Engineering Sulfur Vacancies in Spinel-Phase Co\textsubscript{3}S\textsubscript{4} for Effective Electrocatalysis of the Oxygen Evolution Reaction

Xiaomin Li, Kaitian Zheng, Jiajun Zhang, Guoning Li,* and Chunjian Xu*

ABSTRACT: Restricted by the sluggish kinetics of the oxygen evolution reaction (OER), efficient OER catalysis remains a challenge. Here, a facile strategy was proposed to prepare a hollow dodecahedron constructed by vacancy-rich spinel Co\textsubscript{3}S\textsubscript{4} nanoparticles in a self-generated H\textsubscript{2}S atmosphere of thiourea. The morphology, composition, and electronic structure, especially the sulfur vacancy, of the cobalt sulfides can be regulated by the dose of thiourea. Benefitting from the H\textsubscript{2}S atmosphere, the anion exchange process and vacancy introduction can be accomplished simultaneously. The resulting catalyst exhibits excellent catalytic activity for the OER with a low overpotential of 270 mV to reach a current density of 10 mA cm\textsuperscript{-2} and a small Tafel slope of 59 mV dec\textsuperscript{-1}. Combined with various characterizations and electrochemical tests, the as-proposed defect engineering method could delocalize cobalt neighboring electrons and expose more Co\textsuperscript{3+} sites in spinel Co\textsubscript{3}S\textsubscript{4}, which lowers the charge transfer resistance and facilitates the formation of Co\textsuperscript{3+} active sites during the preactivation process. This work paves a new way for the rational design of vacancy-enriched transition metal-based catalysts toward an efficient OER.

INTRODUCTION

Sustainable energy conversion and storage technologies are being continuously developed and show promise in solving the temporal or spatial intermittency of renewable energy resources, thereby alleviating the energy crisis and environmental deterioration.\textsuperscript{1} The transformation process of renewable energy is usually accompanied by various chemical reactions.\textsuperscript{2,3} Therefore, the oxygen evolution reaction (OER) plays an essential role in solar and electricity-driven water splitting devices, regenerative fuel cells, and rechargeable metal–air batteries.\textsuperscript{4,6–9} However, owing to kinetic energy barriers, the potential required for driving the reaction is much larger than the thermodynamic equilibrium potential (1.23 V vs reversible hydrogen electrode, RHE). Moreover, the large-scale application of noble metal oxides (IrO\textsubscript{2} or RuO\textsubscript{2}) with high activity toward the OER is limited by the scarcity of their reserves and easy corrosion during the reaction.\textsuperscript{10} Therefore, it is challenging to design low-cost and effective electrocatalysts for the OER.

Different from noble metal catalysts, transition metal-based materials (e.g., Mn, Fe, Co, and Ni) with diversity and abundant reserves have been extensively studied.\textsuperscript{11–14} According to the binding energy difference of \( \Delta G_{\text{O}_2} \) – \( \Delta G_{\text{H}_2\text{O}} \), an OER volcano plot was built to provide clues for developing highly efficient catalysts.\textsuperscript{15} Sitting near IrO\textsubscript{2} and RuO\textsubscript{2}, Co\textsubscript{3}O\textsubscript{4} was evaluated as an attractive electrocatalyst for the OER.\textsuperscript{14,16} However, the catalytic activity of spinel-phase Co\textsubscript{3}O\textsubscript{4} is less than expected due to its poor conductivity and overly strong OER intermediate adsorption.\textsuperscript{7,17–19} As cobalt-based inorganic compounds, the electrical conductivity of cobalt sulfides (Co–Ss) is better than that of cobalt oxides (Co–Os) because the gap between their valence and conduction bands is relatively narrow, which promotes OER kinetics.\textsuperscript{15} Furthermore, the low electronegativity of S atoms in Co–Ss alleviates the coordination ability of OH on the catalyst surface, which decreases the overly strong adsorption of \(*\text{OH}, *\text{O}, and *\text{OOH} intermediates (the asterisk represents active metal sites).\textsuperscript{20} Benefitting from the abovementioned features, Co–Ss should be better than Co–Os for the OER. It is noteworthy that a few reports demonstrate that Co–Ss would convert to corresponding (oxy)hydroxides under oxidizing potentials as the precatalyst.\textsuperscript{15,17} Thus, a good understanding of the catalytic mechanism of Co–Ss is essential for the OER.

