S}_{0.11}$ , and Pt/C, respectively (Fig. 5b). The LSV curves of the partially sulfurized samples obtained at 200, 250, and  $350^\circ\text{C}$  were also collected, using which the OPs were calculated to be 176, 151, and 113 mV, respectively (Fig. S8, ESI†). To evaluate the stability of the materials in an acidic electrolyte, electrochemical measurements were also carried out in a sulfuric acid aqueous solution ( $0.5 \text{ M H}_2\text{SO}_4$ ), and results have been shown in Fig. S9 (ESI†). The OPs at a current density of  $10 \text{ mA cm}^{-2}$  for the samples  $\text{Co}_3\text{O}_4$ ,  $\text{CoS}_2$ , and  $\text{CoO}_{0.88}\text{S}_{0.11}$  are determined to be 205, 157, and 116 mV (Fig. S9a, ESI†), respectively, while Fig. S9b (ESI†) shows that the Tafel slopes of  $\text{Co}_3\text{O}_4$ ,  $\text{CoS}_2$ , and  $\text{CoO}_{0.88}\text{S}_{0.11}$  are 180, 121, and  $87 \text{ mV dec}^{-1}$ , respectively. As a comparison, a summarization table (Table S1, ESI†) listing similar HER electrocatalysts reported in the previous work is also provided, revealing that the electrocatalytic performance of this work is comparable to those reported in recent years.

To further study the difference in the HER process of all the three samples, EIS and ECSA measurements were performed and the results were plotted. It can be seen from Fig. 5c that all





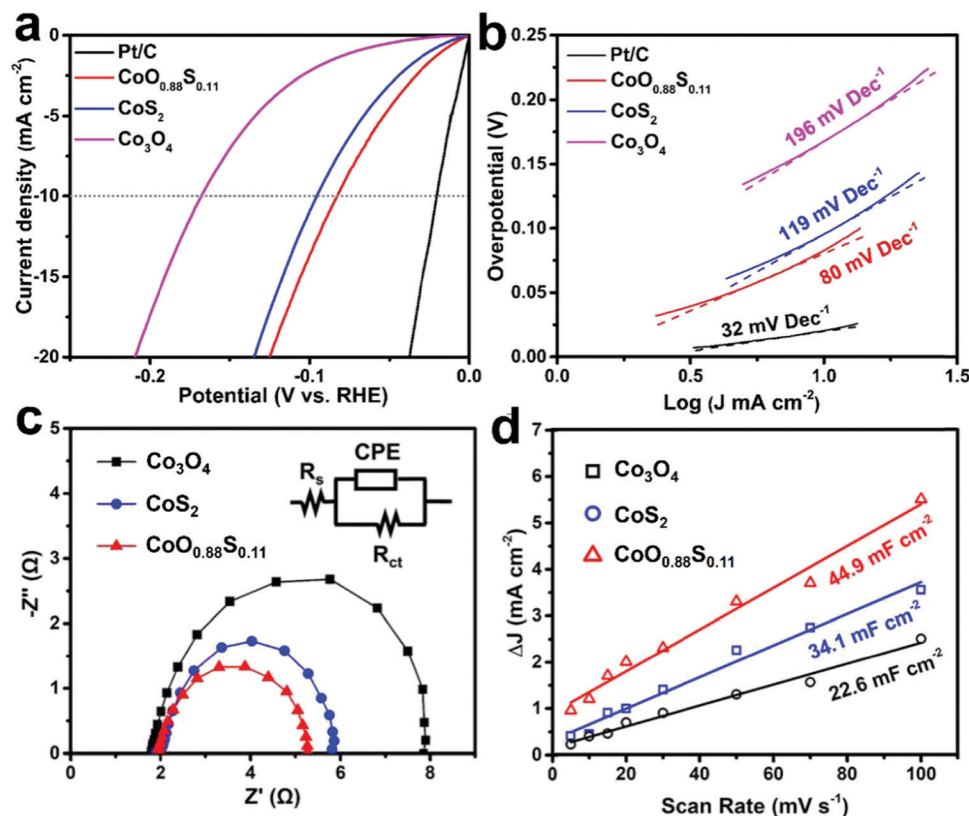


Fig. 5 LSV curves (a), Tafel plots (b), EIS (c), and ECSA (d) of the as-prepared Co<sub>3</sub>O<sub>4</sub>, CoS<sub>2</sub>, and CoO<sub>0.88</sub>S<sub>0.11</sub> samples. LSV and Tafel slope of Pt/C electrode are also shown as a comparison.

