



# Adaptive Amphiphilic Molecular Switch for Coordinated Spin-State and Interfacial Water Regulation Enables Fast Reconstruction for Efficient Oxygen Evolution

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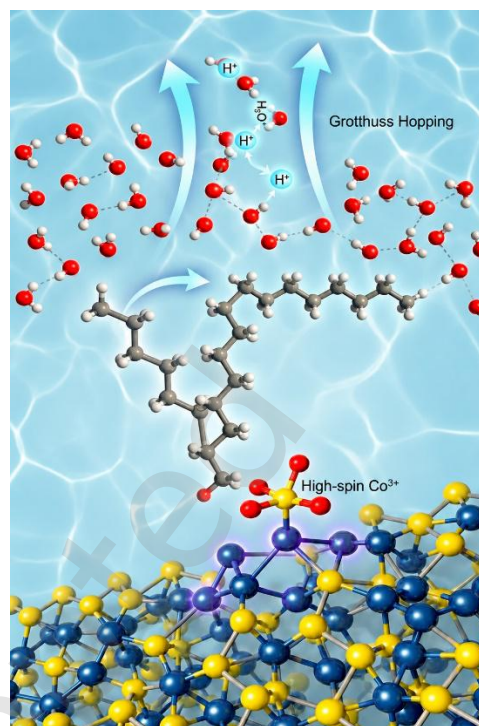
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We propose and validate an entropy–energy competition descriptor for designing adaptive amphiphilic molecular switches, revealing a potential-responsive dual-regulation mechanism wherein the sulfate headgroup dynamically locks cobalt in a high-spin state to facilitate proton-coupled electron transfer, while the dodecyl tail undergoes hinge-like conformational rearrangement that actively polarizes the interfacial hydrogen-bond network into a proton-hopping-favorable medium. This cooperative effect, confirmed by operando spectroscopy and simulations, drives fast reconstruction to achieve 227 mV overpotential and >3000 h durability, and demonstrates broad generalizability across metal sulfide/oxide systems, offering a universal paradigm for descriptor-guided electrocatalyst design.



# Adaptive Amphiphilic Molecular Switch for Coordinated Spin-State and Interfacial Water Regulation Enables Fast Reconstruction for Efficient Oxygen Evolution

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## ABSTRACT

Sluggish catalyst reconstruction limits the oxygen evolution reaction (OER), in part because electronic-state regulation and interfacial mass transport are difficult to coordinate. Here, we establish an entropy–energy competition ratio ( $\zeta = T\Delta S/\Delta E$ , where  $T$  is the absolute temperature,  $\Delta S$  is the spin-transition entropy change, and  $\Delta E$  is the spin-transition energy barrier) as a quantitative descriptor for predicting amphiphile-mediated spin-state regulation. Its predictive capability is validated across amphiphiles with systematically varied headgroups and tail lengths. Guided by this descriptor, sodium dodecyl sulfate (SDS) functions as a potential-responsive molecular switch that couples headgroup-mediated stabilization of high-spin  $\text{Co}^{3+}$  with tail-mediated reorganization of interfacial water, thereby accelerating electrochemical reconstruction. The optimized catalyst requires an overpotential of 227 mV at 10 mA cm<sup>-2</sup> and maintains stable operation for over 3000 h, while the design strategy is extendable across different catalyst systems. These findings establish a descriptor-guided molecular design framework for coordinating electronic and interfacial regulation in reconstruction-driven electrocatalysis.

## KEYWORDS

Spin state regulation, Amphiphilic molecule, Interfacial water structure, Electrochemical reconstruction kinetics, Oxygen evolution

## Introduction

The development of high-efficiency non-precious-metal oxygen evolution reaction (OER) catalysts is crucial for establishing renewable energy systems[1-7]. However, the intrinsically slow kinetics of the OER in alkaline media present a central bottleneck, primarily due to the electrochemical reconstruction that catalysts undergo during operation[8-13]. This process typically involves the dynamic generation and transformation of surface active species on the catalyst, the efficiency of which directly governs the ultimate reaction activity[14-18]. For cobalt-based catalysts, the fundamental equations governing the reconstruction reaction indicate that this process depends not only on the electronic

state and spin configuration of octahedral cobalt centers, but also critically on the structure, orientation, and hydrogen-bond network of water molecules at the electrode/electrolyte interface. These factors collectively govern ion adsorption, proton transfer, and transport pathways during reconstruction[19-25]. For cobalt-based catalysts, however, conventional research strategies have largely focused on single-dimensional tuning, which fails to achieve synergistic modulation of the electronic configuration and interfacial water structure at the intrinsic level, thereby limiting the overall enhancement of reconstruction kinetics.

Ligand modification strategies offer a highly promising approach to addressing these challenges[26-30]. By rationally designing amphiphilic molecules with both electronic



modulation and interface-directing capabilities, it is possible to achieve simultaneous intervention in the spin state of metal centers and the interfacial water microenvironment[31-33]. Sodium dodecyl sulfate (SDS), as a classic amphiphilic molecule, features a hydrophilic head that can serve as a  $\pi$ -donor to effectively modulate electronic structures, while its hydrophobic tail enables the regulation of local polarity at the electrochemical interface. This amphiphilic nature makes SDS a promising candidate for synergistically optimizing both the spin configuration of active centers and the interfacial mass-transfer environment during reconstruction. However, the atomic-scale dynamic behavior and cooperative mechanism of such molecules at complex electrochemical interfaces remain insufficiently explored. Elucidating their working principles is crucial for establishing a new paradigm in catalyst design.

Herein, this work focuses on the dynamic role and synergistic mechanism of amphiphilic molecules in the electrochemical reconstruction of cobalt-based catalysts. For the cobalt center, the ligand effect is intrinsically governed by the interplay between the vibrational entropy contribution and the energetic term of the headgroup ligand field. To integrate these two competing factors into a unified design framework, we first established a theoretical descriptor termed the entropy–energy competition ratio ( $\xi = T\Delta S/\Delta E$ , where  $T$  is the absolute temperature,  $\Delta S$  is the spin-transition entropy change, and  $\Delta E$  is the spin-transition energy barrier), and employed a series of molecular systems with systematically varied headgroup ligand-field strengths and tail-chain lengths to verify its predictive capability for regulating the spin state and catalytic activity, thereby establishing the validity of  $\xi$  as a descriptor for rational catalyst design. On this basis, employing SDS as a potential-responsive molecular switch, and through combined potential-dependent synchrotron X-ray absorption spectroscopy, in situ spectroscopy, multiscale simulations, and electrochemical kinetic analyses, we elucidate its adaptive synergistic mechanism: the hydrophilic sulfate headgroup serves as a donating weak-field ligand that induces and stabilizes high-spin  $\text{Co}^{3+}$  to accelerate initial intermediate adsorption, and dynamically switches the cobalt spin state during reconstruction to boost the proton-coupled electron process; meanwhile, the hydrophobic tail chain undergoes a potential-driven hinge-like conformational transition, actively reshaping the interfacial hydrogen-bond

network by polarizing the long-range ordered, strongly hydrogen-bonded water structure into a flexible medium rich in weak hydrogen bonds, thereby markedly facilitating proton transport via the Grotthuss hopping mechanism. This dual functionality, integrating spin-state regulation with interfacial microenvironment optimization, substantially lowers the surface reconstruction barrier from both electron-transfer and ion-transport perspectives, driving efficient initiation and deep progression of the reconstruction process. Consequently, the optimized SDS-modified  $\text{Co}_9\text{S}_8$  catalyst (CS-300) requires an overpotential of only 227 mV at 10  $\text{mA cm}^{-2}$  and operates stably for over 3000 hours, and this strategy can be extended to different metal centers and catalyst systems, demonstrating good universality. By synergistically optimizing the electronic state and interfacial water environment through rational molecular design, this work provides a quantitative predictive paradigm for developing efficient and stable electrocatalysts.

## Results and Discussion

Thermodynamically, the equilibrium between the high-spin (HS) and low-spin (LS) states is governed by the competition between the spin-transition energy barrier  $\Delta E$  and the entropy change  $\Delta S$ . Here,  $\Delta E$  represents the energy required for the transition from the LS to the HS state, while  $\Delta S$  arises primarily from the change in spin multiplicity and the entropy increase induced by metal–ligand bond-length relaxation. Theoretical thermodynamic analysis (Note S1) reveals that the spin equilibrium depends strongly on the relative magnitude of  $\Delta S$  and  $\Delta E$ . To quantify this competition, we introduce an "entropy–energy competition ratio" descriptor, defined as:

$$\xi = T\Delta S / \Delta E$$

When  $\Delta S$  dominates, the system preferentially stabilizes the HS state; when  $\Delta E$  dominates, the LS state is more readily sustained. Based on this theoretical framework, the influence of SDS introduction on the spin-state evolution of cobalt centers can be predicted (Figure 1a). First, the flexible alkyl tail of SDS adopts a trailing configuration at the interface, increasing vibrational degrees of freedom in the coordination environment and thus significantly enhancing  $\Delta S$ . Second, the sulfate headgroup of SDS undergoes  $\pi$  overlap with the  $t_{2g}$  orbitals of  $\text{Co}^{3+}$  through the oxygen lone-pair-filled p orbitals, forming a lower-energy  $\pi^*$  antibonding orbital that substantially reduces the splitting energy ( $\Delta$ ) between the  $t_{2g}$



and  $e_g$  orbitals. These combined effects shift the spin-state equilibrium toward the entropy-dominated regime, thereby promoting and stabilizing the HS state of cobalt.

To validate the above predictions, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy were employed to monitor the evolution of the local cobalt structure during synthesis in the presence and absence of SDS. As shown in Figure 1b, in the system without SDS, heating for 2 h to 6 h only induced a slight low-energy shift in the absorption edge and limited attenuation in the white-line intensity. In contrast, under SDS addition, the same heating period led to a pronounced decrease in the absorption-edge energy ( $E_0$ ), a rapid reduction in white-line intensity, and an earlier enhancement of post-edge spectral features. These observations indicate that the  $\pi$ -donor character of SDS lowers the ligand-field splitting  $\Delta$ , promoting electron transfer from the  $t_{2g}$  to the  $e_g(\sigma^*)$  antibonding orbitals, thereby enhancing spin polarization and magnetic moment. Fourier-transform EXAFS (FT-EXAFS) spectra further support this conclusion (Figure 1c). In the absence of SDS, the peak corresponding to the first coordination shell shifted to a shorter distance and showed a significant increase in intensity and integrated area from 2 h to 6 h of heating, suggesting that both local and long-range ordering were still being gradually established. In sharp contrast, for the SDS-modified sample, the first-shell peak stabilized at approximately 1.68 Å after just 2 h of heating, attributed to the lengthening of Co–S  $\sigma$  bonds due to electron population in the  $e_g^*$  orbitals. Extending the heating to 6 h maintained the integrated intensity, indicating that the local coordination environment of cobalt underwent earlier restructuring and reached a stable state[34]. Wavelet transform (WT) analysis enables simultaneous resolution of EXAFS signals in both momentum ( $k$ , the photoelectron wave number) space and real ( $R$ , the radial coordinate) space (Figure 1d). For the sample without SDS, after 2 h of heating, the WT intensity was mainly concentrated at  $k \approx 7 \text{ \AA}^{-1}$  and  $R+\Delta R \approx 1.5 \text{ \AA}$ . Upon further heating to 6 h, the intensity peak shifted toward lower  $k$  ( $\sim 6 \text{ \AA}^{-1}$ ) and larger  $R+\Delta R$  ( $\sim 1.8 \text{ \AA}$ ), accompanied by the appearance of a subsidiary feature at low  $k$ . The shift toward the lower- $k$  region reflects an increase in the Co–S bond length and a further ordering of the coordination environment; concurrently, the appearance of an auxiliary peak in the low- $k$  region can be assigned to the

enhanced contribution from Co–Co coordination, indicating a gradual evolution of the local structure toward the standard CS structure. These structural evolution trends are consistent with the improvement in crystallinity observed by X-ray diffraction (XRD) (Figures S1–S5). In contrast, the SDS-modified sample exhibits a markedly earlier structural evolution. For the 2 h-SDS sample, the WT intensity maximum is already located at  $k \approx 6 \text{ \AA}^{-1}$  and  $R+\Delta R \approx 1.7 \text{ \AA}$  and extends into the lower- $k$  region, demonstrating that the average Co–S bond length increases within a shorter reaction time as a result of the perturbation of the Co local structure by SDS coordination. Upon further heating to 6 h, the WT intensity of the 6 h-SDS sample becomes more concentrated in the low- $k$  region ( $\sim 5 \text{ \AA}^{-1}$ ) and is significantly enhanced in the  $R+\Delta R$  range of approximately 2.0–2.2 Å, reflecting the synergistic strengthening of Co–S and Co–Co coordination and the stabilization of the local structure.

To directly visualize the differences in the evolution rate of the cobalt spin states during synthesis, the magnetic properties of the four sets of samples were measured using a vibrating sample magnetometer (VSM)[35]. The magnetization ( $M$ ) versus magnetic field ( $H$ ) curves ( $M$ – $H$ ) reveal that all samples exhibit soft magnetic behavior (Figure 1e). Comparative analysis shows that after 2 h of heating, the introduction of SDS significantly enhances the saturation magnetization ( $M_s$ ) from 0.262 emu g<sup>-1</sup> to 0.317 emu g<sup>-1</sup>, and this enhancing trend persists upon extending the heating to 6 h. The increase in  $M_s$  directly reflects a rise in the total number of unpaired electrons per unit mass, that is, an enhancement of the overall net magnetic moment of the system[36]. However, it should be noted that the magnitude of the macroscopic magnetization is jointly determined by the local magnetic moments and the magnetic exchange interactions between Co sites. To decouple these two contributions, we analyzed the relative Curie constant ( $C_{\text{rel}}$ ) extracted from the magnetization ( $M$ ) versus temperature ( $T$ ) curve ( $M$ – $T$ ) (Figure 1f). According to the Curie–Weiss law,  $C_{\text{rel}}$  is proportional to the square of the local magnetic moment and independent of the magnetic exchange interactions, and can therefore reflect the changes in the single-ion spin state. In the system without SDS, as the heating time increased from 2 h to 6 h, the low-temperature magnetic moment under zero-field cooling (ZFC) decreased from 3.18 emu g<sup>-1</sup> to 1.01 emu g<sup>-1</sup>, and the relative  $C_{\text{rel}}$  obtained from linear fitting

of the high-temperature inverse-magnetization ( $1/M$ ) versus temperature ( $T$ ) curve also decreased from 8.04 to 2.46, indicating a reduction in the effective number of paramagnetic spins. In contrast, the SDS-containing sample retained a higher  $C_{rel}$  value even after 6 h, demonstrating that SDS induces the excitation of cobalt d electrons from the paired  $t_{2g}$  orbitals into the eg  $\sigma^*$  antibonding orbitals, thereby generating a stronger net magnetic moment at an early stage. To further elucidate this phenomenon at the electronic structure level, total density of states (TDOS) analysis based on ab initio molecular dynamics (AIMD) snapshots at 900 K (0 fs and 1000 fs) was performed (Figures 1g, 1h). The  $Co_9S_8$  (CS) sample showed nearly spin-degenerate features near the Fermi level ( $E_F$ ) at both time points. In contrast, the  $Co_9S_8$ -SDS (CS-SDS) sample exhibited spin-polarized occupied states even at 0 fs, with clear exchange splitting near  $E_F$ :  $\alpha$ -spin dominated below  $E_F$ , while  $\beta$ -spin dominated above  $E_F$ . These results indicate that SDS alters the local charge environment of cobalt early in the reaction, promoting the formation and stabilization of a high-spin state dominated by majority spins at an earlier stage[37].

To evaluate the predictive generality of the  $\xi$  descriptor, we further designed three control systems: sodium n-octyl sulfate (CS-SOS), dodecyl phosphate (CS-PC), and sodium hexadecyl sulfate (CS-SHS). Among them, CS-SOS and CS-SHS share the same sulfate headgroup as SDS but possess progressively longer tail chains (C8, C12, and C16), which are expected to systematically modulate the vibrational entropy  $\Delta S$ ; in contrast, CS-PC has the same tail length as SDS, yet its phosphate headgroup provides a stronger ligand

field than sulfate and is thus expected to markedly enlarge the splitting energy  $\Delta E$ . To further quantify the molecular-structure dependence of the entropy-energy competition, we introduced a normalized entropy-energy competition descriptor,  $\xi_{rel}$ , using CS-SDS as the molecular reference. The relative entropy contribution was estimated from the number of internal conformational degrees of freedom of the alkyl chain, whereas the relative energy contribution was determined by the headgroup-dependent ligand-field strength (Table S1). Notably, the calculated descriptor values reproduce the experimentally observed spin-state response: CS-SHS exhibits the highest spin degree, whereas CS-SOS and particularly CS-PC show substantially suppressed spin polarization relative to CS-SDS. A series of phase characterization results indicate that all three molecules were successfully grafted onto the CS surface without altering its intrinsic crystal structure (Figure S6, S7a–c). Further soft X-ray absorption spectroscopy (sXAS) and X-ray photoelectron spectroscopy (XPS) analyses (Figure S7d–i) reveal that CS-SHS exhibits a higher cobalt spin state compared to CS-300, whereas CS-SOS and CS-PC show relatively lower cobalt spin degrees. In addition, fitting of the M-H curves yields saturation magnetization values of 0.237, 0.214, and 0.269 emu for CS-SOS, CS-PC, and CS-SHS, respectively, providing a direct comparison with CS-300, with all samples displaying paramagnetic characteristics (Figure S8). These results further corroborate the theoretical prediction that modulating the vibrational freedom of the tail chain and the coordination field strength of the headgroup can effectively drive the shift in spin equilibrium.