The catalytic activity of cobalt-based compounds is highly influenced by the microchemical environment of cobalt sites, which could be further improved by various strategies.\textsuperscript{21} Defect
engineering, a common and effective modification strategy for modulating the properties of metal centers, could be utilized to improve catalyst activity. Introducing vacancies would modify the electronic structure and regulate oxygenated intermediate formation, which promotes the charge transfer process and the exposure of catalytic sites, thus reducing the kinetic energy barrier for the OER.\textsuperscript{3,22}−\textsuperscript{34} Ba and coworkers studied spinel-structured NiCoO\textsubscript{2} nanosheets rich in oxygen vacancies, concluding that vacancies confined in ultrathin nanosheets increased the number of active sites, which lowered the adsorption energy of H\textsubscript{2}O and promoted OER efficiency.\textsuperscript{35} Xiao and coworkers investigated CoO\textsubscript{2} and identified that the introduction of anion vacancies facilitated the deprotonation of intermediate Co\textsubscript{3}−OOH during the OER process.\textsuperscript{36} Thus, introducing sulfur vacancies to CoS\textsubscript{4} could be favorable for activating the microchemical environment of cobalt sites and exposing more active sites, thereby improving the electrocatalytic activity for the OER. However, there are few reports on engineering vacancies in spinel CoS\textsubscript{4} for the effective electrocatalysis of the OER.

Motivated by the above considerations, we designed a controllable synthesis method to regulate the sulfur vacancy concentration in spinel-phase CoS\textsubscript{4}. A series of hollow dodecahedron frameworks constructed by CoS\textsubscript{4} nanoparticles with sulfur vacancies (H-VS-CoS\textsubscript{4}) were prepared successfully in a H\textsubscript{2}S atmosphere generated from thiourea. Notably, the anion exchange and the introduction of sulfur vacancies were accomplished simultaneously. The morphology, crystalline structure, and electronic structure, especially sulfur vacancies, were systematically studied. Combined with electrochemical tests, the relationship between catalyst activity and its structure was demonstrated. In particular, the roles of the sulfur vacancies in the formation of active sites for OER were investigated. These findings provide insights into the contribution of sulfur vacancies to electrocatalytic OER performance, which is favorable for the advancement of defect engineering.

## EXPERIMENTAL METHODS

### Synthesis of ZIF-67

2-Methylimidazole and Co(NO\textsubscript{3})\textsubscript{2}-6H\textsubscript{2}O were dissolved separately in 60 mL of methanol, and then the clear 2-methylimidazole solution was poured slowly into the orange Co(NO\textsubscript{3})\textsubscript{2} solution at room temperature. Subsequently, the resulting purple solution was constantly stirred at room temperature for 12 h. Finally, the precipitate was obtained by centrifuging, washing, and drying.

### Synthesis of the Hollow Dodecahedron Constructed by Spinel Co\textsubscript{12}O\textsubscript{23} (H-Co3O\textsubscript{4})

The synthesized ZIF-67 was heated to 350 °C in a tube furnace in an inert atmosphere at a ramp rate of 5 °C min\textsuperscript{−1} and maintained at 350 °C for 30 min. Then, the aforementioned material was exposed in air for another 30 min of calcination. Finally, the purple ZIF-67 changed to a black powder, which was named H-Co3O\textsubscript{4}.

### Synthesis of the Hollow Dodecahedron Constructed by Spinel CoS\textsubscript{4} Nanoparticles Rich in Sulfur Vacancies (H-VS-CoS\textsubscript{4})

Briefly, 100 mg of the as-prepared black powder and various amounts of thiourea (300, 400, 500, 600, 700, and 800 mg) were loaded into combustion boats that were placed upstream and downstream in a tube furnace, respectively. To exclude air in the furnace, 30 min of nitrogen gas purging was necessary. After that, the nitrogen gas was switched off, and the furnace was set to 500 °C with a ramp rate of 5 °C min\textsuperscript{−1} and maintained at 500 °C for 2 h. The black powder was collected after natural cooling to ambient temperature and was named S-300-CoS\textsubscript{4}, S-400-CoS\textsubscript{4}, S-500-CoS\textsubscript{4}, S-600-CoS\textsubscript{4}, S-700-CoS\textsubscript{4}, and S-800-CoS\textsubscript{4}.

### Characterization

The morphology and structure of the as-prepared samples were observed by scanning electron microscopy (SEM, FEI, Apreo S LoVac), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM, JEOl, JEM-F200). Furthermore, the specific surface area and porosity of the catalysts were determined by the Brunauer−Emmett−Teller (BET) method. X-ray diffraction (XRD) patterns were obtained with a D8 Advance Bruker X-ray diffractometer to detect the synthesized sample composition and phases. X-ray photoelectron spectroscopy (XPS) measurements were carried out by a Thermo ESCALAB 250 with an Al K\textsubscript{α} radiation source (hv = 1361.0 eV) to obtain the chemical species on the sample surface. Specifically, the binding energies obtained in the XPS spectra were corrected for each specimen by referencing the C 1s peak at 284.8 eV. Moreover, the existence of sulfur vacancies was directly confirmed by means of electron paramagnetic resonance (EPR) on a Bruker model A300 spectrometer at 77 K.