the Nyquist plots show similar semicircles, from which transfer resistances of 6.2, 4.0, and 3.3 Ω can be calculated for Co<sub>3</sub>O<sub>4</sub>, CoS<sub>2</sub>, and CoO<sub>0.88</sub>S<sub>0.11</sub>, respectively. The inset in Fig. 5c shows an equivalent circuit, which contains constant phase element (CPE), electrolyte resistance (R<sub>s</sub>), and charge transfer resistance (R<sub>ct</sub>). The smallest R<sub>ct</sub> value of CoO<sub>0.88</sub>S<sub>0.11</sub> suggests its best electronic conductivity among all the samples, which verified its best HER performance. Next, CV tests (Fig. S10, ESI<sup>†</sup>) were conducted in a non-faradaic potential region

(−0.1 to 0 V, vs. SCE) to estimate the ECSA for the samples (Fig. 5d). Accordingly, the double-layer capacitances (C<sub>dl</sub>) for Co<sub>3</sub>O<sub>4</sub>, CoS<sub>2</sub>, and CoO<sub>0.88</sub>S<sub>0.11</sub> are estimated to be 22.6, 34.1, and 44.9 mF cm<sup>-2</sup>, respectively. The ECSA is considered positively proportional to C<sub>dl</sub>, and thus CoO<sub>0.88</sub>S<sub>0.11</sub> holds the largest ECSA among all the samples. Catalytic materials with higher surface areas usually show better electrocatalytic performance, because they can provide larger numbers of active sites for catalytic reactions.<sup>43,44</sup> Turnover frequency (TOF)

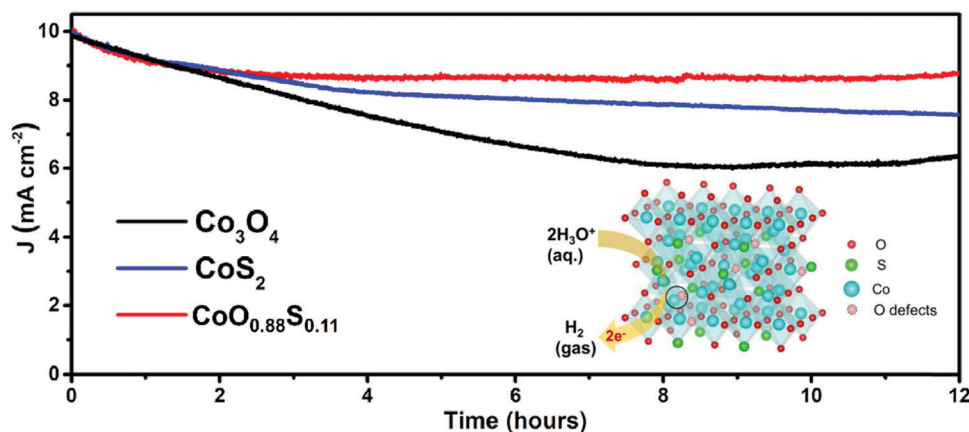


Fig. 6 *i*–*t* curves obtained under the respective OPs of the three samples in 1 M of KOH aqueous solution. The inset schematically shows a HER process enhanced by enriched V<sub>so</sub> of CoO<sub>0.88</sub>S<sub>0.11</sub>.

indicates the numbers of gaseous  $\text{H}_2$  molecules evolved in the HER process at a unit time, which is regarded as the most important parameter to reflect the intrinsic catalytic properties. Herein, the TOFs of all the three samples were calculated and compared according to a calculation method described in a previous work.<sup>27</sup>  $\text{CoO}_{0.88}\text{S}_{0.11}$  yielded a TOF of  $1.589 \text{ H}_2 \text{ s}^{-1}$ , which is much higher than those of  $\text{Co}_3\text{O}_4$  ( $0.307 \text{ H}_2 \text{ s}^{-1}$ ) or  $\text{CoS}_2$  ( $0.806 \text{ H}_2 \text{ s}^{-1}$ ).

Electrocatalytic stability is considered important for practical application. Durability tests were performed with respective OPs to maintain a current density of  $10 \text{ mA cm}^{-2}$  for all the three samples. The obtained results (Fig. 6) show that the current densities of both  $\text{Co}_3\text{O}_4$  and  $\text{CoS}_2$  decrease upon catalytic time, but  $\text{CoS}_2$  keeps a higher current than  $\text{Co}_3\text{O}_4$ . Remarkably,  $\text{CoO}_{0.88}\text{S}_{0.11}$  has shown a much more stable current density after 2 h compared to the other samples, which suggests that it possesses the best durability among all the three samples. Apparently, a quick current decay of  $\text{Co}_3\text{O}_4$  was observed after 2 h, which should be due to its poor conductivity, and the mass loss of the electrode materials during the prolonged cycles.<sup>45</sup> After 12 h, current densities of 8.91, 7.62, and  $6.33 \text{ mA cm}^{-2}$  can be retained for samples  $\text{CoO}_{0.88}\text{S}_{0.11}$ ,  $\text{CoS}_2$ , and  $\text{Co}_3\text{O}_4$ , respectively, indicating the lowest current decay of 10.9% for  $\text{CoO}_{0.88}\text{S}_{0.11}$ .

