The Restructuring-Induced CoOₓ Catalyst for Electrochemical Water Splitting

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ABSTRACT: Restructuring is an important yet less understood phenomenon in the catalysis community. Recent studies have shown that a group of transition metal sulfide catalysts can completely or partially restructure during electrochemical reactions which then exhibit high activity even better than the best commercial standards. However, such restructuring processes and the final structures of the new catalysts are elusive, mainly due to the difficulty from the reaction-induced changes that cannot be captured by ex situ characterizations. To establish the true structure–property relationship in these in situ generated catalysts, we use multimodel operando characterizations including Raman spectroscopy, X-ray absorption spectroscopy, and X-ray reflectivity to investigate the restructuring of a representative catalyst, Co₉S₈, that shows better activity compared to the commercial standard RuO₂ during the oxygen evolution reaction (OER), a key half reaction in water-splitting for hydrogen generation. We find that Co₉S₈ ultimately converts to oxide cluster (CoOₓ) containing six oxygen coordinated Co octahedra as the basic unit which is the true catalytic center to promote high OER activity. The density functional theory calculations verify the in situ generated CoOₓ− layered structures. These electrocatalysts that experience a similar restructuring in OER. Our results also provide insights to design other transition-metal-based materials as efficient electrocatalysts that experience a similar restructuring in OER.

KEYWORDS: operando, X-ray absorption spectroscopy, Raman spectroscopy, oxygen evolution reaction, electrocatalyst

INTRODUCTION

Catalysts often undergo structural changes in working conditions to facilitate the reaction processes. While reversible restructuring can maintain the catalysts’ stability for long-term use, irreversible restructuring has long been believed to degrade their stability, which can lead to a loss of activity due to undesirable changes in catalysts’ compositions and structures. However, recent studies have shown that some materials (e.g., transition metal sulfides) can be unstable at the beginning of the reactions but evolve to new forms of catalysts with compositions and structures different from their initial states. These electrocatalysts, including transition metal chalcogenides, pnictides, and carbides, are called metal X-ides and can exhibit superior activities, even better than the best commercial references. Unfortunately, no agreement has been reached so far on the final structure of these metal X-ides in reactions, and the origin of their superior activity/stability remains unclear.

One type of metal X-ides includes transition metal (i.e., Fe, Co, and Ni) sulfides which are earth-abundant materials and have attracted tremendous attention as a new group of catalysts for water oxidation under alkaline conditions due to their comparable or superior activities compared to RuO₂ and IrO₂. However, there is a lack of agreement on the composition of the “true” catalyst as these materials change at highly oxidative electrochemical conditions for oxygen evolution reaction (OER), a key half reaction to produce hydrogen as a clean fuel. The most prominent theories suggest that under highly oxidative conditions these transition metal sulfides could restructure to metal oxide or (oxy)hydroxide or partially oxidized/(oxy)hydroxidized compounds at the surface (Table S1), which efficiently catalyze the reactions. Much in the literature has indicated that the driving force for oxide (oxy)hydroxides OER is based on the transition metal redox couples (Table S2) such as Co(II)/Co(III), Co(III)/Co(IV), Ni(II)/Ni(III), and Ni(III)/Ni(IV). Unlike treating the metal oxidation state as a reaction center, some literature argued about the structure-dependent active sites for OER (Table S2). For example, Bergmann et al. proposed that the di-μ-oxo bond

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(a square structure formed by metal—oxygen—metal—oxygen) as a unified structural motif is the catalytically active site in the Co(oxyhydr)oxides. Aliki et al. suggested that the cobalt superoxide species as a key intermediate for cobalt oxy-hydroxide OER. Kanan et al. demonstrated that the Co-oxo/hydroxo cluster in cobalt phosphate is the reaction site for OER. Apparently these proposed active sites are different, and some even conflict with each other. We hypothesize that there could be a common building block on the atomic scale for these metal X-ides, acting as the catalytic site to promote the reaction with good stability. The active site could also form different redox centers by absorbing and desorbing OH or aggregating together to form an oxo/hydroxo cluster with different oxidation states.