### Electrochemical Measurements

All electrochemical measurements were taken with an electrochemical workstation (Model CHI660E, Chenhua, Shanghai) and rotating disk electrode (RDE) (ALS/DY2323 Bipotentistat) through the use of a three-electrode system in 1 M aqueous KOH solution at 25 °C. A saturated Hg/HgO electrode and graphite electrode were operated as the reference electrode and counter electrode, respectively. To obtain the working electrode, well-dispersed ink was prepared. Briefly, 4 mg of catalyst powder was added into a mixed solution containing 960 μL of isopropanol and 40 μL of Nafion solution followed by ultrasonic dispersion at 20 °C for 2 h. After that, 5 μL of the resulting ink was dropwise added evenly on a glassy carbon electrode (GCE, d = 0.3 cm, S = 0.0707 cm\textsuperscript{2}) and naturally dried at room temperature. Cyclic voltammetry (CV) at a scan rate of 50 mV s\textsuperscript{−1} for 100 cycles was conducted in a 1 M KOH electrolyte that was bubbled with oxygen gas for at least 30 min. Linear sweep voltammetry (LSV) polarization curves for OER activity were measured at a scan rate of 5 mV s\textsuperscript{−1} by correcting the raw data with 90% iR losses. Notably, according to the Nernst equation (E\textsubscript{OER} = E\textsubscript{Hg/HgO} + 0.098 + 0.059 × pH), the potential of the Hg/HgO reference was calculated to be 0.3046 V. Furthermore, Tafel slopes were calculated from the polarization curves during OER at a current density of 1–20 mA cm\textsuperscript{−2}. Electrochemical double-layer capacitance (C\textsubscript{dl}) was determined in a non-Faradaic portion (0.73–0.83 V vs RHE) with varied scan rates (20, 40, 60, 80, and 100 mV s\textsuperscript{−1}). Electrochemical active surface area (ECSA) was calculated using the formula ECSA = C\textsubscript{dl}/C\textsubscript{g} × GCE (C\textsubscript{g} = 40 μF cm\textsuperscript{2} in 1.0 M KOH). In terms of electrochemical impedance spectroscopy (EIS) tests, Nyquist plots and Bode plots were obtained over a frequency range of 10\textsuperscript{−1} to 10\textsuperscript{4} Hz at an open circuit potential (OCP) of approximately 0.30 V with an amplitude of 5 mV. The stability measurements were conducted via chronopotentiometry (CP) and chronoamperometry (CA) tests in 1 M KOH.

## RESULTS AND DISCUSSION

Scheme 1 illustrates the synthesis process of the H-VS-CoS\textsubscript{4} samples. First, H-Co3O\textsubscript{4} was prepared by the thermal calcination of ZIF-67, which was based on a typical procedure.
with slight modification.\textsuperscript{27} Then, H-V_{2}Co_{3}S_{4} was obtained in a sulfidation and reducing atmosphere built with a self-generated H_{2}S atmosphere derived from the thermal decomposition of thiourea,\textsuperscript{28} and the detailed formation process of H_{2}S can be found in the Supporting Information. By regulating the thiourea dose, the morphology of the electrocatalyst exhibits various features. To visualize the controllable synthesis process, a series of scanning electron microscopy (SEM) images found in the Supporting Information. By regulating the thiourea dose, the morphology of the electrocatalyst exhibits various features. To visualize the controllable synthesis process, a series of scanning electron microscopy (SEM) images (Figure 1a–f) were obtained. In Figure 1a, a hollow dodecahedral structure of H-Co_{3}O_{4} with an average size of approximately 500 nm was successfully synthesized (white dotted circles). To further confirm the morphology of H-Co_{3}O_{4}, transmission electron microscopy (TEM) was carried out. As shown in Figure S1b (H-Co_{3}O_{4}), the centers of the hexagon are brighter than the edges in comparison with Figure S1a (ZIF-67), indicating the successful preparation of hollow dodecahedrons after the thermal calcination. In Figure 1b, a few nanoparticles are randomly distributed on the smooth surface of S-300-CoS. With an increasing thiourea dose, the degree of surface etching for S-400-CoS (Figure 1c), S-500-CoS (Figure 1d), and S-600-CoS (Figure 1e) gradually increases. Furthermore, Figure S2 exhibits that the hollow dodecahedral structure of S-600-CoS is constructed by a large number of nanoparticles with an average size of around 40 nm (red dotted circles). After an overdose of thiourea, nanoparticles on the surface aggregate and the hollow structures are apparently damaged (Figure 1f). Based on the above, the surface morphology and hollow structure of the synthesized catalysts could be well regulated via this method.

As a factor influencing catalytic activities, the surface areas of the samples were measured by the Brunauer–Emmett–Teller (BET) method. As displayed in Figure 2a, the BET specific surface areas (S_{BET}) of H-Co_{3}O_{4}, S-300-CoS, S-400-CoS, S-500-CoS, S-600-CoS, and S-700-CoS are 73.944, 42.489, 29.753, 27.882, 21.876, and 2.579 m^{2} g^{-1}, respectively, demonstrating the decreasing S_{BET} trend, which is consistent with the observation from the SEM images. The hollow structure is gradually damaged because the etching agent (H_{2}S) concentration is enhanced with an increase of the thiourea dose. Moreover, the pore size distribution of samples by the Barrett–Joyner–Halenda (BJH) method is represented in Figure 2b. The main portion of pores for all samples, except S-700-CoS, is distributed within 2–20 nm in the mesoporous region. Such a pore structure could promote gas transfer and extra exposed active sites for the electrocatalytic OER.\textsuperscript{29}