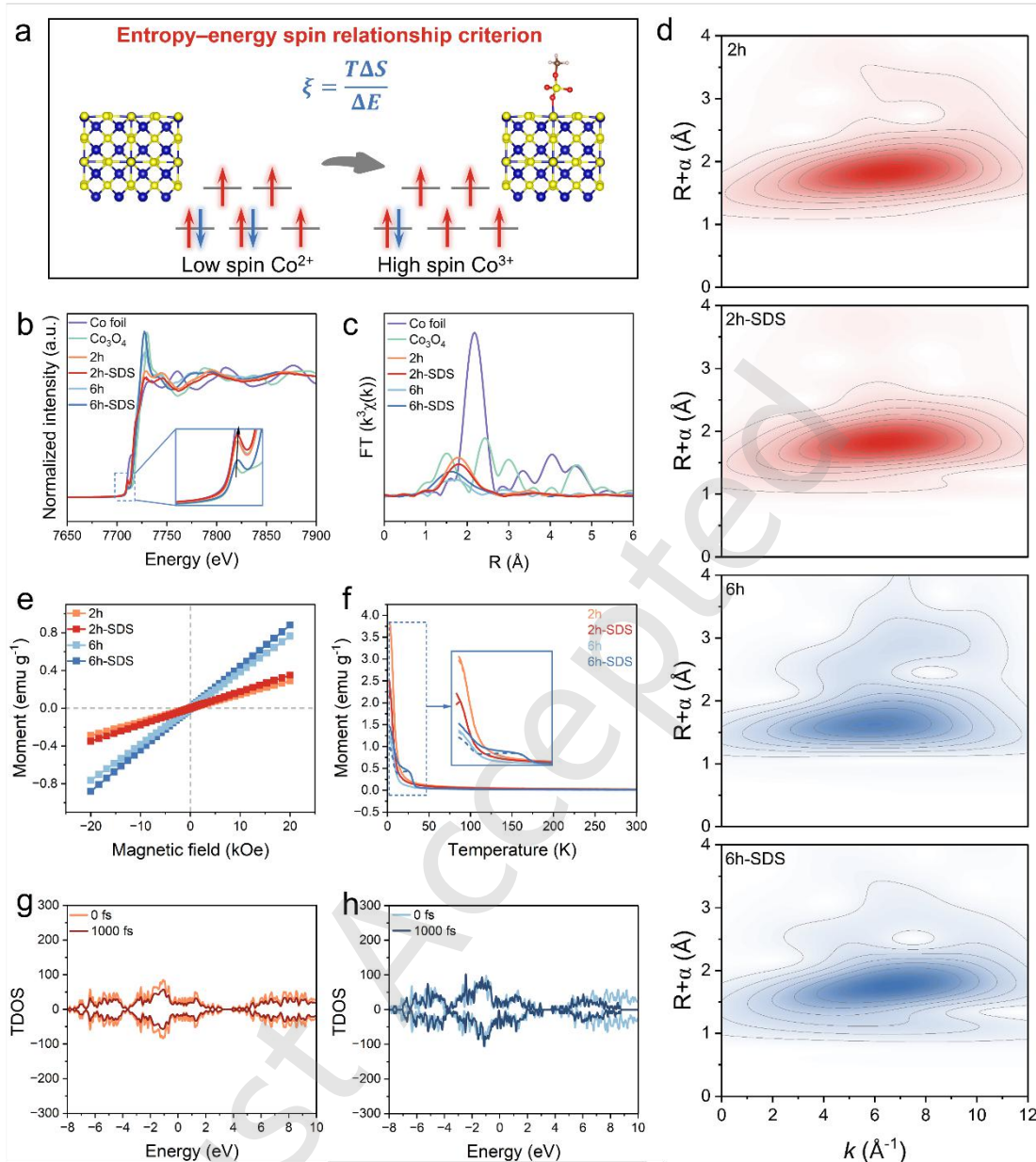


**Figure 1.** a Descriptor of entropy-energy competition influencing spin state. b Co K-edge XANES spectra, c FT-EXAFS spectra, d WT contour plots, e Magnetic hysteresis (M-H) curves, f Magnetic temperature-dependent curves for varying heating durations with or without SDS. Total density of states (TDOS) obtained from ab initio molecular dynamics (AIMD) simulations of g CS, h CS-SDS at varying heating times.

Based on the aforementioned theoretical framework, we selected SDS as a proof of concept molecule and first systematically characterized the phase structure and bonding configuration of the catalyst using XRD and Raman spectroscopy. The XRD patterns (Figure 2a) show that the characteristic diffraction peaks of all samples match well with the standard  $\text{Co}_9\text{S}_8$  reference in the Powder Diffraction File (PDF No. 86-2273), with no detectable additional crystalline phases or obvious phase transformation upon SDS

incorporation. These results demonstrate that SDS modification preserves the bulk  $\text{Co}_9\text{S}_8$  crystallographic framework and long-range structural identity. In contrast to the preserved bulk crystal phase revealed by XRD, Raman spectroscopy probes changes in the local bonding environment and reveals a distinct local structural response to SDS incorporation (Figure 2b). Distinct vibrational peaks were observed at  $480\text{ cm}^{-1}$  ( $E_g$ ),  $520\text{ cm}^{-1}$  ( $F_{2g}$ ),  $610\text{ cm}^{-1}$  ( $F_{2g}$ ), and  $690\text{ cm}^{-1}$  ( $A_{1g}$ ). Notably, the  $A_{1g}$  mode in the CS-300

sample, which corresponds to the symmetric stretching vibration of octahedral  $\text{CoS}_6$  sites, exhibits a clear red-shift toward lower wavenumbers. This shift is directly attributed to the elongation of Co–S bonds induced by SDS incorporation, leading to a reduction in the bond force constant[38]. Therefore, the Raman response does not indicate a change in the overall  $\text{Co}_9\text{S}_8$  crystal phase, but rather reflects a perturbation of the local Co–S coordination environment within the preserved  $\text{Co}_9\text{S}_8$  framework. Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric-differential scanning calorimetry (TG-DSC) results provide direct evidence for the successful incorporation of SDS (Figures 2c, S9). Characteristic absorption peaks of CS-300 at 2922, 2852, and 1471  $\text{cm}^{-1}$  correspond to the stretching vibrations of the methylene tail chain and relevant modes of the sulfate headgroup in SDS, respectively[32]. Moreover, the CS-300 sample exhibits significantly higher electron paramagnetic resonance (EPR) signal intensity and double-integrated area compared to CS, accompanied by pronounced anisotropic broadening and enhanced main spectral features (Figure 2d). The enhancement of the EPR signal directly reflects an increase in the number of unpaired electrons,

which serves as an unambiguous indicator of an elevated concentration of paramagnetic species.

The samples were characterized using transmission electron microscopy (TEM). TEM images (Figure 2e) reveal the presence of amorphous bands on the sample surface, providing direct evidence of the successful integration of CS and SDS in CS-300. High-resolution TEM (HRTEM) lattice analysis shows observed fringe spacings of 0.306 nm and 0.287 nm (Figure 2f), corresponding to the (311) and (111) planes of CS, respectively. To further resolve the spatial distribution of elements in the multicomponent material, high-angle annular dark-field scanning TEM coupled with energy-dispersive X-ray spectroscopy (HAADF-STEM-EDX) was employed for elemental mapping (Figure 2g). The results indicate a homogeneous distribution of Co, S, C, and Na at the nanoscale. This is consistent with findings from scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM-EDX) (Figure S10) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) depth profiling (Figure S11), collectively confirming uniform elemental dispersion from two-dimensional planes to three-dimensional space.



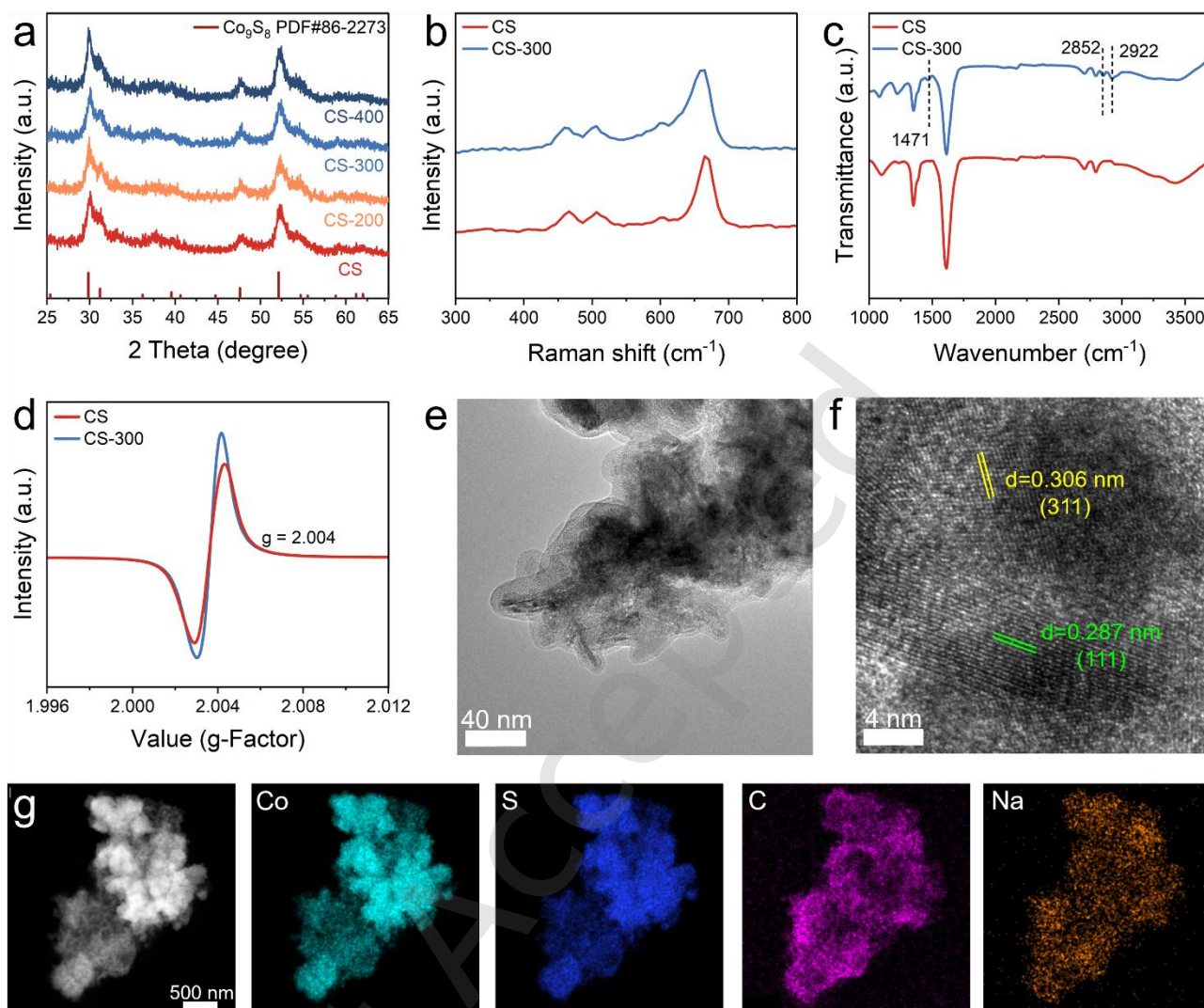


**Figure 2.** **a** XRD patterns of CS and CS-X (X = 200, 300, or 400; X denotes the initial SDS feeding mass in mg). **b** Raman spectra, **c** FT-IR spectra, **d** EPR spectra of CS and CS-300. **e** TEM image, **f** HRTEM image and **g** HAADF-STEM with corresponding elemental mapping images of CS-300.

Co K-edge XANES spectra reveal a marked difference in the cobalt electronic structure between CS and CS-300. Compared with CS, CS-300 exhibits a clear shift of the absorption edge to higher energy and a pronounced increase in white line intensity, indicating that coordination of SDS induces an elevated cobalt valence state. Determination of the absorption edge inflection point by derivative fitting shows that the edge energy of CS-300 is approximately 0.9 eV higher than that of CS, reflecting an increase in edge energy due to a higher effective nuclear charge. Linear combination fitting further reveals that, after SDS modification, the fraction of high-valence cobalt species increases significantly, leading to an elevated average valence state (Table S2); this

result is consistent with XPS (Figures S12–S13). For the pre-edge region (7705–7725 eV, corresponding to the  $1s \rightarrow 3d$  quadrupole transition), baseline-subtracted integration analysis shows that, compared with CS, CS-300 exhibits a notably larger pre-edge area and a slight shift in the centroid energy, indicating a decrease in local symmetry and enhanced  $3d-4p$  orbital mixing. This implies that the introduction of SDS disrupts the local symmetry of the octahedral cobalt sites and increases the covalency of the Co–S bonds. This interpretation is further supported by the R-space spectra of Co-K-edge EXAFS (Figure 3b). The first coordination shell in CS-300 shows slightly elongated bond lengths and increased peak intensity, while the peak of the second shell



shifts from 2.608 Å to 2.915 Å with significant broadening, indicating an increase in the average Co–Co bond distance. Furthermore, wavelet transform analysis reveals that the intensity peak of CS-300 extends toward the lower- $k$  region, indicating a broader Co–S bond length distribution and a longer average bond length compared with CS, which reflects the pronounced alteration of the local Co coordination environment induced by SDS modification (Figures 3c, 3d). Further insights into the spin state and valence information are provided by the analysis of Co-L-edge soft X-ray absorption spectroscopy (sXAS) (Figure 3e)[39]. First, derivative analysis was performed on the baseline-subtracted L<sub>3</sub> edge (770–782 eV). The unmodified CS sample exhibits two distinct local maxima at approximately 778.4 eV and 779.0 eV, with a splitting of about 0.6 eV, corresponding to the  $2p_{3/2} \rightarrow t_{2g}^*$  and  $2p_{3/2} \rightarrow e_g^*$  transitions, respectively. In contrast, the SDS-modified CS-300 displays only a single main peak at ~779.1 eV, with the low-energy shoulder nearly disappearing, indicating a significantly reduced energy gap between the  $t_{2g}$  and  $e_g$  unoccupied states, a hallmark of HS state  $\text{Co}^{3+}$ . Thus, the spectral change of CS-300 suggests that SDS facilitates the entry of  $\text{Co}^{3+}$  into the HS state by lowering the crystal field strength and increasing the degree of coordination symmetry breaking. Second, the main peak and satellite features of the L<sub>2</sub> edge (793–805 eV) were examined. CS shows a sharp main peak at 793.4 eV; CS-300 exhibits a main peak at 793.5 eV but with increased peak width and weakened satellite shoulder. For quantitative comparison, the low-energy shoulder ( $t_{2g}$ ) and the main peak ( $e_g$ ) of the L<sub>3</sub> edge were integrated over the ranges 778–779 eV and 779–781 eV, respectively. The resulting  $t_{2g}/e_g$  area ratio is approximately 0.83 for CS, whereas it decreases to about 0.75 for CS-300, further confirming the enrichment of the HS state. Compared with CS, both the L<sub>3</sub> and L<sub>2</sub> edges of CS-300 shift to higher energies, confirming an increase in the average cobalt valence state. More importantly, the L<sub>3</sub>/L<sub>2</sub> peak area ratio of CS-300 increases from 2.55 to 2.59, and the branching ratio ( $L_3/(L_3+L_2)$ ) rises from 0.718 to 0.721. These increases are directly correlated with a greater number of unpaired electrons and an enhanced spin multiplicity of cobalt ions, unequivocally indicating an increased proportion of HS cobalt species. Collectively, these results further validate the theoretical prediction that SDS promotes the stabilization of the HS state. Corresponding magnetic

measurements show that both CS and CS-300 exhibit paramagnetic behavior at room temperature in the M-H curves (Figure 3f). Compared with CS (0.212 emu), CS-300 exhibits a significantly higher saturation magnetization (0.265 emu) and a lower coercivity, with the hysteresis loop remaining highly reversible, indicating that the enhanced magnetism primarily originates from an increase in the number of paramagnetic centers rather than from the formation of a magnetically ordered structure. M-T curve analysis (Figure 3g) reveals that in the low-temperature region (2–20 K), the magnetic moment of CS-300 (3.87 emu) is markedly higher than that of CS (2.55 emu). With increasing temperature, both samples show a paramagnetic decay trend, yet CS-300 maintains a higher magnetic moment throughout the entire temperature range, further confirming the stabilizing effect of SDS on the HS state of cobalt.