The inset in Fig. 6 shows a schematic illustration of the HER process that has been promoted by enriched  $\text{V}_{\text{so}}$  of  $\text{CoO}_{0.88}\text{S}_{0.11}$ . The Co atoms serve as the main active sites for catalytic reactions, where water molecules are reduced to generate  $\text{H}_2$ .

Additionally,  $\text{V}_{\text{so}}$  present at the lattice of the spinel structure (Co atom and  $\text{V}_{\text{so}}$  indicated by the solid circle) can act as extra active centers for absorbance of  $\text{H}_2\text{O}$  and subsequent reduction. Thus, electrocatalytic  $\text{H}_2$  evolution can be strengthened by such an enhancement. Furthermore, the LSV curves of all the three samples after stability tests were also obtained, as shown in Fig. S11 (ESI†). The results indicate that the catalytic activities of the samples  $\text{Co}_3\text{O}_4$  and  $\text{CoO}_{0.88}\text{S}_{0.11}$  are improved after durable tests (reduced OPs for  $\eta_{100}$ ), while a decay of catalytic properties can be observed for  $\text{CoS}_2$ , which is probably due to its relatively low chemical stability.

The electrocatalytic results have shown that  $\text{CoS}_2$  is superior over  $\text{Co}_3\text{O}_4$ . To further study the role of  $\text{V}_{\text{so}}$  in the  $\text{H}_2\text{O}$  adsorption process, DFT calculations were then extended to simulate the perfect (111) facets without any defects for all the three samples. Fig. 7 showcases the  $\Delta E_{\text{ads}}$  results at sites 1 for  $\text{Co}_3\text{O}_4$  (111) with Co–O terminals (Fig. 7a),  $\text{CoO}_{0.88}\text{S}_{0.11}$  with Co–O terminals (Fig. 7b), and  $\text{CoS}_2$  (111) with Co–S terminals (Fig. 7d), respectively. The absolute values of adsorption energies are in the order of ( $\text{Co}_3\text{O}_4$ ,  $0.18 \text{ eV}$ ) < ( $\text{CoO}_{0.88}\text{S}_{0.11}$ ,  $0.23 \text{ eV}$ ) < ( $\text{CoS}_2$ ,  $0.28 \text{ eV}$ ). Hence,  $\text{CoS}_2$  (111) exhibits the most stable adsorption for  $\text{H}_2\text{O}$  molecules among all the three samples based on a perfect crystalline structure mode. However, our previous ESR results (recall Fig. 3d) have confirmed a remarkable  $\text{V}_{\text{so}}$  enrichment in the  $\text{CoO}_{0.88}\text{S}_{0.11}$  sample, compared to the pristine  $\text{Co}_3\text{O}_4$  or  $\text{CoS}_2$ . Then the  $\Delta E_{\text{ads}}$  at site 1 was also calculated for  $\text{CoO}_{0.88}\text{S}_{0.11}$  (111) with one unit of O vacancy. Interestingly, the absolute value of  $\Delta E_{\text{ads}}$