To investigate the difference in the crystalline structure of the materials, X-ray diffraction (XRD) characterization was performed. As shown in Figure 3a, the diffraction pattern of H-Co_{3}O_{4} matches well with spinel-phase Co_{3}O_{4} (JCPDS no. 74-2120), and S-300-CoS exhibits the diffraction peaks of CoO (JCPDS no. 48-1719) and Co_{3}S_{4} (JCPDS no. 42-1448). The transformation in the crystal structure confirms that a reducing and sulfidation atmosphere is successfully built by the thermal decomposition of thiourea. S-400-CoS, S-500-CoS, and S-600-CoS display similar diffraction patterns at 26.7, 31.4, 38.0, 47.3, 50.2, and 55.0°, which are ascribed to the (220), (311), (400), (422), (S11), and (440) lattice planes of spinel-phase Co_{3}S_{4}, respectively. Especially, the diffraction peaks of S-600-CoS are broader than those of S-500-CoS and S-400-CoS, suggesting the wider distribution of lattice spacing, which implies that more defects might be introduced to S-600-CoS and leads to a decreased crystalline degree.\textsuperscript{30} Influenced by this changed crystal structure, there is a slight difference in peak intensity for the (422) and (S11) planes between S-600-CoS and S-500-CoS or S-400-CoS. As thiourea continues to increase, the diffraction pattern of Co_{1−x}S (JCPDS no. 42–0826) is observed in S-700-CoS and S-800-CoS. Evidently, the composition of materials could be well regulated by controlling the thiourea dose, and a series of spinel-phase Co_{3}S_{4} samples were successfully constructed.

Energy-dispersive X-ray (EDX) spectroscopy elemental mapping and high-resolution transmission electron microscopy (HRTEM) were also carried out to confirm the transformation from H-Co_{3}O_{4} to Co_{3}S_{4} and Co_{1−x}S. In the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and corresponding EDX mappings (Figure 3b,c), Co, O, C, and N as well as Co, S, C, and N are exhibited in H-Co_{3}O_{4} and S-400-CoS, respectively. Especially, the even distribution of C and N elements is derived from the thermal calcination of ZIF-67. The HRTEM image of S-600-CoS (Figure 3d) shows that the lattice spacings of 0.291, 0.160, 0.124, and 0.120 nm are indexed to the (422), (511), and (440) crystal planes of Co_{3}O_{4} (JCPDS no. 74-2120), and S-300-CoS exhibits the dihedral angle of 125°, respectively.
0.343, and 0.512 nm are indexed to the (311), (220), and (111) crystalline planes of Co₃S₄. Furthermore, the interplanar spacing of 0.249 nm belonging to the (101) crystalline plane of Co₁₋ₓS could be observed in S-700-CoS and S-800-CoS (Figure 3e,f), which is consistent with the XRD results, further manifesting the phase conversion to Co₁₋ₓS. The above crystalline planes could also be observed in the selected area electron diffraction (SAED) patterns (Figure 3g–i). Therefore, all the above results demonstrate that hollow dodecahedrons constructed by spinel-phase Co₃S₄ nanoparticles (H-Co₃S₄) are successfully obtained (i.e., S-400-CoS, S-500-CoS, and S-600-CoS), which are transformed from H-Co₃O₄ by a facile and controllable process.