To gain an atomic-scale understanding of the above phenomenon, we performed adsorption and structural optimization of SDS molecules on the octahedral cobalt sites of the constructed CS crystal facet, ensuring that the density functional theory (DFT) calculation model is consistent with experimental observations. Differential charge density analysis (Figure 3h) reveals a pronounced charge depletion around the cobalt atom in the presence of SDS, indicating that the sulfonate anion acts as an electron acceptor, withdrawing electrons from the cobalt center. This reduces the electron count in the cobalt d orbitals, subsequently promoting its valence increase and spin-state transition. Total density of states (TDOS) analysis further elucidates (Figure 3i) that the CS-SDS system exhibits a significantly broadened density of states near the Fermi level and stronger oscillations within the energy range of –6 eV to 2 eV. Simultaneously, the peak intensity below the Fermi level decreases while the peak width increases, suggesting enhanced electron delocalization and effective Coulomb interactions, collectively reinforcing the metallic character of the system. This evolution of the electronic structure is closely linked to the formation of spin-polarized channels induced by high-spin cobalt sites, where unpaired electrons align in parallel spins and can engage in spin-selective coupling with reaction intermediates, thereby significantly facilitating electron transfer processes. This conclusion is strongly supported by work function simulations, Kelvin probe force microscopy (KPFM), and

four-probe resistivity measurements (Figures S14–S16). Combined with a series of additional characterizations (Figures S17–S19), it is confirmed that CS-300 not only exhibits significantly enhanced charge transport capability

but also achieves synergistic optimization of its band structure and surface/interface properties, in excellent agreement with theoretical predictions.

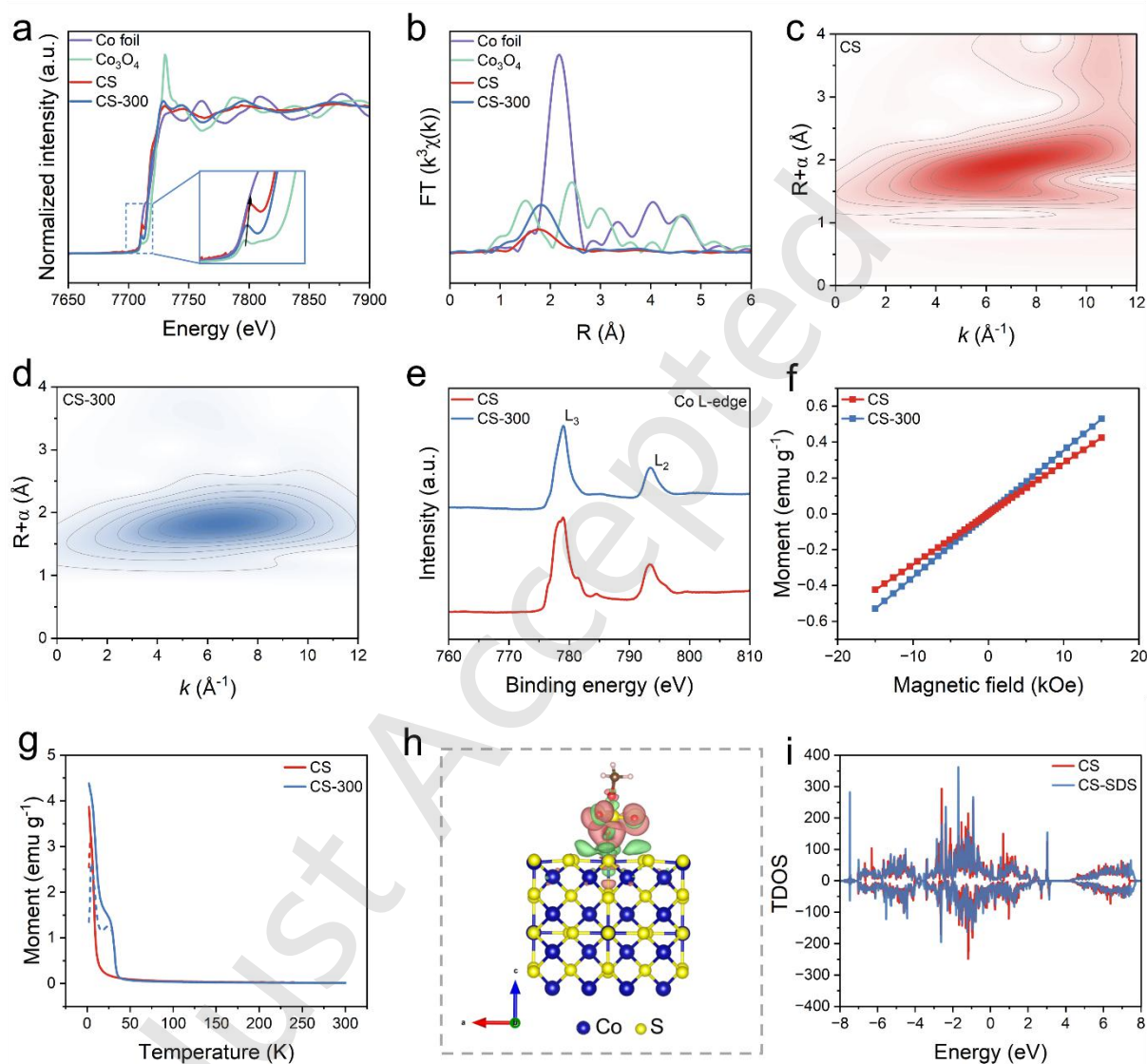


**Figure 3.** **a** Co K-edge XANES spectra and **b** FT-EXAFS spectra of CS and CS-300. WT contour plots of **c** CS and **d** CS-300. **e** Co L-edge sXAS spectra, **f** M-H curves and **g** M-T curves of CS and CS-300. **h** The differential charge density of CS-SDS. **i** The TDOS of CS and CS-SDS.

Building on the in-depth understanding of the catalyst's electronic structure and coordination environment, the OER performance was evaluated in a standard three-electrode system using 1 M KOH electrolyte. Linear sweep voltammetry (LSV) curves and the corresponding Tafel slopes (Figures 4a, 4b) reveal that all SDS-modified CS-X samples exhibit enhanced catalytic activity compared with

pristine CS, indicating that SDS-assisted ligand substitution effectively promotes catalytic performance. Among them, CS-300 demonstrates the most outstanding performance, requiring an overpotential of only 227 mV to reach a current density of  $10 \text{ mA cm}^{-2}$ , with a Tafel slope of  $53.27 \text{ mV dec}^{-1}$ , suggesting faster reaction kinetics. This performance surpasses that of many reported transition-metal-based OER

catalysts (Table S3). Notably, CS-300 shows exceptional stability, maintaining high activity after 3000 h of continuous cycling tests (Figure 4c). Post-durability failure analysis (Figures S20–S26) reveals that both CS and CS-300 undergo surface reconstruction to form amorphous CoOOH species after prolonged operation. Furthermore, the combined FT-IR and TOF-SIMS analyses of the cycled samples show that SDS remains stably present on the CS-300 surface, with its sulfate headgroup still chemically bonded to CS, indicating that SDS is not an inert spectator species but rather an anchored functional ligand that continuously exerts its role (Figure S27). Comparison of the XPS and Raman spectra of the two cycled samples (Figure S28) reveals that the presence of SDS induces a higher oxidation state of cobalt after cycling, which is beneficial for stabilizing high-valence active sites and sustaining catalytic activity. In addition, inductively coupled plasma mass spectrometry (ICP-MS) analysis of the post-cycling electrolyte (Table S4) shows that the amount of cobalt leached from CS-300 is significantly lower than that from CS, demonstrating that SDS effectively suppresses the dissolution of active metals. Collectively, SDS is chemically anchored to the catalyst surface, induces a stable high-valence cobalt state, and inhibits metal dissolution, thereby providing a fundamental guarantee for the long-term stable operation of the catalyst[40].

To probe the origin of the superior intrinsic activity of CS-300, the influence of specific surface area was first ruled out (Figures S29, Table S5). The samples exhibited similar specific surface areas, with CS-300 being slightly lower, indicating that its high activity does not stem from an increase in physical adsorption sites. We therefore turned to electrochemical kinetic methods to investigate the effect of SDS modification on interfacial charge transport and ion behavior. The Nyquist plots from electrochemical impedance spectroscopy (EIS) reveal that CS-300 possesses the smallest diameter of the impedance arc and the lowest real-axis intercept (Figure 4d, Table S6), demonstrating both the lowest intrinsic resistance and the smallest charge-transfer resistance ( $R_{ct}$ )[41, 42]. Furthermore, the imaginary impedance ( $Z''$ ) of CS-300 shows a more concentrated frequency distribution, with a significantly compressed impedance arc in the high-frequency region, reflecting faster electron-transfer kinetics. The interfacial response was analyzed via the imaginary capacitance ( $C''$ ) as a function of

frequency (Figure 4e). In the high-frequency range ( $\geq 10^4$  Hz), both CS-300 and CS exhibit low  $C''$  values, corresponding primarily to dielectric-response characteristics. However, CS-300 displays slightly higher  $C''$  and a notably lower real impedance ( $Z'$ ). In the medium-frequency range (1–100 Hz),  $C''$  increases rapidly, and CS-300 consistently shows higher  $C''$  values than CS, accompanied by a further decrease in the real part of the impedance ( $Z'$ ), indicating more efficient electron conduction and enhanced interfacial ion adsorption during reconstruction. To further probe the mass-transport process, the relationship between  $Z'$  and the reciprocal square root of angular frequency ( $\omega^{-1/2}$ , where  $\omega$  is angular frequency) was examined (Figure 4f). The slope of  $Z'$  versus  $\omega^{-1/2}$  reflects the extent of diffusion limitation within the electrode. At the same  $Z'$  value, CS-300 corresponds to a significantly smaller  $\omega^{-1/2}$ , confirming lower ion-diffusion resistance. Linear fitting yields slopes of 0.32 for CS and 0.17 for CS-300, demonstrating a substantial reduction in both ion-diffusion and electron-transport impedance for CS-300. The smaller fitting intercept for CS-300 further indicates a lower inherent interfacial resistance. These conclusions are additionally supported by in situ EIS, Bode plots, and alternating-current voltammetry (ACV) measurements (Figures S30, S31)[43]. More quantitatively, in the reconstruction region at 1.53 V, the characteristic frequency extracted from the Bode phase response increases from approximately 0.1 Hz for CS to 0.3 Hz for CS-300. According to  $\tau = 1/(2\pi f_c)$ , where  $\tau$  is the characteristic relaxation time and  $f_c$  is the characteristic frequency, the corresponding characteristic relaxation time decreases from 1.59 s to 0.53 s, equivalent to an approximately threefold acceleration of the interfacial response. The associated apparent relaxation rate,  $k_{\text{relax}} = 1/\tau$ , therefore increases from  $0.63 \text{ s}^{-1}$  for CS to  $1.88 \text{ s}^{-1}$  for CS-300. These quantitative kinetic parameters provide direct evidence that SDS substantially accelerates the reconstruction-related interfacial response rather than merely increasing the magnitude of the oxidation current. The electrochemical reconstruction process was characterized by repeated cyclic voltammetry (CV) scans. As shown in Figure S32, the first-cycle CV oxidation feature of CS-300 is substantially more pronounced than that of CS, suggesting an earlier and stronger reconstruction response. To move beyond this qualitative comparison, scan-rate-dependent kinetic analysis was further performed. According

to the power-law relation  $i = av^b$ , CS-300 exhibits a larger anodic  $b$  value ( $\sim 0.75$ ) than CS ( $\sim 0.59$ ), indicating a substantially enhanced surface-controlled response during reconstruction initiation. Further separation using  $i(V) = k_1v + k_2v^{1/2}$ , where  $i(V)$  is the current at potential  $V$ ,  $v$  is the scan rate, and  $k_1$  and  $k_2$  are the fitted capacitive and diffusion-associated coefficients, respectively, reveals that CS-300 retains a markedly larger diffusion-associated contribution over the investigated scan-rate range, demonstrating enhanced  $\text{OH}^-$  transport during the subsequent propagation of reconstruction (Figure S60). Together with the shortened Bode relaxation time, these results quantitatively establish

faster reconstruction-associated kinetics for CS-300. Consequently, CS-300 is activated more rapidly and reaches a relatively stable electrochemical state within fewer cycles. Clearly, CS-300 exhibits more pronounced dynamic electrochemical self-optimization behavior compared to CS. This trend is further corroborated by methanol probe experiments and post-cycling electrochemical surface area (ECSA) results (Figures S33–S35, Table S7), in which CS-300 demonstrates stronger ion affinity and enhanced charge-transfer capability, confirming its faster surface-reconstruction initiation kinetics.

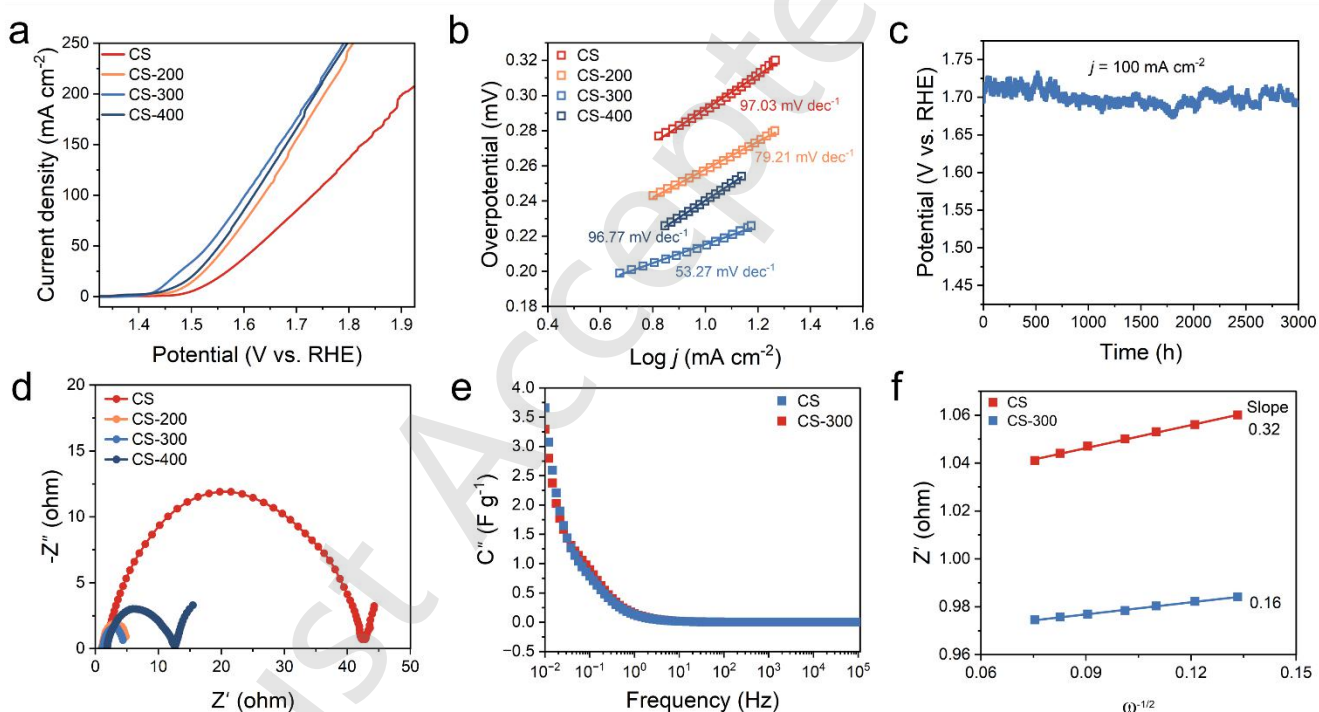


**Figure 4.** **a** LSV curves and **b** Tafel slopes of CS and CS-X (X=200, 300, 400). **c** Cycling stability of CS-300. **d** Nyquist plots, **e** Imaginary capacitance versus frequency curves, **f** Relationship between  $Z'$  and  $\omega^{-1/2}$ .

To elucidate the mechanism by which the introduction of SDS optimizes the electrochemical reconstruction process, we conducted an in-depth investigation using a series of in-situ spectroscopic techniques. First, Co-K-edge XANES was employed to dynamically monitor the local electronic structure of both catalysts under different applied potentials (Figures 5a, 5b). In the potential range of 1.1–1.9 V, the half-width energy and white-line intensity of the CS sample remained largely stable, indicating its structural robustness under reconstruction conditions and the absence of significant

changes in cobalt oxidation state. In contrast, CS-300 exhibited a distinct blue-shift of 1.8 eV at 1.5 V and 1.3 eV at 1.9 V, accompanied by enhanced white-line intensity, signifying a substantial increase in the oxidation state of cobalt centers. This trend is consistent with the Co 2p XPS results obtained at different potentials (Figure S36). Combined with in-situ Raman spectroscopy and synchronous two-dimensional correlation Raman analysis, it is evident that CS-300 significantly lowers the oxidation barrier, enabling highly synergistic kinetics between Co–S bond



breaking and Co–OH formation. EXAFS results also show a consistent trend (Figure S37, S38). Compared with CS, CS-300 exhibits distinct Fourier-transform amplitude features during reconstruction. For CS, the first-shell peak is located at about 1.75 Å, and its amplitude remains almost unchanged from 1.1 V to 1.9 V. The second-shell peak is fixed at 2.42 Å with a slight decrease in amplitude, indicating that the octahedral Co–S coordination remains stable without obvious loss of sulfur ions. In CS-300, however, when the potential increases to 1.5 V and 1.9 V, the first-shell peak shifts from 1.75 Å to 1.47 Å and 1.60 Å, respectively, accompanied by a reduction in amplitude, suggesting that long-range Co–S bonds are gradually replaced by short-range Co–O bonds. Moreover, the integrated area of the second shell in CS-300 increases notably at these potentials, indicating that after sulfur-ligand loss, adjacent Co atoms reconnect via oxygen bridges to form Co–O–Co clusters. To further elucidate the evolution of spin states during the reconstruction process, Co-L edge sXAS was employed to monitor the spin configurations of CS-300 and CS at different potentials (Figure S39). At 1.1 V, the Co  $L_3$  main peak of CS-300 appears at approximately 781.2 eV with pronounced multiplet features, and the branching ratio reaches 0.759, indicating a relatively high-spin-rich Co environment induced by SDS at the initial activation stage. This high-spin-rich state favors the initial adsorption and activation of  $\text{OH}^-$ , thereby facilitating the onset of Co–S bond substitution. Upon increasing the potential to 1.5 V, the branching ratio decreases sharply to 0.617, accompanied by a blue shift of the  $L_3$  feature. Combined with the XANES, EXAFS, and in-situ Raman results, this decrease is attributed to the progressive replacement of Co–S coordination by stronger-field Co–O(H) ligands, which enhances crystal-field splitting and transiently reduces the average spin magnitude of Co during active reconstruction. At 1.9 V, the branching ratio partially recovers to 0.685. At this stage, the catalyst has undergone deeper reconstruction toward a defect-rich and structurally heterogeneous CoOOH-like coordination environment, leading to partial recovery of the spin magnitude rather than restoration of the initial Co–S state. Therefore, the non-monotonic branching-ratio evolution reflects a stage-dependent feedback between ligand exchange and spin-state regulation during reconstruction, rather than a monotonic increase in spin state with applied potential.