To prove our hypothetical theory, we need to understand the detailed restructuring processes for metal X-ides. Clearly, ex-situ characterizations, which are used to detect the pre- and postchemical states of catalysts, cannot meet the requirements to study the reaction kinetics and any short-lived intermediates as well as transition forms of metal X-ides. To find out the true catalytically active sites of metal X-ides, operando characterizations are urgently required, as the structural, compositional, and chemical information can be detected under reaction conditions. In this paper, we focus on a metal sulfide thin film, Co9S8, as a representative example of metal X-ides, as it has excellent OER performance and reasonable stability compared to RuO2,16 Using multimodal operando characterizations including Raman spectroscopy, X-ray absorption spectroscopy (XAS), and X-ray reflective (XRR), we revealed the detailed structure and composition evolution of Co9S8 during OER. We unambiguously identified the edge-sharing CoO6 octahedral clusters as the true active sites for CoO6 formed in OER, which is supported by the density function theory (DFT) calculations.

## Results and Discussion

To investigate the reaction kinetics of as-deposited Co9S8 film, cyclic voltammetry (CV) was employed in 0.1 M KOH solution at a scan rate of 2 mV/s. As shown in Figure 1a for the first cycle, the Co9S8 catalyst exhibited excellent performance, as the operational potential at a current density of 10 mA cm−2 (Epc) is 1.55 V (323 mV overpotential compared to 409 mV for RuO2).16 The first cycle CV curve also exhibits a pronounced irreversible feature as the integrated area of the anodic peaks (positive current values) at voltages less than 1.4 V was much larger than that of the cathodic peaks (negative current values), suggesting the oxidation of the Co9S8 catalyst (Figure 1a). In addition, by investigating the second derivation of the curve,17,18 the anodic band at 1.15–1.4 V has two peaks at 1.27 and 1.31 V (Figure S1a,b), which could be due to the change of the coordination environments for cobalt atoms. Compared to the first cycle, the integrated area of anodic peaks for the following second to fifth cycles is much smaller (Figure 1b), and the 1.05 V anodic peak in the first cycle disappeared, which also indicates an irreversible change in the Co9S8 films. However, the anodic peaks and cathodic peaks in the second to fifth cycles have almost the same integrated area, implying more reversible processes after the first cycles. Note that there is increased overpotential after the first cycle (Figure 1a), suggesting some deactivation of the newly restructured electrocatalyst. This is a common issue for electrocatalysts under alkaline conditions but not our focus in this article.19,20

Figure 1c shows the Tafel plot, where the Tafel slope is a good indicator of the OER kinetics. The Tafel slope was measured to be 60.8 mV/dec, and a slope near 60 mV/dec is suggestive of a rate-limiting chemical step following an electrochemical pre-equilibrium step.1,21 Figure 2a shows

![Figure 1](https://doi.org/10.1021/jacsau.1c00346)

**Figure 1.** (a) First five cycles of the CV curve of the Co9S8 film at a scan rate of 2 mV/s. (b) Enlarged view of panel a indicating the oxidation and reduction peak in the first five cycles. (c) Tafel plot. (The Tafel plot was obtained by chronoamperometry measurements in steps of 10 mV, where a relaxation time of 60 s was used for each step to allow the current to achieve a steady state.) All potentials are iR-compensated.

![Figure 2](https://doi.org/10.1021/jacsau.1c00346)