To confirm the presence of sulfur vacancies for the H-Co₃S₄ samples, electron paramagnetic resonance (EPR) characterization was carried out at 77 K. As shown in Figure 4a, a characteristic EPR peak is observed at the position of the g value of 2.003 in spinel-phase Co₃S₄, which can be assigned to sulfur vacancies, suggesting that sulfur vacancies are successfully introduced in H-Co₃S₄ to form H-V₃-Co₃S₄ samples during the reducing process. Furthermore, the signal intensity of the sulfur vacancies is increased from S-400-CoS to S-600-CoS, which indicates that the sulfur vacancy concentration could be regulated. Since a portion of Co³⁺ could be converted to Co²⁺ to balance the creation of surface vacancies (Scheme 2), X-ray photoelectron spectroscopy (XPS) was used to characterize the difference in cobalt chemical status among H-V₃-Co₃S₄ samples. In XPS full-survey spectra (Figure S3), the main peaks are attributed to Co 2p, S 2p, C 1s, N 1s, and O 1s. Especially, the presence of the O element is caused by physically adsorbed oxygen on the surface structural defects when exposed to air. In the corresponding Co 2p high-resolution XPS spectra (Figure 4b), the Co²⁺ 2p₃/₂ and Co³⁺ 2p₃/₂ fitting peaks of S-400-CoS, S-500-CoS, and S-600-CoS are located at approximately 781.8 and 778.8 eV, respectively, which correspond to Co²⁺ and Co³⁺ on the surface of Co₃S₄. The left column of Figure 4d shows that the ratio of the relative peak areas of Co²⁺ 2p₃/₂ to Co³⁺ 2p₃/₂ gradually increases from S-400-CoS to S-600-CoS. The highest Co²⁺ concentration is found in S-600-CoS, and combined with the EPR result, the increase in Co²⁺ originates from the increased number of sulfur vacancies. In the S 2p spectra for H-V₃-Co₃S₄ (Figure 4c), the core peaks at around 162.8 eV (S 2p₁/₂) and 161.7 eV (S 2p₁/₂) correspond to metal–sulfur bonds (Co—S), while the peaks at 162.4 eV (S 2p₁/₂) and 161.3 eV (S 2p₁/₂) are ascribed to the sulfur vacancies. Notably, the relative intensity of sulfur vacancy-related peaks gradually increases from S-400-CoS to S-600-CoS. As depicted in the
right column of Figure 4d, the peak area ratio of sulfur vacancy to Co−S in the S 2p3/2 spectrum is 0.27 for S-400-CoS, and this proportion increases to 0.73 for S-600-CoS (to 0.52 for S-500-CoS), indicating the highest sulfur vacancy concentration in S-600-CoS. Also, the shift of the Co3+ peaks to lower binding energy (0.3 eV) and the broadening of the S 2p peaks (the half-width at half-maxima of S 2p3/2 peaks increases from 0.29 to 0.35 eV) suggest that the degree of electron delocalization for H-VS-Co3S4 is enhanced with an increased sulfur vacancy concentration.38 In the C 1s high-resolution XPS spectra for H-VS-Co3S4 (Figure S4), the peaks at around 284.8, 285.7, and 288.8 eV represent C−C/C=C, C≡N, and N−C≡N, respectively. Moreover, the N 1s XPS spectra show that two fitting peaks at around 399.1 and 400.9 eV are attributed to N−C≡N and graphitic N.39 Notably, the H-VS-Co3S4 samples show the same C and N structure without S doping in the corresponding XPS spectra, indicating that thiourea does not interact with C and N frameworks, which would not affect the study of sulfur vacancies in spinel Co3S4. The above results indicate that the hollow dodecahedrons prepared from the thermal calcination of ZIF-67 are mainly supported by C and N frameworks. According to the above analysis, the conversion from H-Co3O4 to H-Co3S4 and the simultaneous introduction of sulfur vacancies are accomplished in a H2S atmosphere, and the number of sulfur vacancies, and thus, Co2+, could be regulated by controlling the thiourea dose.

To study the OER performance of H-VS-Co3S4, linear sweep voltammetry (LSV) polarization curves of the as-prepared samples were obtained by a conventional three-electrode electrochemical cell in a 1 M KOH electrolyte. As shown in Figure 5a, S-600-CoS exhibits a remarkably small onset potential ($E_{\text{onset}}$) of 1.47 V (vs RHE) and requires an overpotential of 270 mV to reach a current density of 10 mA cm$^{-2}$, which is much lower than those of RuO2, the other samples (Figure 5c), and the analogous catalysts (Table S1), indicating its excellent electrocatalytic performance for OER.40−49 Tafel slopes, calculated from the LSV polarization curves, are usually employed to study the reaction kinetics of OER. In an electrocatalytic reaction, a smaller Tafel slope is commonly a sign of a good electrocatalyst, and different Tafel slope values represent different rate-determining steps (RDSs).50 As displayed in Figure 5b, the smallest value (59 mV dec$^{-1}$) belongs to S-600-CoS, indicating that S-600-CoS has the best catalytic activity for OER. Compared with 120 and 30 mV dec$^{-1}$, the Tafel slopes of H-Co3O4, S-300-CoS, S-400-CoS, S-500-CoS, and S-600-CoS (59−87 mV dec$^{-1}$) are closer to 60 mV dec$^{-1}$, suggesting that the whole electrocatalytic process of those catalysts is mainly determined by the reaction between the *OH intermediates and OH$^−$ ($^*\text{OH} + \text{OH}^− \rightarrow ^*\text{O} + \text{H}_2\text{O}$).51,52 Different from the above catalysts, S-700-CoS has a Tafel slope of 101 mV dec$^{-1}$, which is closer to 120 mV dec$^{-1}$, demonstrating that the first electron transfer reaction is the RDS ($^*\text{OH} \rightarrow ^*\text{OH}^−$). Based on the previous studies, the oxidation of Co2+ to Co3+ or a higher oxidation state of Co3+ to Co4+ is critical for generating active *OOH sites, which is beneficial for OER.53,54 To investigate the preactivation process of H-VS-Co3S4, cyclic voltammetry (CV) was employed. As shown in Figure 5d, the signal
peaks at around 1.25 V (A1, B1, and C1) and 1.48 V (A2, B2, and C2) represent the oxidation process of Co2+ to Co3+ and Co3+ to Co4+, respectively.\textsuperscript{55,56} For H-VS-Co3S4 samples, the signal intensities of A1 and A2 are stronger than those of B1 and B2 as well as C1 and C2, signifying that more Co2+ generated by sulfur vacancy introduction undergo the preoxidation process to form a higher oxidation state of cobalt (Co3+ and Co4+) for S-600-CoS. After CV preactivation, as shown in Figure S5, the oxidation peaks of A1, B1, and C1 disappear, and the reduction peaks of Co4+ to Co3+ (A3, B3, and C3) appear. The absence of

Figure 5. Electrochemical tests toward OER. (a) Polarization curves. (b) Tafel slopes. (c) Summarized overpotentials at a current density of 10 mA cm\textsuperscript{-2} and Tafel slopes of the samples. (d) First CV curves of H-VS-Co3S4 and S-700-CoS.