According to the fundamental reaction of electrochemical reconstruction ( $M(\text{II})\text{-OH} \rightarrow M(\text{III})\text{-O} + \text{H}^+ + e^-$ , where M denotes the metal center), its kinetics are governed not only by the electron-transfer step but also closely depend on the adsorption of  $\text{OH}^-$  and the desorption/transport of protons, processes that are highly sensitive to the structure of water molecules at the electrode/electrolyte interface. Following the Grotthuss proton-hopping mechanism, doubly coordinated water (2HB) helps lower the energy barriers for hydrogen-bond breaking and reformation, thereby facilitating the proton-coupled electron transfer[44]. Guided by this understanding, we employed in-situ Raman spectroscopy to monitor in real time the dynamic evolution of the interfacial water structure during the electrochemical reconstruction of CS and CS-300 (Figures 5c, 5d, Table S8). Quantitative analysis reveals that the ordering of the interfacial hydrogen-bond (H-bond) network increases significantly for CS during reconstruction. With increasing potential, the Raman peak area corresponding to strongly H-bonded, tetra-coordinated water (4HB) gradually increases, while the 2HB/4HB peak-area ratio decreases accordingly. This indicates a transformation of the water structure at the CS surface from a loose, weakly H-bonded state to a dense cluster of strong H-bonds. In contrast, CS-300 maintains a relatively high 2HB/4HB ratio even at high potentials, demonstrating a continuous enrichment of weakly H-bonded 2HB water at its interface during reconstruction. This result confirms that the introduction of SDS effectively weakens the interfacial H-bond network, favoring proton Grotthuss hopping and thereby accelerating the kinetics of electrochemical reconstruction. To exclude the possible contribution of the bulk electrolyte to the interfacial water signal, we collected in-situ Raman spectra of both samples at open-circuit potential (OCP) (Figure S40). The results show no significant differences in the spectral features or relative intensities of interfacial water between CS and CS-300 at OCP, and the trends are distinctly different from those observed under applied potentials. This confirms that the potential-dependent evolution of the 2HB/4HB ratio originates primarily from restructuring of the water structure at the electrode/electrolyte interface rather than from the background contribution of the bulk electrolyte. Furthermore, to verify the potential influence of electrolyte concentration on our conclusions, we repeated the in-situ Raman

measurements in a low-concentration electrolyte (0.1 M KOH) (Figure S41). Although the overall signal intensity is attenuated due to the lower ionic strength, the peak-fitting results show that the potential-dependent trend of the 2HB/4HB relative intensity is fully consistent with that observed in 1 M KOH, demonstrating that changes in electrolyte concentration do not alter the qualitative conclusions regarding the evolution of the interfacial water structure. To gain deeper insight into the evolution of the interfacial water structure, we further performed dynamic analysis of the solution-side H-bond network using in situ attenuated total reflection-surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) (Figures 5e, 5f). The results show that as the potential increases, the 2HB/4HB ratio of CS exhibits a general decreasing trend: approximately 0.28 at 1.1 V, dropping rapidly to 0.17 as the potential shifts positively to 1.3 V, and rebounding only slightly to 0.26 at 1.9 V. This indicates that with increasing electric field strength, the interfacial water gradually transforms from a loose, weakly hydrogen-bonded network into a denser, strongly hydrogen-bonded cluster. In contrast, the 2HB/4HB ratio of CS-300 remains consistently and significantly higher than that of CS, and continues to increase further at high potentials. These spectroscopic data indicate that CS-300 not only exhibits stronger overall O–H stretching signals but also shows a significantly greater increase in the 2HB signal relative to 4HB upon potential elevation. This confirms that its interfacial water network possesses a more flexible and dynamic H-bond structure. Such a weakened and readily reconfigurable H-bond environment is highly conducive to rapid proton hopping conduction through the interfacial water network, thereby significantly boosting the overall kinetics of the electrochemical reconstruction process. This phenomenon can be attributed to the "head-to-head" overlap of the d-orbitals of high-spin  $\text{Co}^{3+}$  in CS-300, forming spin-polarized channels. The spin angular momentum of the unpaired electrons in these channels exhibits higher symmetry matching with the O 2p orbitals of the reactants, enabling efficient coupling between spin symmetry and electron transfer during reconstruction. Concurrently, the presence of the hydrophobic SDS tail strongly polarizes surrounding water molecules, weakening the original H-bond network and creating an expansive, transitional water layer that provides a flexible pathway for oxygen-intermediate

migration. It should be noted that all in-situ spectroscopic measurements described above were normalized to eliminate absolute intensity variations arising from differences in sample state or fluctuations in measurement conditions. To assess whether the O–H stretching signals could be significantly affected by hydroxyl vibrations from the reconstructed CoOOH surface layer, we further performed in situ ATR-SEIRAS measurements on CS-300 after prolonged electrochemical cycling, for which the surface reconstruction had reached a stable CoOOH-rich state (Figure S42). After identical baseline correction and integrated-area normalization over 2700–3800  $\text{cm}^{-1}$ , the spectra collected at 1.1, 1.5, and 1.9 V showed nearly overlapping O–H line shapes with no systematic potential-dependent redistribution. This control indicates that hydroxyl species associated with the reconstructed CoOOH layer contribute predominantly a quasi-static background in this spectral region. Therefore, the pronounced potential-dependent redistribution observed during the initial reconstruction process is primarily associated with reorganization of the interfacial hydrogen-bond network rather than with changes in CoOOH surface O–H vibrations. Accordingly, the data analysis focuses on the potential-dependent evolution of the relative intensities of characteristic peaks to reflect structural changes in the hydrogen-bonding network of interfacial water, rather than relying on absolute peak areas for quantitative comparison. To further exclude potential interference from potential-induced changes in the optical properties of the catalyst itself, we collected ultraviolet–visible (UV–Vis) spectra after potentiostatic relaxation of the samples at two test potentials (1.1 V and 1.9 V) (Figure S43). The results show no significant change in the absorbance curves between the two potentials, demonstrating that the optical properties of the catalyst remain stable within this potential window and do not affect the quantitative analysis of the in-situ spectra. Moreover, a low optical power density was maintained throughout the measurements to minimize self-absorption effects, thereby ensuring the intrinsic reliability of the spectral lineshapes and intensities. Furthermore, the relatively stable proportion of non-hydrogen-bonded (0HB) water throughout the potential window further demonstrates that SDS introduction enhances performance primarily by optimizing the ordering of the interfacial water structure, rather than merely increasing the content of free water.

Furthermore, we evaluated the OER activities of CS-SOS (236 mV), CS-PC (243 mV), and CS-SHS (225 mV). Interestingly, the activity trend was found to correlate positively with the variation in  $\zeta$  (Figure S44). The contribution of specific surface area to the enhanced activity was first ruled out through ECSA measurements. Based on the mechanistic analysis described above, the following insights can be gleaned. For CS-SOS, which possesses a shorter alkyl chain than SDS, the interfacial  $\Delta S$  is relatively low, resulting in a limited weakening effect on the hydrogen-bonding network; the medium-to-long-range hydrogen-bonding structure remains relatively rigid, leading to slightly lower activity than that of CS-300. For CS-SHS, which features a longer alkyl chain, the activity is very close to that of CS-300, implying that excessively long carbon chains, which influence the extended long-range hydrogen-bonding network, do not afford additional benefits for OER performance. Moreover, high-purity SHS is substantially more expensive than SDS, rendering it economically unfavorable. For CS-PC, despite having the same tail chain length as SDS, the strong-field induction of its headgroup reduces the spin state, thereby weakening the adsorption strength of intermediates and the electron exchange rate, ultimately resulting in diminished activity. To further elucidate the respective functional contributions of the hydrophilic headgroup and the hydrophobic tail chain of the SDS molecule, we separately synthesized a sodium sulfate-modified CS sample containing only the sulfate headgroup (CS-SO<sub>4</sub><sup>2-</sup>) and a dodecanol-modified CS sample containing only the dodecyl hydrophobic chain (CS-C12). Electrochemical measurements (Figure S45) show that the overpotential of CS-SO<sub>4</sub><sup>2-</sup> at 10 mA cm<sup>-2</sup> is 273 mV, while that of CS-C12 is as high as 345 mV, both significantly higher than that of CS-300. Although CS-SO<sub>4</sub><sup>2-</sup> induces a certain degree of spin state elevation of the cobalt centers through the coordination of the sulfate headgroup, its ability to stabilize the high-spin state is limited due to the absence of the vibrational entropy contribution from the hydrophobic tail chain. Moreover, the lack of the tail chain also prevents effective modulation of the interfacial water hydrogen-bonding network, thereby restricting the enhancement of catalytic performance. In contrast, CS-C12 contains only the hydrophobic dodecyl chain, which cannot form effective electronic interactions with the cobalt sites. Instead, the

disordered packing of the hydrophobic chains on the surface hinders the contact of the electrolyte with the active sites, severely suppressing interfacial mass transfer. To exclude potential-dependent surface-coverage variation as a major origin of the different behaviors of the headgroup- and tail-only controls, we further tracked the characteristic sulfate-derived and C12-chain-derived fragments of CS-SO<sub>4</sub><sup>2-</sup> and CS-C12, respectively, by potential-resolved TOF-SIMS (Figure S46-47). After identical normalization, the characteristic fragment signals remain nearly unchanged over the investigated reconstruction-potential range, indicating that neither control undergoes substantial potential-induced depletion or desorption. To verify the generality of this strategy, we extended SDS modification to other catalyst systems, including cobalt-based oxide (Co<sub>3</sub>O<sub>4</sub>) and nickel-based sulfide (Ni<sub>3</sub>S<sub>2</sub>). Phase characterizations confirmed that SDS was successfully grafted onto the surfaces of Co<sub>3</sub>O<sub>4</sub> and Ni<sub>3</sub>S<sub>2</sub> without altering their intrinsic crystal structures (Figures S48-S50). Combined electronic structure and magnetic analyses revealed that, after SDS modification, the spin state of cobalt in Co<sub>3</sub>O<sub>4</sub> shifted toward the high-spin direction, and the spin state of nickel in Ni<sub>3</sub>S<sub>2</sub> exhibited a similar trend. The M-H curves further demonstrated a significant increase in saturation magnetization, confirming that SDS induces an enhancement of the spin polarization degree (Figure S48g, h). Electrochemical measurements showed that the overpotentials of SDS-modified Co<sub>3</sub>O<sub>4</sub>-SDS and Ni<sub>3</sub>S<sub>2</sub>-SDS at a current density of 10 mA cm<sup>-2</sup> were significantly lower than those of the corresponding unmodified samples, indicating markedly improved OER activity (Figures S51-S52). Importantly, we further performed potential-dependent in situ Raman spectroscopy to directly probe the interfacial-water structure in these two catalyst families (Figure S53). Relative to the corresponding unmodified Co<sub>3</sub>O<sub>4</sub> and Ni<sub>3</sub>S<sub>2</sub> catalysts, both SDS-modified systems exhibit an enhanced contribution from weakly hydrogen-bonded 2HB water and maintain a higher 2HB/4HB ratio over the reconstruction-potential range. This evolution closely parallels that observed for CS-300, demonstrating that the SDS-mediated weakening and reorganization of the interfacial hydrogen-bond network is not restricted to the CS system. Together, these results establish cross-system transferability of the coupled electronic-state/interfacial-water regulation mechanism

across representative metal sulfide and oxide catalysts.

Further AIMD simulations provide critical evidence for the evolution of the interfacial water structure during reconstruction from the perspective of water geometry and dynamic behavior. As shown in Figure 5g, near the unmodified CS surface, water molecules exhibit a broad distribution of distances relative to the reference centroid (extending to about 0.94 Å), indicating the presence of long hydrogen-bonded chains within the interfacial water layer, which favors the formation of strongly hydrogen-bonded, tetra-coordinated water clusters. Upon introduction of SDS, this distance distribution shifts overall toward shorter ranges and narrows significantly, suggesting that SDS compresses the radial thickness of the interfacial water layer and suppresses the formation of long-range water chains. A comparison of the mean-square displacement (MSD) evolution over time for CS and CS-SDS reveals distinct dynamic differences (Figure 5h). Within a 2-ps simulation period, the MSD of water molecules at the CS surface reaches about 5.83 Å<sup>2</sup>, whereas that of the CS-SDS system increases only to 0.37 Å<sup>2</sup>. This result demonstrates that the introduction of SDS markedly suppresses the diffusive motion of interfacial water molecules, confining their

dynamics to a limited region closer to the electrode surface. Analysis based on the radial distribution function,  $g(r)$ , further elucidates the spatial distribution differences of the interfacial water layers between CS and CS-SDS (Figure 5i). Within the 0–0.4 Å range, the  $g(r)$  of the SDS-modified system is slightly higher than that of CS, indicating a greater accumulation of water molecules in the immediate vicinity of the reference site. In the 0.4–0.6 Å interval, the  $g(r)$  of the modified system decreases noticeably and fully decays to zero beyond 0.8 Å, while the CS system still retains a weak tail signal. This implies that the hydrophobic tail of SDS promotes a more localized distribution of water molecules, reducing the density at medium- to long-range distances and thereby restricting the extension of long-range hydrogen-bond networks. The disappearance of the tail peak in  $g(r)$  further confirms that SDS breaks the originally extended, linked hydrogen-bond structure on the CS surface. Consequently, the redistribution of  $g(r)$  induced by SDS signifies an overall weakening of the interfacial hydrogen-bond network, which not only helps lower the energy barrier for hydrogen-bond breaking but also creates more low-energy pathways for proton migration.



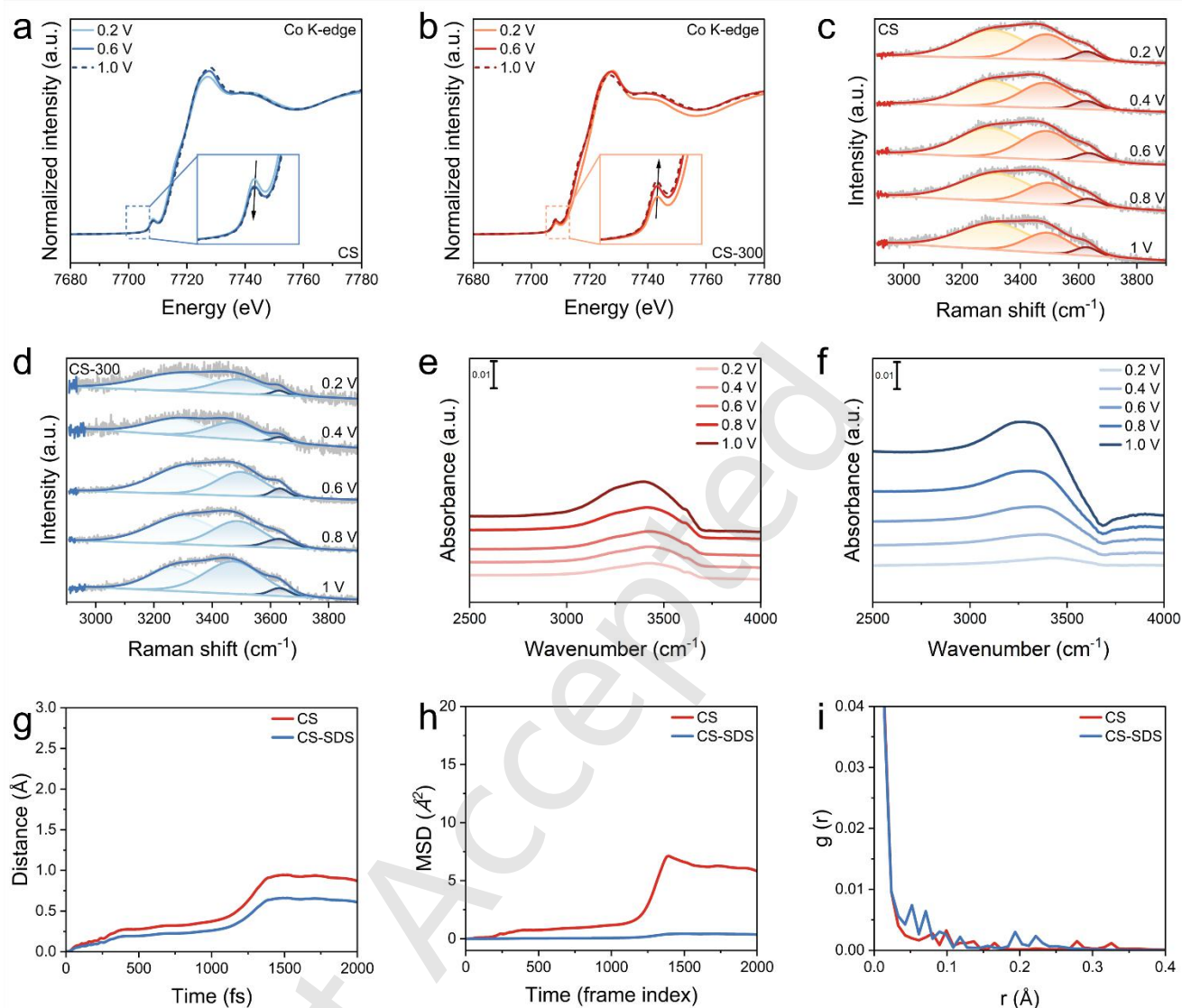


**Figure 5.** Dynamic monitoring of Co-K edge XANES for **a** CS and **b** CS-300 under different potentials. In-situ Raman spectra of interfacial water structure for **c** CS and **d** CS-300. In-situ ATR-SEIRAS spectra of interfacial water structure for **e** CS and **f** CS-300. **g** Variation of the distance between Co centers and OH<sup>-</sup> particles, **h** Mean square displacement of OH<sup>-</sup> as a function of time, **i** Radial distribution function during the reconstruction process from AIMD simulations.