**Figure 2.** (a) In situ Raman spectra for the Co9S8 film at various constant applied potentials. The arrow indicates the sequence of the applied potential, and each applied potential (vs RHE) is labeled on the side of the spectrum. (b) Raman spectra of (1) an as-deposited Co9S8 film and (2, 3) the film subjected to one-week air exposure (~70% relative humidity). For the air-exposed sample, Raman spectra were taken at (2) a particle-like region and (3) a featureless region. For comparison, the plot also includes the OCV spectrum as shown in Figure 2a.
the representative operando Raman spectra taken at different applied potentials for the Co$_9$S$_8$ film on a glassy carbon electrode in 0.1 M KOH (enlarged data shown in Figure S2). The applied potential was increased stepwise from 0.9 to 1.75 V and then decreased to 0.9 V (vs RHE), with a step interval of 0.1−0.2 V. The Raman spectrum of the as-deposited Co$_9$S$_8$ film shows two distinct peaks at 338 and 403 cm$^{-1}$. Prolonged air exposure could oxidize Co$_9$S$_8$ to form Co$_3$O$_4$ (Figure 2b), and humid air could accelerate this oxidation process. Therefore, the Co$_9$S$_8$ samples were always stored under dry ambient Ar. Upon the immersion of the Co$_9$S$_8$ film in the 0.1 M KOH, the open circuit voltage (OCV) was found to gradually increase from 0.840 to 0.846 V (Figure S3). This OCV increase was probably due to the oxidation of Co$_9$S$_8$ in the alkaline electrolyte. (Note that the O$_2$ dissolved in the electrolyte was not intentionally removed.) After the OCV was stabilized, the Raman spectrum was taken on the sample. As shown in Figure 2, no Raman peak is shown at 338 or 403 cm$^{-1}$, but instead the spectrum shows pronounced peaks at 482, 523, and 689 cm$^{-1}$, which match with the E$_g$, F$_{2g}$, and A$_{3g}$ modes of spinel Co$_3$O$_4$, respectively.$^{23−26}$ In addition, the spectrum also shows a minor peak at 502 cm$^{-1}$, and this peak could be ascribed to CoOOH, which often forms on the Co$_3$O$_4$ surface.$^{24,25,27}$ These results suggest that after the relaxation at OCV, the crystalline phase of Co$_9$S$_8$ disappeared, at least below the Raman detection limit, and converted to Co$_3$O$_4$ and CoOOH. This conversion was confirmed by the XPS measurement on an OCV-relaxed sample (Figure S4). In fact, this spontaneous conversion is consistent with the Pourbaix diagram, as Co$_3$O$_4$ is suggested by the Pourbaix diagram to be the thermodynamically stable phase in 0.1 M KOH.$^{21,25,28}$ Moreover, our electrochemical characterization results also indicate that the conversion from Co$_9$S$_8$ to Co$_3$O$_4$ was kinetically fast in the alkaline solution.

The above Raman features remained almost the same when a bias potential was applied and increased up to 1.0 V. However, when the potential was further raised to 1.1 V, the peaks belonging to Co$_3$O$_4$ (i.e., 482, 523, and 689 cm$^{-1}$) largely diminished while the peak of CoOOH at 502 cm$^{-1}$ became more pronounced. In addition, a new broad band at 602 cm$^{-1}$ appeared in the spectrum, and this broad band may also be a signature of CoOOH.$^{25,27,29}$ These results suggest that a change of Co$_3$O$_4$ to CoOOH occurred at 1.0−1.1 V, where an anodic peak was observed in the CV curve (Figure 1b). When the applied potential was further raised to 1.4 V and above, all the peaks belonging to Co$_3$O$_4$ disappeared, which suggests a complete conversion to CoOOH. Notably, the band at 602 cm$^{-1}$ gradually shifted to 585 cm$^{-1}$ as the potential increased from 1.25 to 1.5 V. The red-shift of the 602 cm$^{-1}$ band is suggested to be indicative of the oxidation of the Co(II) and Co(III) toward Co(IV).$^{35}$ This assignment is also consistent with the CV curve, where a pronounced anodic peak was observed at 1.3 V.$^{6,30}$ Notably, the redshift of the band occurred monotonically, which suggests that the entire CoOOH was oxidized collectively. Above 1.6 V, substantial oxygen bubbling appeared.