Figure 6. (a) Scan rate-dependent current densities of all samples. LSV polarization curves normalized by (b) BET and (c) ECSA for H-VS-Co3S4 and S-700-CoS. (d) Nyquist diagrams, with the inset showing an enlarged EIS spectrum, and (e) the fitting value of the $R_{ct}$ of the samples, with the inset showing the fitting electrical equivalent circuit. (f) Bode angle diagrams of H-VS-Co3S4.
A1, B1, and C1 suggests that Co2+ are irreversibly transformed to Co3+ by the preactivation process. Furthermore, the oxidation peak intensity of A2 is still stronger than those of B2 and C2 after preactivation, and the corresponding reduction peaks (A3, B3, and C3) also show a tendency of increased peak intensity from S-400-CoS to S-600-CoS, which indicates the formation of more active Co3+ for S-600-CoS. In terms of S-700-CoS, there is no oxidation process of Co3+ to Co4+ before and after CV preactivation (Figure S6), suggesting that no active Co3+ is formed, which leads to a poor OER performance. As a result, during the CV preactivation process, more Co2+ generated by introducing sulfur vacancies are irreversibly transformed to more Co3+ active sites for S-600-CoS, favorable for efficient electrocatalytic performance.

Compared with \( S_{BET} \), the electrochemical active surface area (ECSA) is considered as the most indicative measure of the effect of surface area because the determination is in the electrolyte rather than gas.57 In this work, the ECSA was determined by the double-layer capacitances (\( C_{dl} \)) of catalysts measured by CV curves at a scan rate from 20 to 100 mV s\(^{-1}\) within the non-Faradaic region (Figure S7). Figure 6a presents the linear relationship between current density and scan rate for all investigated samples. Evidently, the ECSA (Table S2) of S-600-CoS (0.22 cm\(^2\)) is larger than those of H-Co3O4 (0.17 cm\(^2\)), S-300-CoS (0.14 cm\(^2\)), S-400-CoS (0.20 cm\(^2\)), S-500-CoS (0.21 cm\(^2\)), and S-700-CoS (0.18 cm\(^2\)), indicating that more active cobalt centers are accessible for OER and thereby enhancing electrocatalytic OER activity. The difference in intrinsic activity in the H-VS-Co3S\(_4\) samples could be illustrated in LSV polarization curves normalized by \( S_{BET} \) and ECSA (Figure 6b,c). Excluding the contribution of the specific surface area and increased active cobalt sites, the specific activity of S-600-CoS excels among H-VS-Co3S\(_4\) samples as well as S-700-CoS, which further confirms that the intrinsic activity is improved, attributed to the enriched sulfur vacancies.

To obtain further insight into the kinetics of the electrocatalytic reactions, electrochemical impedance spectroscopy (EIS) measurement was carried out. In the Nyquist diagrams (Figure 6d), S-600-CoS has the smallest semicircles, suggesting its lowest charge transfer resistance (\( R_{ct} \)). To obtain the \( R_{ct} \) value, an electrical equivalent circuit composed of two capacitive/resistive elements was obtained based on the variation law of total impedance response. In Bode diagrams, a horizontal line is observed within a frequency region, indicating that a resistive behavior is dominant. Moreover, a capacitive behavior within a frequency region is described by a straight line with a slope of \(-1\).58,59 As shown in Figure S8, a resistance behavior is observed at high frequency (10\(^4\) to 10\(^6\) Hz) among all samples. However, two frequency-dependent linear zones (10\(^{-1}\) to 10\(^2\) and 10\(^2\) to 10\(^4\) Hz) can be individuated with different slopes other than \(-1\) and 0, exhibiting the complicated capacitive/resistive behavior, which results in the presence of two capacitive/resistive elements in the corresponding equivalent circuit. In the fitting electrical equivalent circuit (the inset in Figure 6e), \( R_s \), \( R_{ct} \), and CPE\(_1\) represent the uncompensated electrolyte resistance, charge
transfer resistance, and double-layer capacitance, respectively. The CPE2-R2 loop is attributed to the dielectric properties and resistivities of the catalysts. In particular, the $R_{ct}$ of S-600-CoS exhibits the lowest value of 11.54 $\Omega$, which is attributed to a higher degree of electron delocalization by introducing vacancies. Bode phase diagrams, which can concretely describe the phase angle relaxation as a function of frequency, can be utilized to emphasize the specific role of the vacancies. According to previous studies, the middle-frequency region (10$^2$ to 10$^4$ Hz) is associated with the chemical reaction on the surface. In Figure 6f, the phase peak intensity of S-600-CoS is strongest among the H-VS-Co$_3$S$_4$ samples in the middle-frequency region, which indicates that the surface oxidation process of S-600-CoS is fastest. Hence, it could be concluded that the introduction of sulfur vacancies could enhance the degree of electron delocalization and accelerate the charge transfer process, which alleviates the sluggish kinetics and facilitates catalytic OER performance.