To elucidate the regulatory mechanism of SDS on the interfacial water structure during electrochemical reconstruction, understanding its dynamic behavior is essential. Based on AIMD simulations under a positive bias potential, the real-time evolution of the SDS molecule was tracked, and its surface dynamics were categorized into four consecutive stages (Figures 6a, 6b, S54). In the initial stage (0–200 fs), the root-mean-square displacement (RMSD) of SDS increases slowly, reaching a maximum below 0.1 Å<sup>2</sup>, while its velocity autocorrelation function (VACF) exhibits pronounced oscillations. This indicates that the molecule is

strongly confined within a surface adsorption well, undergoing primarily localized vibrations, with electrostatic attraction between the anionic headgroup of SDS and the CS surface being the dominant interaction. As the applied positive potential persists, the system enters a slow-diffusion stage (200–600 fs). The RMSD gradually rises to about 0.3 Å<sup>2</sup>, though the increase rate slows and fluctuates, while the VACF amplitude begins to decay. This reflects an enhancement in translational freedom and a weakening of velocity memory, stemming from the positive potential-induced reduction in electron density at Co centers,

which partially neutralizes the negative charge of the SDS headgroup. Concurrently,  $\text{OH}^-$  from the electrolyte begins to attack the Co–S bonds, initiating initial surface reconstruction and collectively weakening the SDS–surface binding. Between 600 fs and 700 fs, the RMSD curve enters a plateau, and the VACF amplitude decays to nearly zero, indicating that the SDS molecule resides in a nearly balanced metastable state. During this period, the disruption of Co–S bonds by  $\text{OH}^-$  continues, and charge neutralization of the headgroup by the positive potential becomes more pronounced, leading to a near cancellation of surface repulsion and residual attraction on the molecule. In the final stage, the RMSD exhibits exponential growth, surging from  $0.3 \text{ \AA}^2$  to over  $1.0 \text{ \AA}^2$  within 1 ps, while the VACF decays to zero. This marks the rapid displacement of the SDS center-of-mass away from the electrode surface, with its kinetic behavior following an Arrhenius-type pattern. To further visualize the evolution of SDS, COMSOL multiphysics simulations were performed (Figure 6c). Initially, SDS lies flat on the surface, with its headgroup embedded in a low-potential region. As the voltage increases, the electric field weakens the electrostatic attraction between the headgroup and the surface, causing some headgroups to lift and migrate toward higher-potential regions while the hydrophobic tail remains anchored. This results in a bent, “hinge-like” configuration that undergoes slow diffusion, consistent with the stage of gradual RMSD increase and VACF decay observed earlier. With further voltage increase, more headgroups lift, and the tail gradually detaches in a segment-by-segment dynamic process, transitioning the molecule to a semi-upright posture. Subsequently, oxygen intermediates generated on the surface occupy the original adsorption sites, further weakening tail-surface interactions. Finally, under the combined effects of fluid shear and solvation, the hydrophobic tail of SDS becomes fully upright, creating a localized low-polarity microenvironment at the interface. This induces rearrangement of interfacial water molecules and disrupts the original long-range, strongly hydrogen-bonded network on the CS surface (Figure S55). The conformational evolution of SDS molecules induced by potential polarization was further tracked in real time at the atomic scale using in-situ ATR-SEIRAS (Figure 6d). In the low-potential region from the open-circuit potential (OCP) to 1.2 V, only minor changes were observed in the symmetric ( $\nu_s \approx 1084 \text{ cm}^{-1}$ ) and

asymmetric ( $\nu_{as} \approx 1219/1248 \text{ cm}^{-1}$ ) stretching vibrations of the  $\text{SO}_4^{2-}$  headgroup, while the  $\text{CH}_2$  scissoring vibration ( $\approx 1468 \text{ cm}^{-1}$ ) remained nearly unchanged. This indicates that the headgroup remains firmly attached to the catalyst surface, with the hydrophobic tail chains adopting a flat, well-ordered arrangement. Under these conditions, the direction of the vibrational dipole moment is nearly parallel to the electrode surface, resulting in a negligible normal component of the surface-enhanced field. As the potential increased to 1.3–1.5 V, the integrated area of the  $\text{SO}_4^{2-}$  region ( $1000\text{--}1150 \text{ cm}^{-1}$ ) sharply rose from 0.054 at OCP to 0.88 at 1.4 V, attributed to the headgroup lifting off from the surface potential well and tilting outward, thereby increasing the perpendicular component of the vibrational dipole moment. Concurrently, the  $\text{CH}_2$  scissoring peak exhibited significant broadening, reflecting enhanced van der Waals interactions arising from the increased density of tail chains within the confined interfacial space. Upon further increasing the potential to 1.6–1.8 V, the system entered a metastable state; the integrated intensity of the  $\text{SO}_4^{2-}$  stretching vibrations plateaued ( $\approx 1.46$ ), and the growth of the  $\text{CH}_2$  scissoring peak slowed, suggesting that the headgroup had partially lifted while the tail chains had not yet fully detached. At higher potentials, the symmetric  $\text{SO}_4^{2-}$  peak continued to intensify with little further change in the  $\text{CH}_2$  scissoring peak, indicating partial disordering of the headgroup orientation and stepwise detachment of the hydrophobic tails. To directly verify the potential-dependent coverage changes of SDS, TOF-SIMS depth profiling was performed on the CS-300 electrode surface after relaxation at each potential (Figure S56). At low potentials, strong interfacial coordination results in a flat-lying adsorption configuration of SDS, with the hydrophobic tail chains tightly confined to the electrode, leading to suppressed secondary ion yields due to spatial shielding effects. As the potential increased to 1.3–1.5 V, the electric-field-induced molecular reconstruction caused the headgroup to lift, and the tail chains became progressively exposed as the tilt angle increased. At 1.5 V, the secondary ion intensity of the tail-chain fragments reached a maximum, and the corresponding mapping images revealed extensive homogeneous yellow regions, indicating that most SDS molecules were in a semi-upright configuration with fully exposed tail chains and maximum coverage. Upon further increasing the potential to 1.7 V, localized spots appeared on

the surface, bright features and voids were evident in the total ion images, and the tail-chain fragment signals decreased, suggesting that the molecules became more upright, resulting in a slight reduction in the surface exposure of the tail chains.

Based on AIMD simulations, we compared the total density of states (TDOS) of the initial (0 fs) and final (1000 fs) structures (Figure 6e). The results show a high degree of overlap in the TDOS across major energy ranges between the two states, with negligible differences in spin-polarized integration. This indicates that the evolution of the SDS chain structure does not significantly alter the electronic structure or magnetic moment of the cobalt sites, confirming that their electronic characteristics are preserved over the reconstruction time scale. Furthermore, calculations of the adsorption energies of  $\text{Co}^{3+}$  for OH and O in the two structures (Figure 6f) reveal differences in the proton-desorption capability of the system. The results show that the high-spin  $\text{Co}^{3+}$  induced and maintained by CS-SDS exhibits stronger adsorption for  $\text{OH}^-$ , creating a thermodynamically favorable condition for the subsequent nucleophilic attack step in reconstruction. In addition, compared with CS, CS-SDS shows stronger adsorption for the O intermediate formed after deprotonation, indicating that the deprotonation process is more energetically spontaneous, thereby accelerating proton dissociation during reconstruction. This originates from the  $e_g$  orbitals of high-spin  $\text{Co}^{3+}$ , which point directly toward the ligands and possess strong  $\sigma$ -bonding capability. The deprotonation of OH can be viewed as a synchronous process of O–H bond cleavage and Co–O bond strengthening: the  $d_{z^2}$  component of the  $e_g$  orbitals enhances overlap with the  $p_z$  orbital of O, forming a strong  $\sigma$  bond that stabilizes the deprotonated product. To bridge the dynamic AIMD trajectory with the static electronic-structure calculations, representative CS-SDS configurations were extracted from different stages of the AIMD trajectory and independently subjected to electronic-structure and adsorption-energy calculations (Figure S57, Table S9). Rather than treating CS-SDS as a single static adsorption configuration, these snapshots capture the progressive conformational evolution of SDS from the initially surface-confined state toward increasingly tilted/displaced configurations. The corresponding TDOS reveals a progressive enrichment of electronic states near the  $E_F$  as the SDS configuration evolves, while the overall spin-

polarized character of the Co centers remains preserved. This indicates that SDS conformational adaptation does not simply switch off its electronic regulation; instead, it continuously modulates the accessibility and electronic response of the interfacial Co sites. Consistently, the calculated  $\text{OH}^-$  adsorption energy becomes progressively more favorable along the same conformational trajectory, demonstrating that the dynamic reorientation of SDS enhances the affinity of the interfacial Co sites toward  $\text{OH}^-$  rather than merely representing a passive desorption event. To directly track the spatial distribution and content evolution of reaction intermediates, depth-profiling imaging of  $\text{OH}^-$  and  $\text{O}^-$  distributions in the two samples at different potentials was performed using TOF-SIMS (Figures 6g, 6h, S58). As the potential increased from 1.1 V to 1.9 V, the  $\text{OH}^-$  signal in both samples increased significantly, with CS-300 showing a much greater enhancement than CS. At 1.5 V and 1.9 V, CS-300 maintained higher  $\text{OH}^-$  intensity throughout the entire sputtering depth range, with an integrated intensity approximately twice that of CS, and the sputtering time corresponding to the signal full-width at half-maximum extended from 64.7 s for CS to 82.7 s. These results demonstrate that SDS-mediated regulation of the interfacial water network effectively reduces the barrier for  $\text{OH}^-$  transport toward the metal center imposed by the hydration shell, not only promoting rapid enrichment of  $\text{OH}^-$  on the catalyst surface but also driving its deeper penetration into the bulk phase. This was further validated by temperature-programmed desorption tests (Figures S59–S60). Additionally, comparison of the  $\text{O}^-$  signal intensity further reveals that CS-300 exhibits a stronger  $\text{O}^-$  signal, indicating that this system is more conducive to stabilizing oxygen species generated after reconstruction, thereby enhancing the structural stability and reaction sustainability of the electrochemical reconstruction process.

Based on the results above, we combine the reconstruction curves obtained from galvanostatic tests to discuss the mechanism by which SDS accelerates reconstruction kinetics in stages (Figure S60). Both samples exhibit three typical stages: initial activation, accelerated reconstruction, and stabilization. During the initial activation stage, the potential rises gradually as reconstruction proceeds, reflecting that the pre-activation process relies on the initial adsorption and activation of  $\text{OH}^-$ . Because the SDS

headgroup induces cobalt centers into a high-spin state, enhancing their adsorption affinity for relevant intermediates,  $\text{OH}^-$  can more efficiently displace Co–S bonds under positive bias, thereby significantly lowering the energy barrier for initiating reconstruction. This kinetic advantage is directly reflected in the potential-time curve, where CS-300 shows a steep potential rise at around 50 s, notably earlier than CS (~90 s), indicating an earlier entry into the accelerated reconstruction stage. The subsequent accelerated reconstruction stage involves lattice-oxygen insertion and  $\text{S}^{2-}$  leaching, accompanied by continuous increases in metal-ion valence and migration, a rapid kinetic process governed by proton–electron cooperative transfer. This view is supported by the kinetic b- and k- values obtained during reconstruction, ICP measurements after reconstruction, and variable-potential XPS results (Figures S61–S63). In this stage, continuous and rapid deprotonation and structural rearrangement occur, where the deprotonation process is regulated by both Co–O covalency and the interfacial water structure. Notably, the unique amphiphilic structure of SDS endows it with excellent surface/interface-modulation capability. Its headgroup-induced high-spin  $\text{Co}^{3+}$  strengthens Co–O covalency, reducing the proton-transfer barrier. Simultaneously, the potential-driven upright orientation of the hydrophobic tail induces water-molecule rearrangement at the interface, disrupting the long-range strong hydrogen-bond network and thereby promoting proton-hopping desorption. In the final stabilization stage, the surface has transformed into thermodynamically more stable  $\text{CoOOH}$ , and further bulk reconstruction is limited by

slow ion diffusion in the bulk phase, with deprotonation mainly occurring at surface active sites. However, CS-300 undergoes deeper reconstruction, generating more  $\text{CoOOH}$  and coordination defects, and exhibits a slightly lower steady-state potential, demonstrating superior electrocatalytic performance. This further confirms SDS acts as a potential-responsive molecular switch that pre-stabilizes a high-spin-rich Co state for reconstruction initiation and subsequently enables dynamic spin-state adaptation as the local coordination environment evolves, while optimizing the interfacial water structure via potential-responsive conformational changes of its hydrophobic tail, thereby steering the reconstruction reaction toward a more thorough and efficient pathway.

To elucidate the mechanism underlying the enhanced OER performance of the post-reconstruction materials, DFT calculations were performed to simulate the TDOS of the heterostructures formed after reconstruction in both systems. The results show that both structures exhibit a small band gap near the Fermi level, indicating a quasi-metallic character after reconstruction. However, the TDOS of CS-SDS@ $\text{CoOOH}$  is significantly higher, suggesting easier electron transitions from the valence to the conduction band and thus improved conductivity. Gibbs free-energy calculations based on this model (Figure S64) reveal that the rate-determining step (RDS) for CS@ $\text{CoOOH}$  is the conversion of  $^*\text{O}$  to  $^*\text{OOH}$ , with an energy barrier of 2.05 eV. For CS-SDS@ $\text{CoOOH}$ , although the RDS remains the same, the barrier is reduced to 1.55 eV, indicating markedly improved reaction kinetics (Figure 6i).