When the applied potential was reduced stepwise, the Raman spectra indicated that the structural change of the cobalt compound was generally reversed: the 585 cm$^{-1}$ band shifted back to 597 cm$^{-1}$, and the Co$_3$O$_4$ peaks reappeared when the potential was reduced below 1.4 V. However, this change was not completely reversible as the width of the 689 cm$^{-1}$ peak was larger than that at the beginning (fwhm increased from 8.7 to 11.7 cm$^{-1}$). The increased peak width is suggestive of lowered crystallinity, which can be attributed to the irreversible crystalline-to-amorphous structure changes. At a high applied potential (1.6 V vs RHE and above) part of CoOOH becomes amorphous and cannot be converted back to crystalline Co$_3$O$_4$ when the applied voltage is reduced. This crystalline-to-amorphous structure change was also supported by the grazing incidence diffraction (GID) in Figure S9.

To further confirm the change of Co$_9$S$_8$ oxidation state and local structure, we conducted operando XAS. Since the thin film Co$_9$S$_8$ was grown by atomic layer deposition (ALD) with $\sim$20 nm, all signals collected by the bulk sensitive XAS can be used to determine the surface local structures. The pristine material Co$_9$S$_8$ shows an oxidation state around +2.1 (Table S3), and it is very unstable in the electrolyte (Figure 3a), which is also confirmed by operando Raman results and a Pourbaix diagram.$^{21,25,28}$ Once Co$_9$S$_8$ was immersed into the electrolyte, it was oxidized from +2.1 to +2.2, which were calculated based on the linear relationship between the Co XANES edge and oxidation states (Figure 3b). As the applied voltage is increased, the Co XANES edges shift to higher energy, suggesting the further oxidizing of Co. It was found that Co was first oxidized to +2.5 followed by an oxidation to +2.9, +3.1, and finally slightly above +3.2 at a potential of 1.75 V (vs RHE; Figure 3b, Table S3). When decreasing the applied potential back to open circle voltage (OCV, approximately 0.88 V vs RHE), the oxidation state of Co has a descending trend. The change of Co oxidation state is consistent with the operando Raman experiments, which also reflect the reduction and oxidation peaks in the CV measurements. However, incomplete reversibility is also observed, as the oxidation state of Co after returning to OCV is around +2.7 which is higher than that of the pristine sample. This irreversibility change could be caused by the transformation of Co$^{3+}$ to Co$^{3+}$ coordinated in octahedral sites in low crystallinity Co$_3$O$_4$(OH)$_2$, and some of these octahedral sites could be nonreducible Co$^{3+}$, which do not play a role in catalyzing
coordination is left at 1.4 V vs RHE. This small amount of
it is possible that CoO6 is the smallest structure building block
performed model-based EXAFS
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indicating the formation of a reduced Co nanoparticle.
Co9S8 structural evolution of Co 9S8 during the reaction, we
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reason for the instability of Co9S8.
The evolution of Co local structures under the applied
potential is shown in Figure 3c. At OCV, the phase-
uncorrected EXAFS of the catalyst has a broad peak around
1.55 Å that should be a result of the combination of Co−O and
Co−S scattering compared to the EXAFS of CoO and
Co9S8 standards, suggesting the mixture of the two phases.
This is consistent with XANES at OCV that shows the partial
oxidation of Co. As the applied potential is increased, the first
peak in EXAFS (around 1.72 Å in OCV) shifts to 1.42 Å that is
caused by the predominant Co−O scattering. The structure of
the original Co9S8 catalyst is likely to be gradually oxidized to
the CoOx structure, which is also consistent with Raman
spectroscopy findings. To generate further insights into the
structural evolution of Co9S8 during the reaction, we
performed model-based EXAFS fitting by combining Co9S8
and CoO crystal structures (Figures 3d, S6–S7; Table S4 and
S5). The fitted results clearly show an increasing trend of both Co−O and Co−Co coordination numbers (CNs) as the
applied potential is increased, and Co−S coordination mostly
exists in the pristine state and at OCV. Only a small fraction
(around 13.3% compared with pristine Co9S8) of Co−S coordination is left at 1.4 V vs RHE. This small amount of
remaining Co−S may be due to the incomplete S leaching at
OCV. As the applied potential is increased, the conversion of
Co−S coordination to Co−O coordination takes place. It is
noted that the first shell of Co atoms around 1.9 Å reaches full
coordination with six Co−O bonds, representing an octahe-
dron (CoO6) that can be found in spinel Co9O4 or CoOOH as
confirmed by the Raman experiments. However, the second shell Co−O−Co is undercoordinated (less than 12 in CoO or
slightly less than 6 in CoOOH), suggesting a cluster-like structure without long-range ordering.8−10 When the applied
potential is increased, Co−O and Co−Co CNs increase,
contributing to the increase of the oxidation state of Co. When
reversing the applied potential back to OCV, the Co−O and
Co−Co CNs decrease, and both stay undercoordinated,
indicating the formation of a reduced Co nanoparticle.