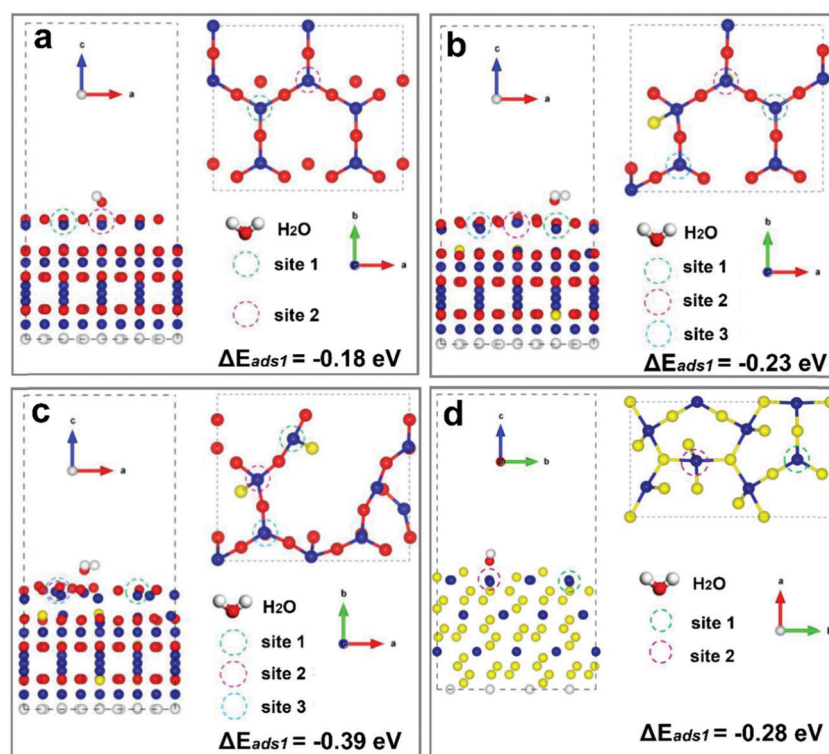


Fig. 7 Diagrams of  $\text{H}_2\text{O}$  adsorption sites for the (111) facets without any defects (a, b, and d) for  $\text{Co}_3\text{O}_4$  (a),  $\text{CoO}_{0.88}\text{S}_{0.11}$  (b), and  $\text{CoS}_2$  (d), respectively, and that of  $\text{CoO}_{0.88}\text{S}_{0.11}$  (111) with one unit of O vacancy (c).





was increased from 0.23 to 0.39 eV, which is much higher than that of CoS<sub>2</sub>. These results strongly validated that the presence and enrichment of vacancies can play a very significant role in the adsorption of water molecules.

In addition, further calculations for adsorption sites 2 with perfect lattices have obtained the  $\Delta E_{\text{ads}}$  values of  $-0.03$ ,  $-0.27$ , and  $-0.66$  eV for Co<sub>3</sub>O<sub>4</sub>, CoO<sub>0.88</sub>S<sub>0.11</sub>, and CoS<sub>2</sub>, respectively, which suggests that CoS<sub>2</sub> is a very good electrocatalytic candidate for HER. However, in fact it is very difficult to remove all the defects within the crystalline structures. For CoS<sub>2</sub> (111), the  $\Delta E_{\text{ads}}$  of site 1 decrease to  $-0.15$  eV when there is one unit of S vacancy, compared to  $-0.28$  eV obtained without any defects. Therefore, a proper S substitution of Co<sub>3</sub>O<sub>4</sub> by partial and slight sulfurization to enrich surface defects reported herein is a rational strategy to optimize the intrinsic catalytic properties.

## 4. Conclusions

In summary, CoO<sub>0.88</sub>S<sub>0.11</sub> electrocatalysts with enriched V<sub>so</sub> were prepared *via* a partial sulfurization process of spinel Co<sub>3</sub>O<sub>4</sub> with exposed (111) facets. The introduction of S atoms into the crystalline lattice of spinel Co<sub>3</sub>O<sub>4</sub> has led to the generation and preservation of lattice distortion with V<sub>so</sub>. The as-formed CoO<sub>0.88</sub>S<sub>0.11</sub> PS with V<sub>so</sub> exhibit a higher ECSA and better electronic conductivity compared to pristine Co<sub>3</sub>O<sub>4</sub> and CoS<sub>2</sub>. The DFT calculations have verified that enriched V<sub>so</sub> can significantly increase the adsorption energies of H<sub>2</sub>O during the HER process. In virtue of the presence of V<sub>so</sub>, high ECSA, and good charge transfer properties, CoO<sub>0.88</sub>S<sub>0.11</sub> PS have demonstrated a low OP ( $\eta_{10} = 83$  mV) with an enhanced TOF ( $1.589 \text{ H}_2 \text{ s}^{-1}$ ) for HER when used as an electrocatalyst for water splitting. This research work provides a new path for surface defect engineering of cobalt based materials with improved physical and chemical properties as efficient electrocatalysts.

## Author contributions

T. Zhu conceived the idea and designed the experiments; J. Pan carried out the experiments, and collected and analyzed the data; Y. Xiao, A. Q. Pan, and S. Q. Liang provided assistance in analyzing the data; T. Zhu wrote the manuscript and S. Q. Liang provided assistance in the revision; T. Zhu and S. Q. Liang provided financial support to this work.

## Conflicts of interest

The authors declare no conflict of interest.

## Acknowledgements

This work was financially supported by the start-up grant of Central South University (No. 202045001), Innovation-Driven Project of Central South University (No. 2019CX028), the Huxiang Assembly Program for High-level Talents (Department of Science and Technology of Hunan province, China, No.

2018RS3018), and the National Natural Science Foundation of China (Key Program, No. 51932011). The authors also thank Prof. Lei Han from Hunan University for his valuable comments and discussion.

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