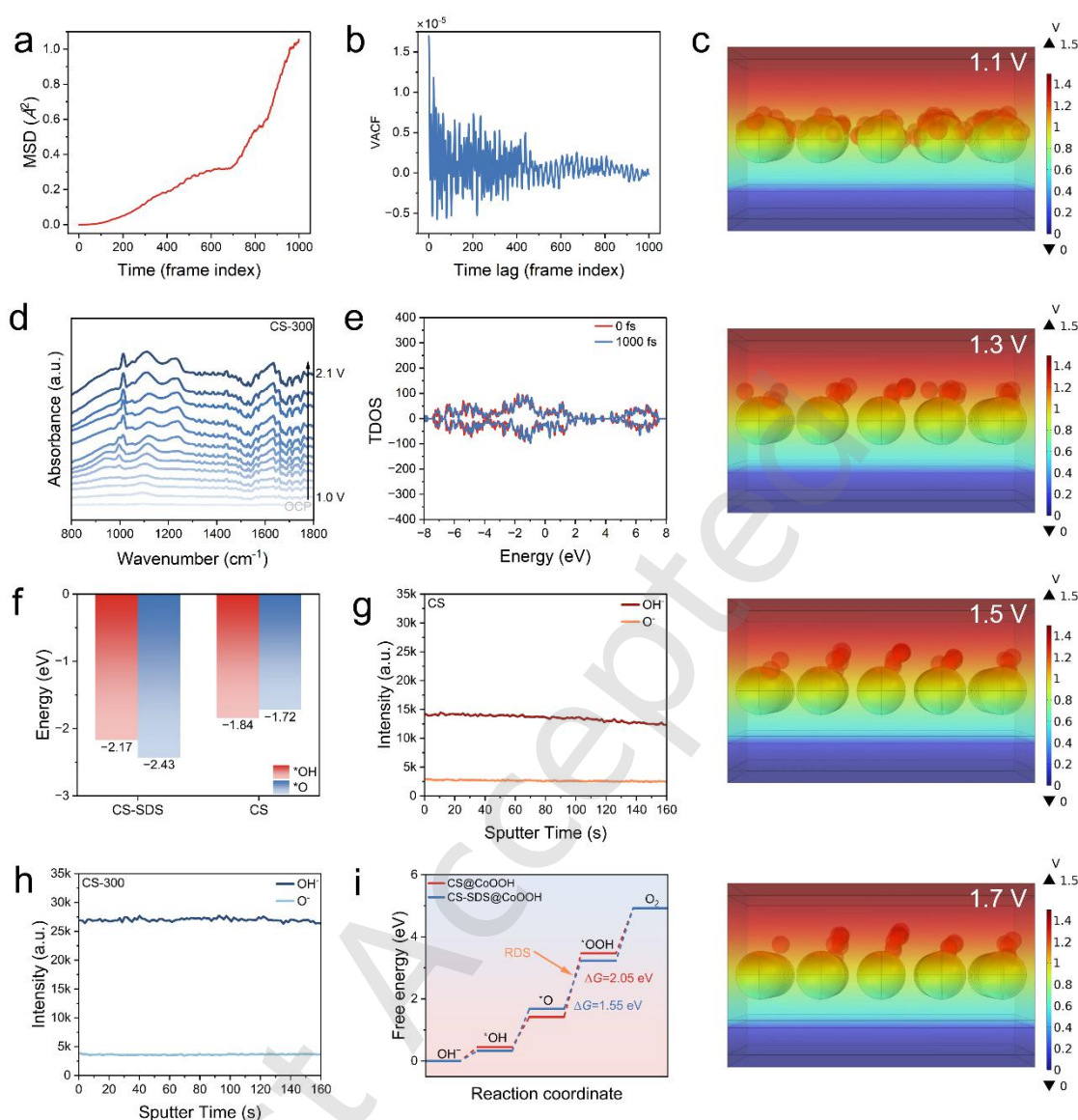


**Figure 6.** **a** Time-dependent root MSD curve of SDS desorption, and **b** VACF of SDS in AIMD simulations. **c** COMSOL visualization simulation of the microscopic physical process of SDS desorption under forward voltage. **d** In-Situ ATR-SEIRAS dynamic monitoring of the conformational evolution process of SDS during reconstruction. **e** Comparison of the total density of states (TDOS) and **f** \*OH and \*O adsorption energies before and after SDS conformational changes. Longitudinal concentration depth profile for OH<sup>-</sup> and O<sup>-</sup> of **g** CS and **h** CS-300. **i** Gibbs free energy diagrams for CS@CoOOH and CS-SDS@CoOOH of OER.

## Conclusions

In summary, we establish an entropy–energy competition ratio ( $\xi = T\Delta S/\Delta E$ ) as a quantitative descriptor for predicting amphiphile-mediated spin-state regulation and use it to guide adaptive molecular regulation of electrochemical reconstruction. Validation across amphiphiles with varied headgroups and tail lengths, together with its correlation with OER activity, supports  $\xi$  as a rational

molecular design descriptor. Guided by this descriptor, SDS acts as a potential-responsive molecular switch that couples headgroup-mediated spin-state regulation with tail-mediated reorganization of interfacial water, thereby coordinating electronic and mass-transport processes to accelerate catalyst reconstruction. This coordinated regulation enables the optimized CS-300 catalyst to achieve an overpotential of 227 mV at 10 mA cm<sup>-2</sup> together with stable operation for over



3000 h. Its extension to different metal centers and material systems further suggests that adaptive amphiphilic regulation can serve as a broadly applicable strategy for reconstruction-driven electrocatalysis. More broadly, this work advances molecular modifiers from empirical additives toward predictable and adaptive interfacial regulators, providing a descriptor-guided framework for coupling electronic-state and microenvironment engineering in reconstruction-driven electrocatalysis.

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## Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

## Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

**Electronic Supplementary Material:** Supplementary material (further details of the in-situ Raman spectroscopy measurements, TEM images, SEM images, XRD, XPS spectra, XAS spectra, etc.) is available in the online version of this article at <https://doi.org/10.26599/NRE.2026.9120285>.

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# Adaptive Amphiphilic Molecular Switch for Coordinated Spin-State and Interfacial Water Regulation Enables Fast Reconstruction for Efficient Oxygen Evolution

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## 1. Experimental

### 1.1 Materials

Cobalt sulfate heptahydrate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ), thiourea ( $\text{CH}_4\text{N}_2\text{S}$ ), sodium dodecyl sulfate (SDS), ethylene glycol (EG), N,N-dimethylformamide (DMF), and potassium hydroxide (KOH) were all purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd. All chemicals used were of analytical grade and were used without further purification.

### 1.2 Synthesis of $\text{Co}_9\text{S}_8$ (CS)

The process began by dissolving cobalt sulfate heptahydrate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ) in a mixture of N,N-dimethylformamide (DMF) and ethylene glycol (EG). After sonication for several minutes, thiourea was added, followed by another 15 minutes of sonication and then magnetic stirring for 5 minutes. The resulting mixture was transferred to a Teflon-lined stainless steel autoclave, sealed, and heated to 190 °C for 12 hours. Finally, the autoclave was allowed to cool naturally to room temperature. The obtained precipitate (CS) was washed three times sequentially with deionized water and ethanol, and then dried overnight in a vacuum oven at 60 °C to yield the CS product.

### 1.3 Synthesis of CS-X (X = 200, 300, and 400)

The synthesis of CS-X (X = 200, 300, and 400, where X denotes the initial SDS feeding mass

in mg) was carried out using a method essentially the same as that for CS, with the only difference being the addition of a certain amount of SDS during the dissolution process for co-mixing.

#### **1.4 Verification of the Synthetic Method for Universal Small- Molecule Functionalization**

The synthesis followed the same procedure as described above, except that the small molecules were replaced, respectively, by sodium n-octyl sulfate (CS- SOS), dodecyl phosphate (CS- PC), sodium hexadecyl sulfate (CS- SHS), sodium sulfate (CS-SO<sub>4</sub><sup>2-</sup>) and lauryl alcohol (CS-C12).

#### **1.5 Synthesis methods for Co<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>-SDS, Ni<sub>3</sub>S<sub>2</sub>, and Ni<sub>3</sub>S<sub>2</sub>-SDS**

For the synthesis of Co<sub>3</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub>-SDS, 0.5 g of cobalt(II) acetate tetrahydrate was first dissolved in an appropriate amount of ammonia solution and stirred in air for 10 min to ensure thorough dispersion. The resulting suspension was then transferred into a reaction vessel and reacted at 150 °C for 3 h. After the reaction, the vessel was cooled to room temperature, and the products were washed three times by alternating centrifugation with deionized water and ethanol, followed by vacuum drying at 60 °C to obtain Co<sub>3</sub>O<sub>4</sub> powder. The preparation of Co<sub>3</sub>O<sub>4</sub>-SDS was carried out in the same way, except that an appropriate amount of SDS was added to the above solution.

For the synthesis of Ni<sub>3</sub>S<sub>2</sub> and Ni<sub>3</sub>S<sub>2</sub>- SDS, the procedure is similar to that described for Co<sub>3</sub>O<sub>4</sub>, except that nickel nitrate is used as the precursor, a piece of nickel foam is placed in the reaction system, and the reaction temperature is increased to 190 °C. The remaining steps are the same: after the reaction, cool to room temperature, wash by centrifugation, and vacuum dry. For Ni<sub>3</sub>S<sub>2</sub>- SDS, follow the same procedure but add an appropriate amount of SDS to the solution.

#### **1.6 Characterization**

XRD pattern was recorded on a Bruker AXS D8 Advance X-ray diffractometer with a Cu K $\alpha$  radiation target (40 V, 40 A). TEM characterization was performed using an FEI Tecnai G2F20 microscope. Atomic-level HAADF-STEM images and the corresponding STEM-EDS elemental maps were measured on an FEI Titan Themis Z 3.1 equipped with a SCOR spherical aberration corrector and a monochromator. The probe convergence angle was 80 mrad, and camera length was 115 mm in the STEM mode. The morphologies were observed by scanning electron microscopy (SEM, Hitachi model (SU8010). The surface charges were determined by Zeta potential measurements using a Mastersizer 2000 potential analyzer. The absorption properties



were studied by UV-vis diffuse reflectance spectrometry (UV-vis-DRS, Shimadzu UV-3600) spectrometer. The Brunauer–Emmett–Teller (BET) specific surface areas were measured by an ASAP 2020 micropolitics surface instrument equipped with a porosity analyzer. Thermogravimetry analysis ( $T_g$ ) was tested using a NETZSCH STA449F3 QMS403D\Bruker V70. The surface elements were identified by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB-250Xi) with monochromatic Al  $K\alpha$  radiation. The temperature programmed reduction ( $H_2$ -TPR) was used to measure the reduction properties of the samples by utilizing an AutoChem II 2920 V3.05 under the condition of 10 vol%  $H_2$  balanced with Ar. And the temperature was ramped from ambient temperature to 850 °C at 10 °C min<sup>-1</sup>. For characterization of the acid sites on surfaces, ammonia-temperature-programmed desorption ( $NH_3$ -TPD) were carried out on an AutoChem II 2920 V3.05 analyzer. And the temperature was ramped from ambient temperature to 500 °C at 10 °C min<sup>-1</sup> under an equilibrium atmosphere of 5%  $NH_3$  and He. The magnetic properties of the synthesized samples were investigated using the SQUID-VSM system. The magnetic hysteresis loops from -1.5 to 1.5 T were measured at room temperature and the ZFC and FC were measured at a magnetic field of 500 Oe in the temperature range from 2 to 300 K. The chemical bonds were investigated by Raman spectroscopy (Renishaw) equipped with an excitation light source of 532 nm. Further details about bonding were collected by Fourier transforms infrared (FT-IR, Nexus670) spectrometry. The electronic states and transitions were studied by electron paramagnetic resonance (EPR, EMPplus-10/12). TOF-SIMS measurement was performed on a TOF-SIMS 5-100 instrument (ION-TOF GmbH) using a 30-keV  $Bi^{3+}$  as analysis beam for negative and positive polarity measurements. Co L-edge NEXAFS spectra was performed at the Catalysis and Surface Science End-station at the BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. Co K-edge X-ray absorption spectra including XANES and EXAFS profiles were collected at BL11B station at the Shanghai Synchrotron Radiation Facility (SSRF).

For in-situ testing measurements, In-situ Raman spectra were obtained using a Renishaw Raman spectrometer. In-situ attenuated total reflectance infrared (ATR-IR) measurements of the catalyst were conducted using a Nicolet iS50 spectrometer coupled with an electrochemical workstation. For quantitative analysis of the interfacial-water spectra, all spectra within a given dataset were processed using an identical procedure. For the in-situ Raman spectra, the

background in the O-H stretching region (2700—3800  $\text{cm}^{-1}$ ) was first removed using the same baseline-correction procedure, after which the total integrated area of the O-H envelope was normalized to unity. The relative populations of different hydrogen-bonding configurations were then obtained by fitting the normalized O-H envelope using identical peak-position and linewidth constraints for all potentials. The 2HB/4HB value was calculated from the integrated areas of the corresponding fitted components,  $A_{2\text{HB}}/A_{4\text{HB}}$ , rather than from peak heights. No external Raman reference peak was used for this analysis. For ATR-SEIRAS, the spectrum collected at open-circuit potential (OCP) was used as the reference spectrum for each electrode. Potential-dependent difference spectra were obtained as  $\Delta A = -\log(S_E/S_{\text{OCP}})$ , where  $S_E$  and  $S_{\text{OCP}}$  denote the single-beam signals at the applied potential and OCP, respectively. For analysis of the interfacial-water region, the 2700—3800  $\text{cm}^{-1}$  envelope was baseline corrected and normalized by its total integrated area before peak deconvolution. The same fitting model and constraints were applied to all potentials, and only fitted integrated-area ratios were used for quantitative comparison.

For quasi-in-situ XPS measurements, The quasi-in-situ OER mechanism was studied in a glove box connected to the XPS instrument through a vacuum channel. CS soaked in 1 M KOH electrolyte was used as a blank sample, while the samples treated at different overpotentials were transferred to the analysis chamber for XPS measurements.

### 1.7 Electrochemical measurements

The electrochemical measurements were performed in a standard three-electrode cell containing 1 M KOH (purified) electrolyte connected to a CHI-760E electrochemical workstation (CHI Instruments, Inc., Shanghai) at 25 °C. A Hg/HgO was used as the reference electrode, a Pt plate was employed as the counter electrode, and a catalyst loaded on nickel felt served as the working electrode. The working electrodes were prepared by mixing 8 mg of the catalyst, 470  $\mu\text{L}$  of DI water, 480  $\mu\text{L}$  of ethanol, and 50  $\mu\text{L}$  of a 5-wt.% Nafion solution under sonication for 1 h to obtain a uniform ink suspension. After sonication and magnetic stirring, ink was loaded onto the nickel felt ( $1 \times 1.5 \text{ cm}^2$ ) followed by drying at room temperature to yield electrodes. All potentials were recorded against a reversible hydrogen electrode (RHE), which can be calculated by the Nernst equation ( $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \times \text{pH} + 0.098$ ). The linear sweep voltammetry (LSV) polarization curves were recorded after activating the catalysts by chronoamperometry (CA)

measurements (1.53 V vs. RHE, 30 min). All LSV ( $5 \text{ mV s}^{-1}$ ) and CV ( $100 \text{ mV s}^{-1}$ ) measurements were carried out without iR correction.

The Tafel slopes ( $b$ ) were calculated as  $\eta = a + b \times \log j$ , where  $\eta$  represents the overpotential, and  $j$  denotes the current density.

The electrochemical impedance spectroscopy (EIS) measurements were performed at frequencies ranging from 0.01 Hz to 100 kHz at an overpotential of 300 mV and a voltage amplitude of 5 mV.

The electrochemical active surface area (ECSA) of each catalyst was measured through the double-layer capacitance ( $C_{dl}$ ) obtained from the CV profiles at various scan rates of 20, 40, 60, 80, and  $100 \text{ mV s}^{-1}$  in a non-Faradic window of 0.975 to 1.075 V vs. RHE.

The ECSA of each catalyst was calculated according to the following equation:

$$\text{ECSA} = C_{dl}/C_s$$

where  $C_s$  represents the specific capacitance ( $0.04 \text{ mF cm}^{-2}$ ).

The mass activity ( $MA$ ) was calculated according to the following equation:

$$MA = j/m$$

where  $m$  and  $j$  are the catalyst loading and current density, respectively.

The specific activity ( $SA$ ) was calculated according to the following equation:

$$SA = MA/A_{\text{BET}}$$

where  $A_{\text{BET}}$  stands for the BET specific surface area.

## 1.8 DFT calculations

The density functional theory (DFT) calculations were all conducted using the Vienna ab initio software package (VASP). The core–valence interaction and exchange–correlation energy were described by the projector augmented wave (PAW) method and the Perdew–Burke–Ernzerhof (PBE) functional, respectively. To ensure accuracy, the energy cutoff and energy convergence criterion were set to 500 eV and  $10^{-5}$  eV, respectively. Also, the residual forces were converged to values less than  $0.02 \text{ eV \AA}^{-1}$ . The Brillouin zone was sampled using a Monkhorst–Pack  $k$ -point mesh, with actual spacings set to be less than  $0.015 \text{ \AA}^{-1}$ .

## 1.9 AIMD simulation

The Ab initio molecular dynamics simulation (AIMD) simulations were carried out with NVT ensemble using Cambridge Sequential Total Energy Package (CASTEP) at an energy cutoff

of 400 eV and convergence of  $1.0 \times 10^{-4}$  eV atom<sup>-1</sup>. A Nose-Hoover thermostat was used to maintain the temperature at about 300 K. The generalized-gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) was used for exchange-correlation interactions, and an explicit water model was applied during AIMD simulations. The explicit water model was composed of 5 H<sub>2</sub>O molecules simulating the aqueous solution, and a time step of 1 femtosecond (fs) was used as the simulation step size. A 2 picoseconds (ps) trajectory was then generated and used for analysis. The center of mass vector ( $r_\sigma$ ) was employed as the average position of the mass point system mass distribution according to the formula:

$$r_\sigma = \frac{\sum_i m_i r_i}{M}$$

where  $m_i$  refers to the mass of each component, and  $r_i$  represent the vector diameter of each position relative to a fixed point in a system.  $M = \sum_{i=1}^n m_i$  means the total mass of the system.

In addition, the AIMD simulations was employed to simulate the evolution of the electronic structure of the material under high-temperature synthesis. By combining quantum mechanics and classical mechanics calculations, the evolution of the system was described through the simultaneous solution of the atomic and electronic equations of motion.

**Note S1.** Derivation of a Physical Descriptor for SDS-Induced Relaxation of Co High-Spin States.

Under an octahedral field coordination environment, cobalt ions exhibit an equilibrium between low-spin (LS) and high-spin (HS) states. The low-spin state features a larger crystal field splitting, with electrons paired in lower-energy orbitals, resulting in lower energy and greater stability. However, the limited number of spin-polarized channels in this state restricts electron transfer; additionally, due to lower degeneracy, the associated spin entropy is also reduced. In contrast, the high-spin state has electrons partially occupying higher-energy antibonding orbitals, leading to higher energy and lower stability, but it provides more spin-polarized channels, thereby accelerating reaction rates. At the same time, the higher degeneracy of the high-spin state increases its contribution to spin entropy.