The loss of long-range ordering of the in situ generated
CoO2 is further confirmed by operando XRR and GID
measurements on Co9S8 thin films (see Supporting Infor-
amation for details). For the as-deposited catalyst thin film, Kiessig
fringes in XRR can be observed, suggesting a smooth surface.
As the applied potential is increased, these fringes quickly
disappear, indicating that the surface was roughening. No
crystalline diffraction peaks are identified from GID,
confirming the formation of short-range ordering materials in
OER, which is consistent with the lack of long-range ordering
indicated by EXAFS and could also be the reason for irreversible reconstruction observed by operando XAS.

Although the Co9S8 catalyst goes through both composi-
tional and long-range-to-short-range ordering structural
evolution, the CoO2 octahedron remains during OER. In our
previous studies, the octahedral site in the spinel structure is
the active site for OER,34,35 and e− theory for transition metal
perovskite oxides is based on the electronic structure of the metal−oxygen octahedron.56 However, some octahedral Co5+ in
CoOOH is not reducible and has low activity in OER, and
some are reducible and have high activity in OER.5 Therefore,
it is possible that CoO2 is the smallest structure building block
and the surface Co atoms bridged by di−µ-oxo bonds in these
octahedrons are active sites as the catalytic center for this type
of metal X-ide. To verify our hypothesis, we performed DFT
calculations by building a small cluster of CoO2 as shown in
Figure S10. Except for the di-µ-oxo site, the octahedral
coordination geometry of each peripheral Co ion is completed
by nonbridging oxygen ligands (including water and hydroxide). The average Co−O bond length between the central Co atom and the surrounding six O atoms is 1.86 Å, which is in accordance with the experimental result (Co−O: 1.90 Å for the first shell). This result also indicates that the central Co atom is in a +3 oxidation state, the same as that of the Co of the octahedral site in Co9O4.37 Recent studies have shown that the oxidation states of surface atoms are
determined using atomic projections of the magnetic moments
and the smaller the magnetic moments of the atoms, the higher
the oxidation states.38 In the Co9O2.H23 cluster model, it is
estimated that there are two oxidation states of Co, namely, Co3+ and Co2+, due to the overlap between the atom-projected magnetic moments of Co ions in various oxidation states. Next, the possible OER mechanisms are explored in an alkaline
environment. For path 1 in Figure 4a and Table S7, step #1:

![Figure 4](https://doi.org/10.1021/jacsau.1c00346)

**Figure 4.** Gibbs free energy diagrams of OER at all possible active sites on the Co9O2.H23 cluster. (a) Path 1 and (c) path 2 in an alkaline environment. Structural optimization of the second electrochemical step to produce O2 on the Co9O2.H23 cluster, (b) Changes of O1−H, O2−Co, and H−O3 bond lengths in path 1. (d) Changes of O−Co1 and O−Co2 bond lengths in path 2. Red, cyan, and blue spheres indicate O, H, and Co atoms, respectively.