The OER stability of S-600-CoS was evaluated by chronopotentiometry (CP) and chronoamperometry (CA) tests. As shown in Figure 7a and the inset, the potential to attain 10 mA cm$^{-2}$ for S-600-CoS remains nearly unchanged after 20 h; in the meantime, the current density remains stable after 20 h of running at a constant potential of 1.5 V (vs RHE), exhibiting the excellent OER stability of S-600-CoS under alkaline conditions.

To study the change of surface structure during the electrochemical process, various characterizations were employed, and the samples that stabilized after activation were denoted as H-V$_5$Co$_3$S$_4$-O (i.e., S-400-CoS-O, S-500-CoS-O, and S-600-CoS-O). As shown in Figure 7b, the XRD pattern of H-V$_5$Co$_3$S$_4$-O exhibits analogous diffraction peaks at 20.2, 37.0, and 38.9°, which are indexed to the (003), (101), and (012) lattice planes of $\gamma$-CoOOH (JCPDS no. 14-0673), respectively, indicating an evident transformation to $\gamma$-CoOOH with comparison to the H-VS-Co$_3$S$_4$ samples. The broadened peaks signify poor crystallinity, which could be caused by the existence of defects. Furthermore, the Raman spectra of H-V$_5$Co$_3$S$_4$-O also display a formation of $\gamma$-CoOOH. In Figure 7c, three bands could be observed at around 465, 505, and 667 cm$^{-1}$, which are assigned to the Co-O(H), $E_g$, and $A_1g$ modes, respectively. Therefore, H-V$_5$Co$_3$S$_4$ samples as the precatalysts for OER undergo reconstruction to $\gamma$-CoOOH during the preactivation process. As the sample with the best OER catalytic activity, S-600-CoS-O exhibits a similar TEM image (Figure 7d) to S-600-CoS with a hexagon structure, suggesting that this electrocatalyst still maintains an original structure constructed with C and N frameworks after phase transformation. In the HRTEM image (Figure 7f), the lattice spacings of 0.143 and 0.245 nm are indexed to the (110) and (101) facets of $\gamma$-CoOOH, respectively, offering the formation of $\gamma$-CoOOH. Consequently, even the dispersion of Co, O, C, and N elements could be observed throughout the single hexagon in HAADF-STEM with EDX spectroscopy elemental mapping patterns (Figure 8g).

To confirm the presence of vacancies after preactivation, an EPR test was carried out at 77 K. As illustrated in Figure 8a, a characterized signal at a $g$ value of 2.005 is observed, which is
attributed to the oxygen vacancies in γ-CoOOH. Furthermore, this signal trend to strengthen with the increase of the thiourea dose, which is consistent with the increasing trend of sulfur vacancy concentration before preactivation. Consequently, the highest vacancy concentration can still be found in S-600-CoS-O among the H-V2-Co3S4-O samples after undergoing a reconstruction process from Co3S4 to γ-CoOOH. XPS characterization was performed to reveal the valence state for H-V2-Co3S4-O samples and further confirm the existence of oxygen vacancy (VO) in γ-CoOOH. In full-survey XPS spectra (Figure S9), the main peaks are ascribed to Co 2p, O 1s, C 1s, and N 1s, respectively. In the C 1s and N 1s XPS high-resolution spectra for H-V2-Co3S4-O (Figure S10), the peaks at around 284.8, 285.7, and 288.8 eV represent C=C, C=O, and N=C=O, and the binding energies at 399.1 and 400.9 eV correspond to N=C=N and graphitic N, respectively, which are the same C- and N-related structures before OER activation, indicating that the hollow dodecahedrons after OER activation are unchanged and still supported by the C and N frameworks. In the Co 2p high-resolution XPS spectra (Figure 8b), four fitting peaks at 779.30, 781.03, 794.30, and 796.42 eV are assigned to Co3+ 2p3/2, Co2+ 2p3/2, Co3+ 2p1/2, and Co2+ 2p1/2, respectively. Notably, the ratio of the relative peak areas of Co3+ 2p3/2 to Co2+ 2p3/2, Co3+ 2p1/2, and Co2+ 2p1/2 gradually increases from S-400-CoS-O to S-600-CoS-O (Figure 8d). This result confirms through CV analysis that more active Co3+ generated by sulfur vacancy introduction converts to high-valence Co3+ through the OER preactivation process. Accordingly, S-600-CoS-O has the most Co3+ active sites among the H-V2-Co3S4-O samples. In the O 1s XPS spectra (Figure 8c), the binding energies at 533.53, 532.09, 531.19, and 530.04 eV are attributed to the adsorption of water molecules on γ-CoOOH, oxygen from the OH groups, VO, and Co-O, respectively. Furthermore, the relative intensity of the vacancy-related peaks gradually increases from S-400-CoS-O to S-600-CoS-O. As depicted in the right column of Figure 8d, the peak area ratio of VO to Co-O is 0.43 for S-400-CoS-O, and this proportion increases to 1.38 for S-600-CoS-O (to 0.86 for S-500-CoS-O), demonstrating the highest oxygen vacancy concentration in S-600-CoS-O. Based on the above EPR and O 1s XPS results, the vacancy concentration trends to increase from S-400-CoS-O to S-600-CoS-O, which results from the increased sulfur vacancy tendency. Especially, the fitting peaks of VO and Co-O slightly shift to lower binding energy from S-400-CoS-O to S-600-CoS-O (−0.12 and −0.13 eV), suggesting enhanced electron delocalization with an increased vacancy concentration. Therefore, S-600-CoS with the most sulfur vacancies has the most Co3+ active sites and exhibits an enhanced electron delocalization, leading to the best OER performance.