Therefore, we understand that the spin state equilibrium is determined by the competition between the energy barrier and the entropy change. The energy barrier  $\delta E$ , defined as the energy difference for the transition from low-spin to high-spin state, primarily tends to suppress the formation of the high-spin state. The entropy change  $\delta S$  reflects the increase in entropy due to the

higher degeneracy during the transition from LS to HS and can be expressed by the formula  $\delta S = k_B \ln(g_{HS}/g_{LS})$ , where  $g_{HS}$  and  $g_{LS}$  are the degeneracies of the high-spin and low-spin states, respectively. The total entropy change consists of contributions from the following three parts:

1. Spin degeneracy entropy ( $S_{\text{spin}}$ ): arising from the difference in spin degeneracy.
2. Coordination configuration entropy ( $S_{\text{vib}}$ ): originates from changes in the vibrational modes of coordination bonds.
3. Solvent reorganization entropy ( $S_{\text{solv}}$ ): caused by changes in the degrees of freedom of the surrounding solvent molecule rearrangement.

That is,  $\Delta S = \Delta S_{\text{spin}} + \Delta S_{\text{vib}} + \Delta S_{\text{solv}}$

Based on the aforementioned analysis, we further derive the thermodynamic relationship of the spin equilibrium equation. The interconversion between spin states can be analogized to a chemical reaction, specifically the reversible transition between the low-spin (LS) and high-spin (HS) states:



Therefore, the equilibrium constant of this reaction can be expressed as:

$$K = e^{\frac{-\Delta G}{k_B T}} = e^{\left(\frac{\Delta E - T\Delta S}{k_B T}\right)}$$

Herein,  $\Delta E$  is defined as the effective energy barrier. After analyzing the equilibrium constant, the expression for the Gibbs free energy change can be derived as:  $\Delta G = \Delta E - T\Delta S$ ,  $T$  is the temperature, and  $\Delta S$  is the entropy difference.

It can be seen that the spin equilibrium is simultaneously influenced by the synergistic effects of the energy barrier and the entropy change. To quantitatively characterize the competitive relationship between the two in spin crossover, we propose the descriptor "Entropy–Energy Competition Ratio" which measures the relative contributions of entropy change and energy barrier:

$$\zeta = \frac{T\Delta S}{\Delta E} = \frac{T(\Delta S_{\text{spin}} + \Delta S_{\text{vib}} + \Delta S_{\text{solv}})}{(P_0 - \Delta_0) - (P_s - \Delta_s)}$$

Where  $P_0$  and  $\Delta_0$  are the electron pairing energy and splitting energy of unmodified SDS, respectively.  $P_s$  and  $\Delta_s$  are the electron pairing energy and splitting energy of SDS after modification, respectively.

An analysis of the physical meaning of this descriptor reveals that  $\zeta$  reflects the relative



contributions of entropy change and the energy barrier. When  $\xi > 1$ , the entropy change dominates, and the spin transition equilibrium favors the stability of the HS state. When  $\xi < 1$ , the energy barrier effect dominates, and the system tends to maintain the stability of the LS state. Based on  $\Delta G = \Delta E - T\Delta S$  and  $\xi = T\Delta S / \Delta E$ , we obtain  $\Delta G = \Delta E(1 - \xi)$ . Therefore,  $\xi = 1$  corresponds to  $\Delta G = 0$ , representing the critical condition at which the entropy contribution and energy penalty are exactly balanced. When  $\xi > 1$ , the entropy term dominates and favors the HS state, whereas when  $\xi < 1$ , the energy term dominates and tends to stabilize the LS state.

Based on the above analysis, we further explore the physical mechanism by which SDS promotes the spin elevation of Co ions. Firstly, the hydrophilic head group of the SDS molecule ( $\text{RSO}_4^-$ ) interacts electrostatically with the Co center, its high electronegativity endows it with significant electron-withdrawing capability, facilitating electron density redistribution. Secondly, the flexible long hydrophobic tail of SDS forms a tailing structure at the interface, increasing the vibrational degrees of freedom of the coordination structure and thereby enhancing the entropy change  $\Delta S$ . At the same time, SDS reduces the crystal field splitting energy  $\Delta$ , lowering the energy barrier  $\Delta E$ , which shifts the spin equilibrium of the system toward the entropy-dominated region. Based on these effects, the expression for the fraction of the high-spin state in the system can be derived as:

$$n_{HS} = \frac{K}{1+K} = \frac{1}{1+e^{\left(\frac{\Delta E - T\Delta S}{k_B T}\right)}} = \frac{1}{1+e^{\frac{\Delta E}{k_B T}(1-\xi)}}$$

Based on the above discussion, the modification effect of the SDS molecule increases the entropy–energy competition ratio  $\xi$ , from which, according to the aforementioned formula, it can be inferred that the fraction of the high-spin state in the system correspondingly increases. Meanwhile, the increase in entropy further lowers the Gibbs free energy, facilitating faster formation of the crystalline phase at relatively lower temperatures.

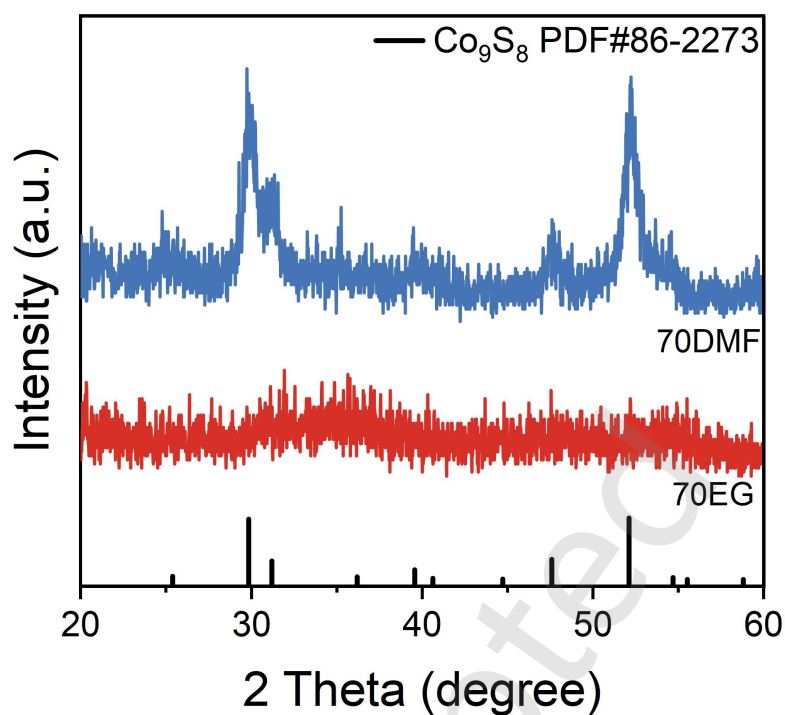


**Figure S1.** XRD patterns of  $\text{Co}_9\text{S}_8$  obtained under the same temperature and time conditions in different solvent environments (70 mL ethylene glycol and 70 mL dimethylformamide).

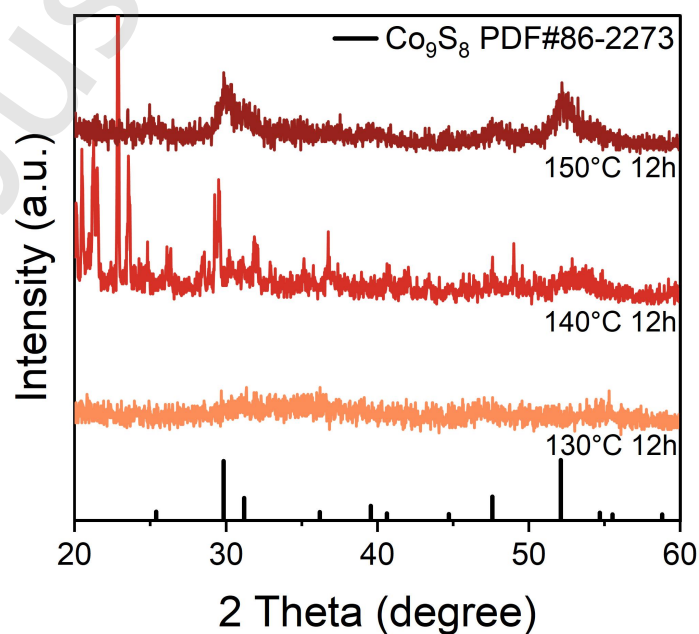


**Figure S2.** XRD patterns of  $\text{Co}_9\text{S}_8$  obtained at different heating temperatures under the same heating duration.