The reaction starts from the deprotonation of *OH to generate a H2O molecule and the "O group by the addition of the first
OH" at the Co2 site, in which the oxidation states of Co1 and
Co2 atoms remain unchanged. Step #2: The *O combined
with the second OH" as the initial state is optimized into a di-
µ-OH and the released O2 molecular, as shown in Figure 4b.
Both the Co1 and Co2 ions (+3) are reduced to +2. Step #3:
The third OH" is preferentially adsorbed on the Co2 site due
to coordinative unsaturation of Co2, causing Co1 to be
oxidized to +3 and no change in the Co2 oxidation state (+2).
Step #4: the deprotonation of di-µ-OH completes the four-
electron transfer of OER by the addition of the fourth OH". In
this reaction step, all the Co ions return to the initial oxidation
states (see Figure S10). For path 2 in Figure 4c and Table S8,
step #1: The reaction begins with the first OH" adsorbed at the
di-µ-O site to form di-µ-O2 and "H2O at the Co2 site, in
which the Co1 and Co2 ions are reduced from the +3 to the +2 oxidation state. Step #2: The deprotonation of $^{+}\text{OH}$ at the Co2 site produces an $^{*}\text{OH}$ by the addition of the second $\text{OH}^−$. At the same time, $\text{di}-\mu$-O$_2$ spontaneously desorbs in the optimization process, as shown in Figure 4d. Step #3: The third $\text{OH}^−$ is preferentially adsorbed on the bridge site between Co1 and Co2. Step #4: This step is the same as the fourth step of path 1. The above results indicate that the adsorption of different intermediates can cause the continuous changes in the oxidation states of Co ions to determine the active sites in OER. When the free energy diagrams at the equilibrium potential of 0.402 V are analyzed, the rate determination step is the deprotonations of $^{+}\text{OH}$ at Co2 site for path1 and $\text{di}-\mu$-OH site for path2 with an overpotential of 0.86 and 0.69 V, respectively. Our results reveal that the $\text{OH}^−$ at the bridge site is more prone to deprotonation than that of the OH adsorbed onto Co ions. Co atoms bridged by $\text{di}-\mu$-oxo bonds with $\text{di}-\mu$-oxo are active sites in OER, and Co1–Co2 with $\text{di}-\mu$-oxo are active sites in OER, which is in good agreement with the experimental results. Note that our calculation only chooses Co1 and Co2 as the reaction surfaces. Other surface atoms such as Co3, Co5, Co6, and Co7 have equivalent roles after deprotonations at $\text{di}-\mu$-OH sites. In addition, no change of Co (Co4) at the center of the nanocluster confirms our hypothesis that only surface Co atoms bridged by $\text{di}-\mu$-oxo bonds are active in reactions. These results also imply that the overall activity and stability of the in situ generated CoO$_x$ could be related to the size of the nanocluster. The continuous growth of the CoO$_x$ nanocluster leads to the low ratio of active surface $\text{di}-\mu$-oxo Co–Co motifs and high amount of inactive central Co atoms, which affect the long-term performance of the metal X-ides.

**CONCLUSIONS**

In summary, we have combined operando XAS, XRR, and Raman spectroscopy together with DFT calculations to reveal the restructuring processes of Co$_9$S$_8$ as one example of metal X-ides for OER. We have shown that the Co$_9$S$_8$ transfers into an entirely different CoO$_x$ structure consisting of edge sharing octahedral CoO$_x$ nanoclusters with $\text{di}-\mu$-oxo Co–Co motifs on the surface, which is the true catalytic center. The top oxygen in CoO$_x$ octahedrons can adsorb reaction intermediates ($\text{OH}^−$), and the bridging Co–O–Co in $\text{di}-\mu$-oxo Co–Co motifs can be easily broken to form the vacancies or unsaturated coordination to facilitate the OER. Compared with the edge-sharing octahedral CoO$_x$, the restructuring Co$_9$S$_8$ in OER induces crystalline-to-amorphous conversion in addition to Co$_9$S$_8$-to-CoO$_x$ change. The composition and structure transformations in this restructuring process are beneficial to providing abundant active sites for the OER. The leaching of S ions also helps create the vacancies in the materials to facilitate the participation of lattice oxygen in the OER, which is another benefit compared other CoO$_x$ bulk materials. Our results demonstrate that for catalysts that experience complicated restructuring processes, operando characterizations are essential to understanding the reaction kinetics and related reaction mechanisms. This strategy is also reflected in a recent study using operando surface-enhanced Raman spectroscopy to point out the formation of super cobalt oxide as the possible reaction center.\(^{22}\) In addition, previous studies (Table S1) also suggest some other metal X-ides ($X=C, P, N, Se,$ etc.) may also be either completed or partially oxidized to metal oxide during the OER. If such restructuring occurs in metal X-ides, the metal–oxygen octahedral clusters with surface $\text{di}-\mu$-oxo metal–metal motifs can act as the active sites to promote the OER. Although some work has shown that the metal X-ides do not undergo any restructuring, the surface-active sites may still contain such building block similar to what we found here. For example, Nath’s group has shown that nickel telluride will form some telluride-based edge sharing octahedra instead of an oxygen-based octahedra structure, which favors the OH adsorbing for OER. Therefore, we come up with a new hypothesis that the edge sharing octahedra units are the basic reaction center for OER in the alkaline medium, but the composition in the units can be modified to enhance the OER performance. Our findings and strategy on identifying metal X-ides’ active site can aid future research in the development of advanced electrocatalysts for the energy conversion and storage systems.