Combined with the above discussions and analysis, the conversion from H-Co3O4 to spinel-phase Co3S4 and the simultaneous introduction of sulfur vacancies could be accomplished in a H2S atmosphere by the thermal decom- position of thiourea. The morphology and composition of the samples as well as the concentration of the introduced sulfur vacancies can be well regulated by controlling the thiourea dose. In the OER process, the H-V2-Co3S4 samples act as the precatalyst and S-600-CoS exhibits the best electrocatalytic activity, which is attributed to the introduction of more sulfur vacancies, specifically for the following two aspects: (i) The increase in Co3+ active sites. In the preoxidation process, more Co3+ sites generated by introducing sulfur vacancies could irreversibly transform to active Co3+ sites, leading to a favorable OER performance. (ii) The enhancement in charge transfer rate. After preactivation, an increased vacancy trend can be inherited and contributes to a higher degree of electron delocalization, thus improving the charge transfer rate of the electrocatalysis process. Therefore, engineering sulfur vacancies in spinel Co3S4 could promote the kinetics of the electrocatalytic reactions and enhance the electrocatalytic activity for OER.

**CONCLUSIONS**

In summary, a facile synthesis strategy realizes the simultaneous transformation from H2O2 to spinel-phase Co3S4, and the introduction of sulfur vacancies by thermally decomposing thiourea, which is attributed to the sulfidation and reducing role of H2S. Furthermore, morphology, composition, and electronic structure, especially the concentration of sulfur vacancies, could be well regulated. The resulting H-V2-Co3S4 can effectively catalyze OER, having a low overpotential (270 mV to 10 mA cm−2), low onset potential (Eonset = 1.47 V vs RHE), small Tafel slope (59 mV dec−1), and low charge transfer resistance (Rct = 11.54 Ω). Notably, benefitting from the introduction of more sulfur vacancies, the formation of more active Co3+ sites via a preactivation process and enhanced charge transfer rates lead to excellent OER performance. Hence, this work provides an avenue for the construction of transition metal-based catalysts with an abundance of vacancies, which affords further insights into defect engineering in the field of electrocatalysis.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01423.

Additional data of structure characterizations and electrochemical tests, including TEM images of ZIF-67 and H-Co3O4; SEM image of S-600-CoS; CV curves and Bode plots of all samples; etc. (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

Guoning Li — School of Thermal Engineering, Shandong Jianzhu University, Jinan 250101, China; Email: liguoning20@sdjzu.edu.cn

Chunjian Xu — School of Chemical Engineering and Technology, State Key Laboratory of Chemical Engineering, Chemical Engineering Research Center, Tianjin University, Tianjin 300072, China; Email: cjxu@tj.edu.cn

Authors

Xiaomin Li — School of Chemical Engineering and Technology, State Key Laboratory of Chemical Engineering, Chemical Engineering Research Center, Tianjin University, Tianjin 300072, China

Kaitian Zheng — School of Chemical Engineering and Technology, State Key Laboratory of Chemical Engineering, Chemical Engineering Research Center, Tianjin University, Tianjin 300072, China; orcid.org/0000-0002-2263-144X; Email: cjiangxu@tj.edu.cn
Jiajun Zhang — Particles and Catalysis Research Group, School of Chemical Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c01423

Author Contributions
X.L. was in charge of conceptualization, methodology, investigation, writing the original draft, and validation. K.Z. was in charge of the methodology, software, formal analysis, and reviewing and editing the draft. J.Z. was in charge of validation, visualization, and reviewing and editing the draft. G.L. was in charge of supervision and conceptualization. C.X. was in charge of supervision and reviewing and editing the draft.

Notes
The authors declare no competing financial interest.

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