**EXPERIMENTS AND METHODS**

**ALD Growth of Co$_9$S$_8$**

Atomic layer deposition (ALD) of Co$_9$S$_8$ thin films was performed in a home-built tubular ALD reactor at 120 °C, using bis(N,N′-di-tert-butylacetamidinato)cobalt(II) and H$_2$S as the precursors.\(^{39,40}\) The films used for electrochemical and operando Raman measurements were deposited on flat glassy carbon (GC) substrates (1 × 1 cm$^2$). The thickness for all of the Co$_9$S$_8$ films was about 20 nm, as measured by X-ray fluorescence (Rigaku, ZSX Primus II). Co$_9$S$_8$ films with the same thickness were deposited on Si substrates for operando XRR measurements.

**Electrochemical Measurements**

The electrochemical measurements were performed in an electrochemical workstation (CHI 660E), using a standard three-electrode configuration. An ALD-Co$_9$S$_8$-coated GC electrode was used as the working electrode. Hg/HgO and Pt electrodes were used as the reference and counter electrodes, respectively, and 0.1 M KOH aqueous solution was used as the electrolyte. All the electrochemical measurements were taken at room temperature. The RuO$_2$ benchmarking electrode was made by drop-casting 16 μL of a RuO$_2$ ink onto a GC electrode to afford a RuO$_2$ loading amount of 0.20 mg cm$^{-2}$. The RuO$_2$ ink was made by ultrasonically dispersing 5 mg of RuO$_2$ (99.9 wt %, Aladdin) in a mixed solution of 0.1 mL of Nafion, 0.9 mL of water, and 1.0 mL of ethanol.

**Operando Raman Measurement**

**Operando Raman** spectra were taken by a confocal Raman microscope (LabRAM HR Evolution, Horiba), using a 532 nm laser for excitation (Laser Quantum Ltd.). The laser was focused with a 100× objective lens to reach a spot size of 1 μm, and the laser power was about 100 mW. A custom-designed electrochemical cell was used for the operando Raman measurement. The GC working electrode was sealed in the cell, which had a transparent window to allow the laser light to pass through. Ag/AgCl and Pt wire electrodes were used as the reference and counter electrodes, respectively, and 0.1 M KOH was used as the electrolyte. During the operando Raman experiment, each Raman spectrum was taken at a constant applied potential. The applied potential was stepwise changed from 0.9 to 1.75 V (vs RHE). At each potential step, the applied potential was first held for 5 min to stabilize the electrochemical current before collecting the Raman spectra. The current was monitored with the electrochemical workstation (CHI 660E). The acquisition of each Raman spectrum took about 5 min. The Raman spectra were also taken at multiple locations on the sample, and no appreciable difference was observed, which suggests negligible sample damage by the Raman laser.

**Operando Surface X-ray Scattering Experiments**

**Operando** XRR experiments were carried out at 12-ID-D, Advanced Photon Source (APS) at Argonne National Laboratory (ANL) using an eight-circle diffractometer equipped with a Pilatus 100k 2D
detector. Specular reflectivity data were collected to probe surface normal properties such as surface roughness and electron density contrast for Co9S8 thin films. To perform operando measurements, thin film material was mounted on a custom designed electrochemical cell with Pt wire and Ag/AgCl as the counter and reference electrodes, and electrochemical data acquisition was done by using a Gamry Reference-600 electrochemical workstation under an O2 gas flow of 30 sccm in 0.1 M KOH. Several potential points were selected based on preliminary cyclic voltammetry (CV) runs and were held for at least 15 min before acquiring XRR data. XRR data were background subtracted and corrected for active area and polarization. Moreover, out-of-plane grazing-incidence diffraction (GID) measurements were done after the electrochemical experiments to probe the surface-specific crystal structure of the film.

**Operando X-ray Absorption Spectroscopy**

Operando XAS experiments were carried out at SBM-D, APS of Argonne National Laboratory. Both Co K-edge XANES and EXAFS were measured under fluorescence mode by a Vortex ME4 detector. Twenty-nanometer-thick Co9S8 was deposited by the same ALD process on carbon fiber paper with 100-μm thickness as the working electrode. Pt wire and Ag/AgCl were used as the counter electrode and reference electrode, respectively. All three electrodes were mounted on a custom-designed operando XAS fluorescence cell, and the electrochemical measurements were done using a Gamry Reference-600 electrochemical workstation under an O2 gas flow at 30 sccm in 0.1 M KOH electrolyte. Several potential points were selected and held for at least 15 min to collect data to make sure the reaction completed. All XAS data analyses were performed with the Athena software package to extract XANES and EXAFS. Fourier Transform of Co K-edge EXAFS was performed by using the Hanning window function with k-weights of 2. For model-based EXAFS analysis, all of the scattering paths were generated by the FEFF calculation function in Artemis based on the crystal structure of CoO and Co9S8. The generated scattering paths were then calibrated by performing the FEFFIT of the EXAFS data of the CoO reference sample, mainly to obtain the amplitude reduction factor (S02) values. With S02 (0.71) known, all EXAFS data of the catalyst materials were fitted with such generated amplitudes using corelineement fitting. All of these EXAFS fittings are done with a k-range from 3 to 12 Å−1. An integral method was used to determine the Co oxidation state with Co K-edge XANES.

**DFT Calculations**

All spin-polarized DFT calculations were performed using the revised Perdew–Burke–Ernzerhof (RPBE) exchange correlation functional of the generalized gradient approximation (GGA) as implemented in VASP 5.4.4. The projector augmented-wave (PAW) method was used to describe the core–valence interaction, and a plane-wave cutoff energy was set to 400 eV to approximate the valence electron densities. The DFT+U method with an effective coulomb integral (U − J) of 5.02 eV for the octahedral sites in bulk Co3O4 was adopted to describe the strong correlation of the localized Co 3d states. Convergence was achieved when all atomic forces and energies were below 0.01 eV Å/Å and 10−6 eV, respectively. The dispersion correction was considered by using the DFT-D3 method to describe the van der Waals interactions. An edge-sharing molecular cobaltate cluster (MCC) was utilized to simulate the molecular dimensions of our experimental Co9S8 octahedral clusters, namely, Co3O6H3. For the isolated cluster, interactions between periodic images are negligible in a 15 × 15 × 15 Å3 unit cell, and thus single gamma-point sampling was used for Brillouin zone integration. Details on the calculations of Gibbs free energies are presented in the Supporting Information.

**Author Contributions**

These authors contributed equally. Z.F., X.W., and H. Z. conceived the project and designed the experiments. X.W. and Q.W. carried out the synthesis and electrochemical measurements. M.W., Z.F., and Q.M. carried out the operando XAS measurements and data analysis. Z.H. and Y.C. carried out the operando Raman measurements. W.S., Y.D., and H.Z. performed operando XRR measurements. X.B. and Y.L. performed the DFT calculations. M.W. and Z.F. prepared Supplementary discussion and results for Raman spectrum, XPS, and XRR; the calculation details of Gibbs free energies; supplementary figures and tables for electrochemical characterization, Raman spectrum, XPS, XAS, and DFT (PDF)

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The authors declare no competing financial interest.

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