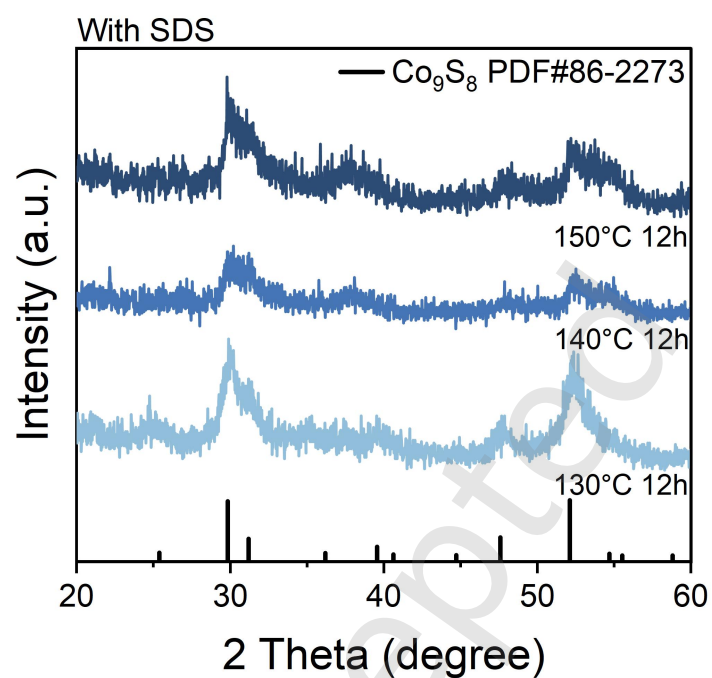


**Figure S3.** XRD patterns of CS-SDS obtained at different heating temperatures under the same heating duration.

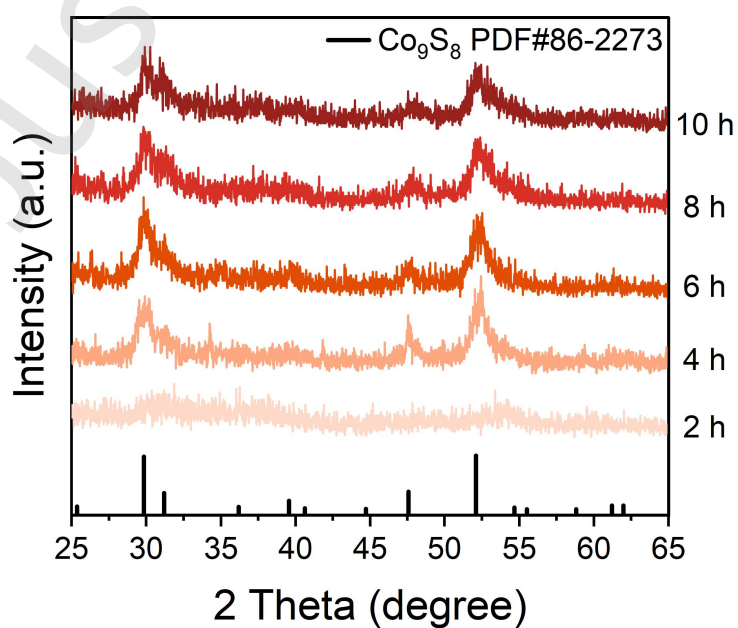


**Figure S4.** XRD patterns of CS obtained at different heating durations under the same heating temperature.

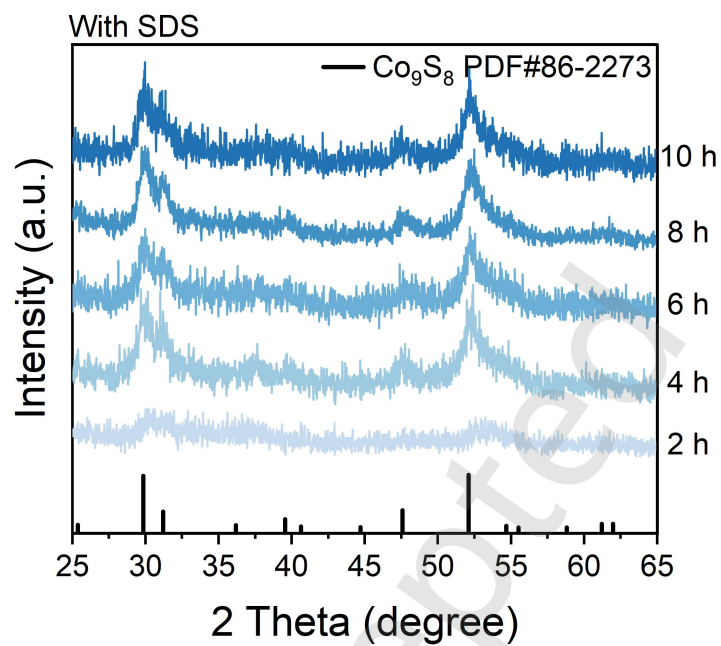


**Figure S5.** XRD patterns of CS-SDS obtained at different heating durations under the same heating temperature.

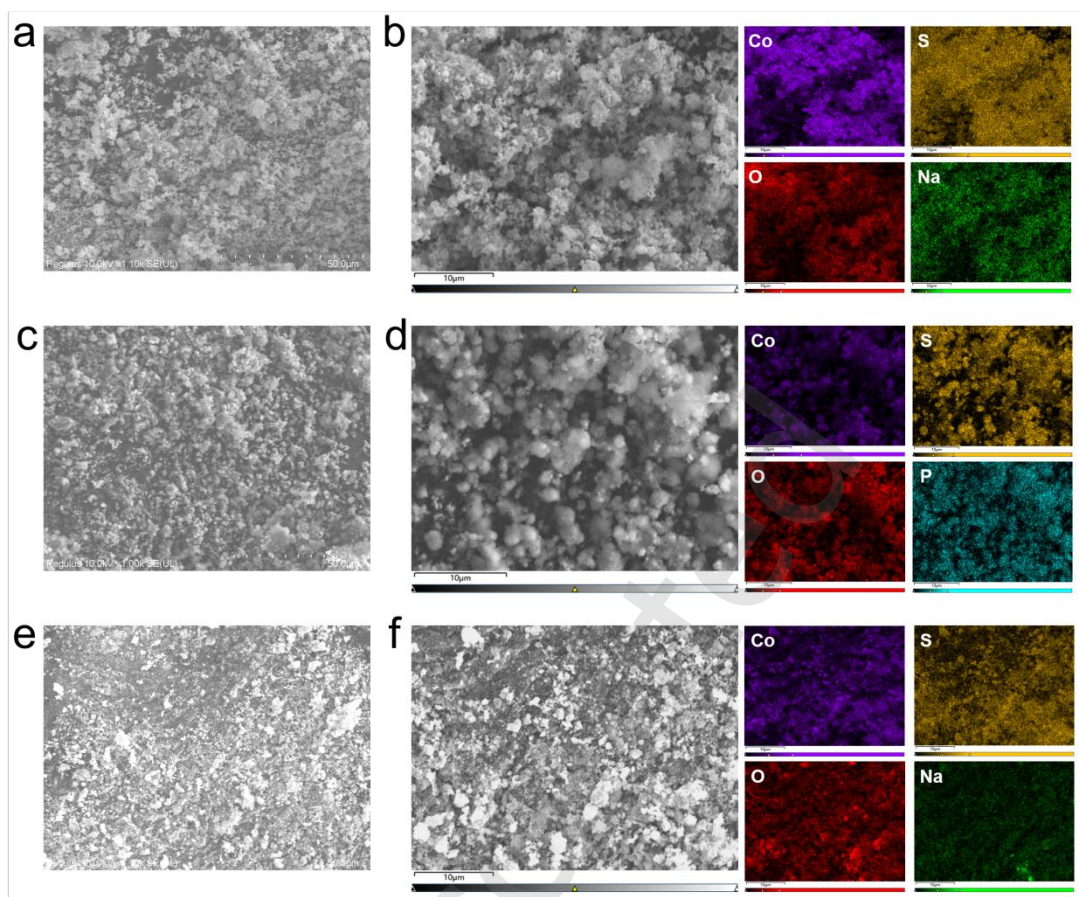


**Figure S6.** SEM image and SEM-EDX image of (a, b) CS-SOS, (c, d) CS-PC and (e, f) CS-SHS.



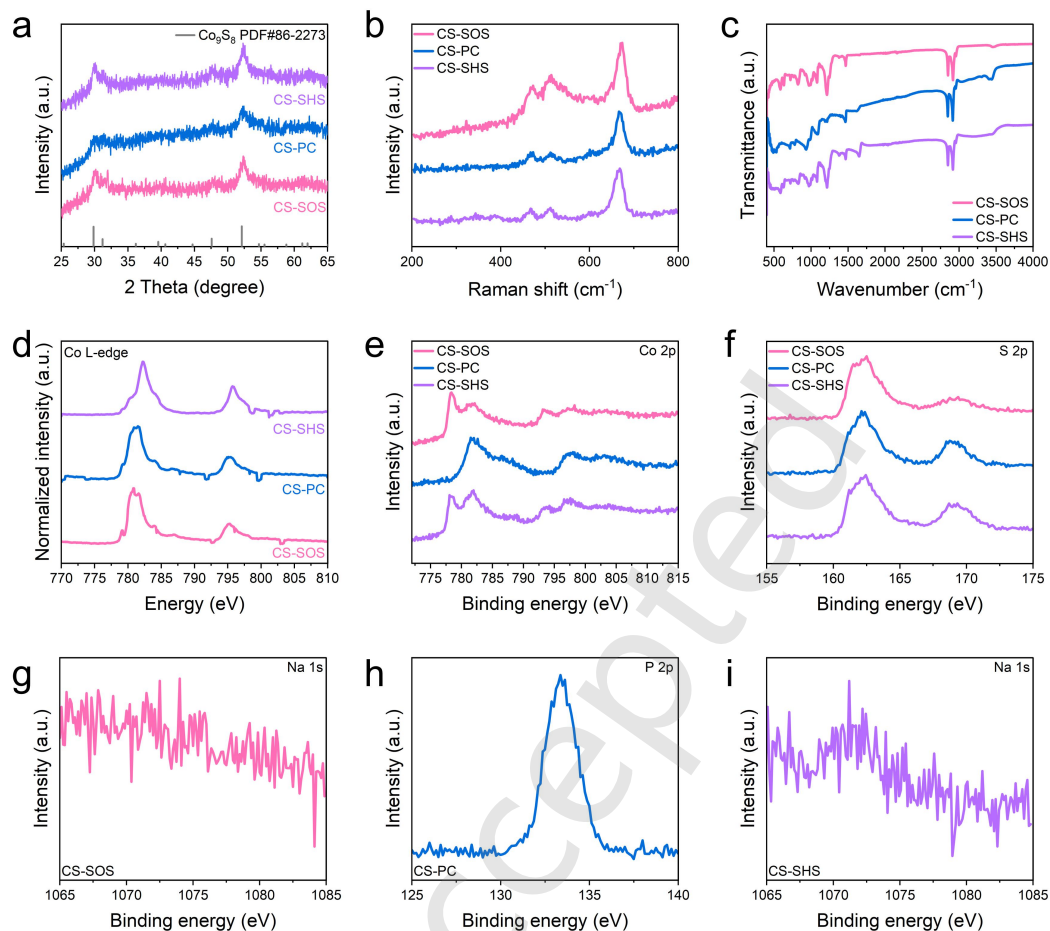


**Figure S7.** (a) XRD patterns, (b) Raman spectra, (c) FT-IR spectra (d) sXAS spectra of CS-SOS, CS-PC and CS-SHS. (e) Co 2p and (f) S 2p high resolution XPS spectra of CS-SOS, CS-PC and CS-SHS. (g) Na 1s high resolution XPS spectra of CS-SOS. (h) P 2p high resolution XPS spectra of CS-PC. (i) Na 1s high resolution XPS spectra of CS-SHS.

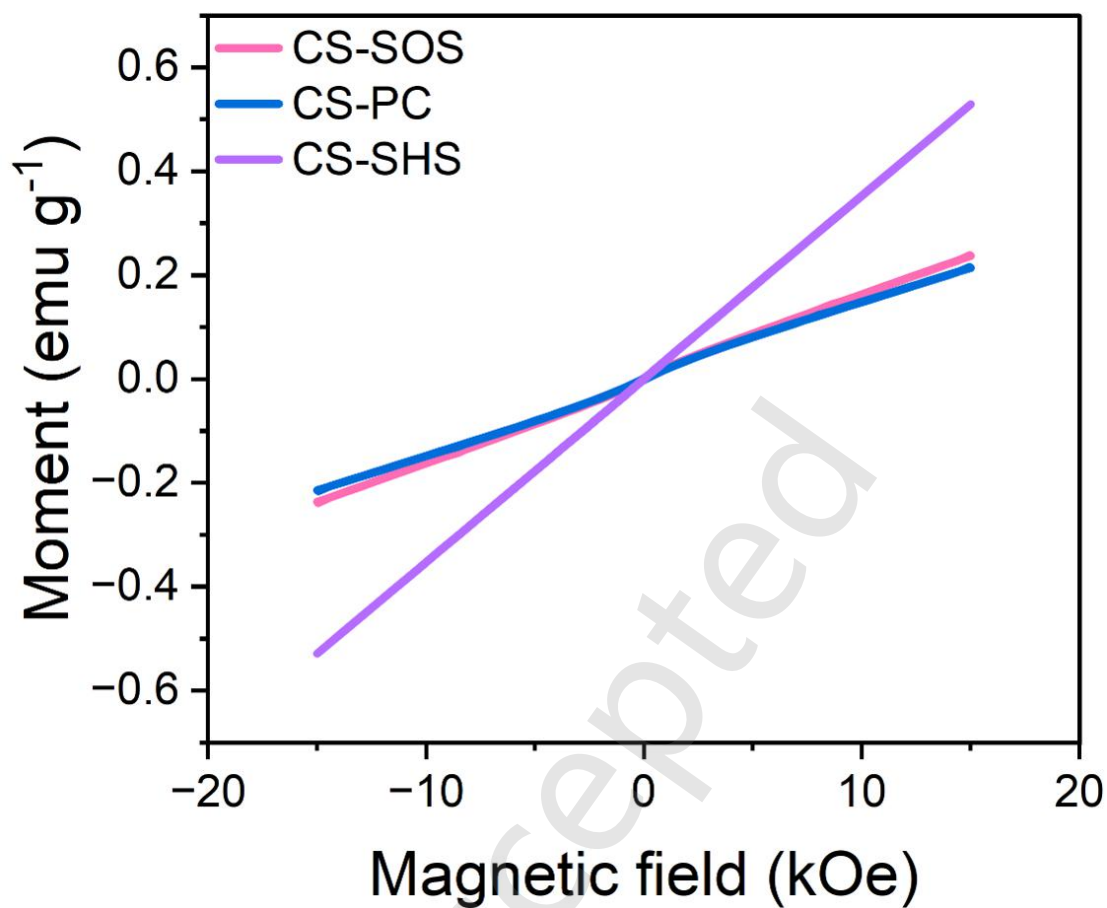


**Figure S8.** M-H curves of CS-SOS, CS-PC and CS-SHS.

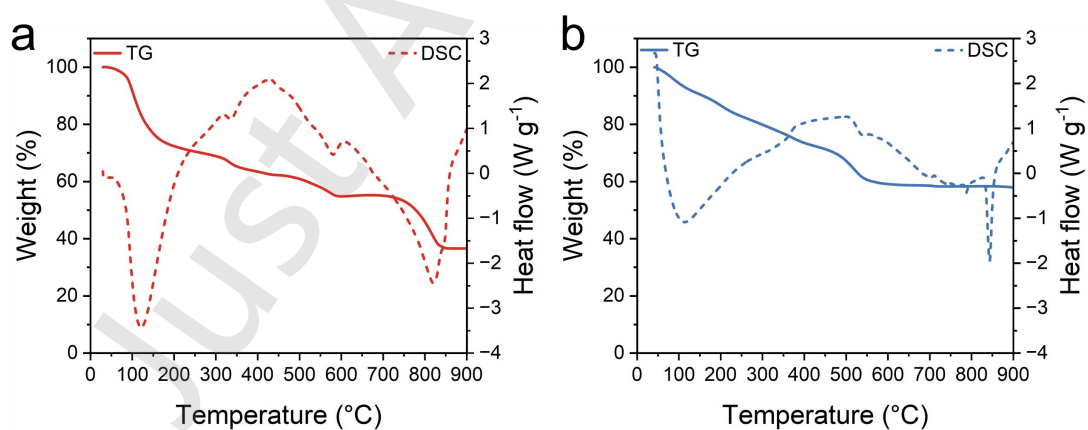


**Figure S9.** TG-DSC curves of (a) CS and (b) CS-300.

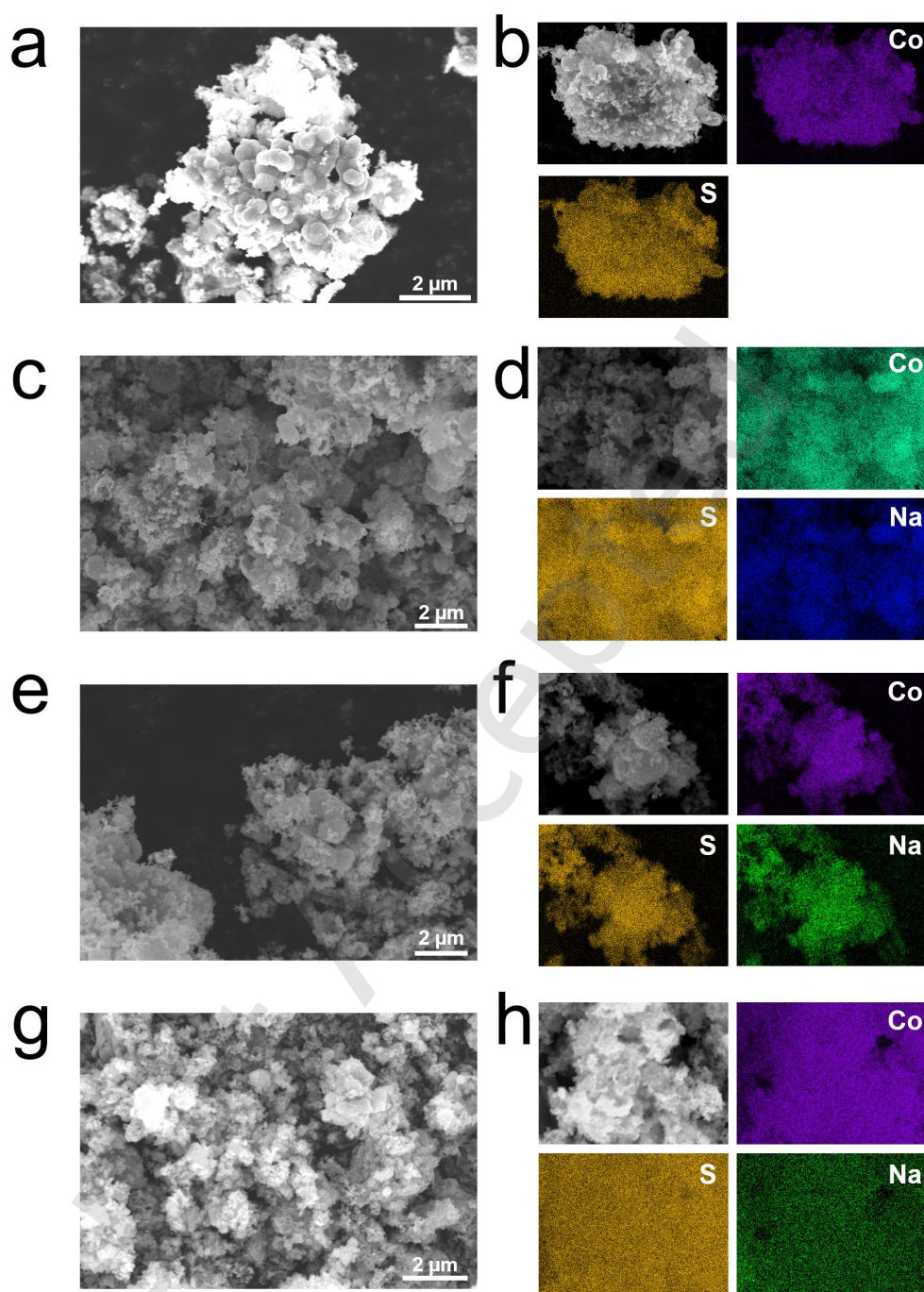


**Figure S10.** SEM images of (a) CS, (c) CS-200, (e) CS-300, and (g) CS-400. SEM energy dispersive spectrum (EDS) mappings of (b) CS, (d) CS-200, (f) CS-300, and (h) CS-400.

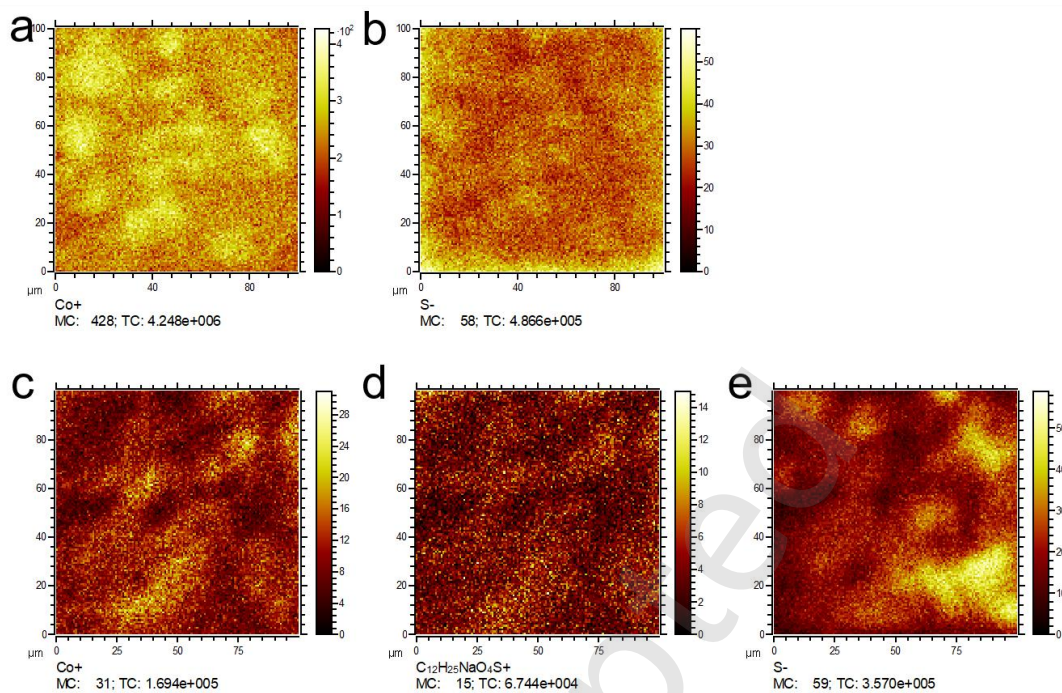


**Figure S11.** Ion distribution maps of (a-b) CS and (c-e) CS-300 measured by TOF-SIMS.

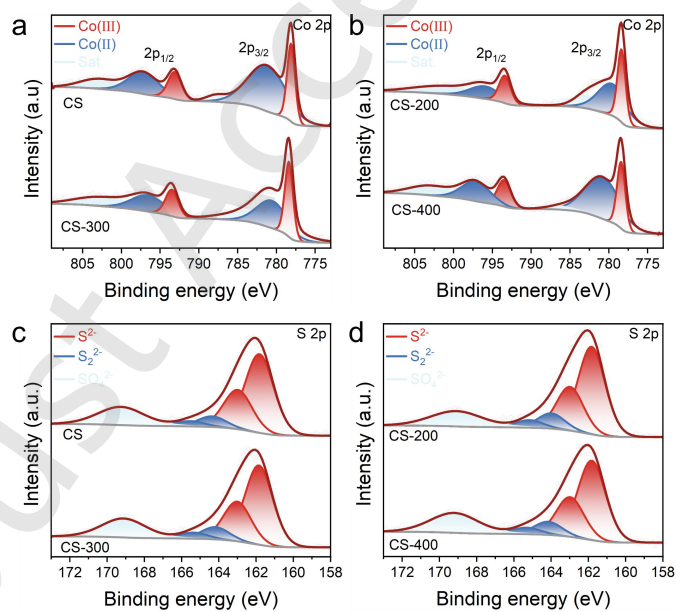


**Figure S12.** High-resolution XPS spectra of Co 2p for (a) CS, CS-300 and (b) CS-200, CS-400. S 2p for (c) CS, CS-300 and (d) CS-200, CS-400.



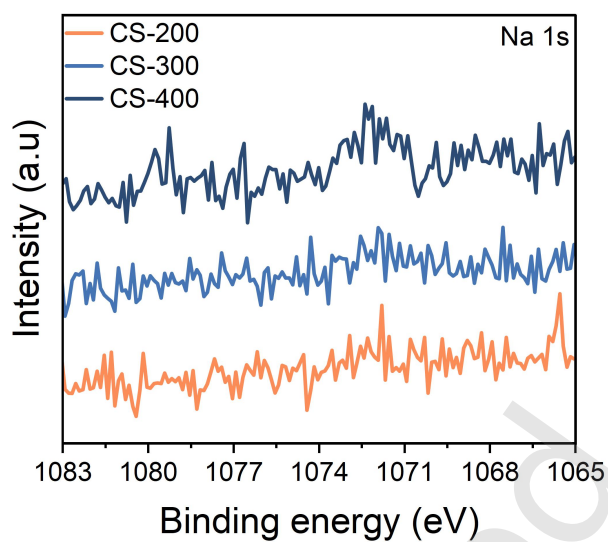


**Figure S13.** High-resolution XPS spectra of Na 1s for CS-200, CS-300 and CS-400.

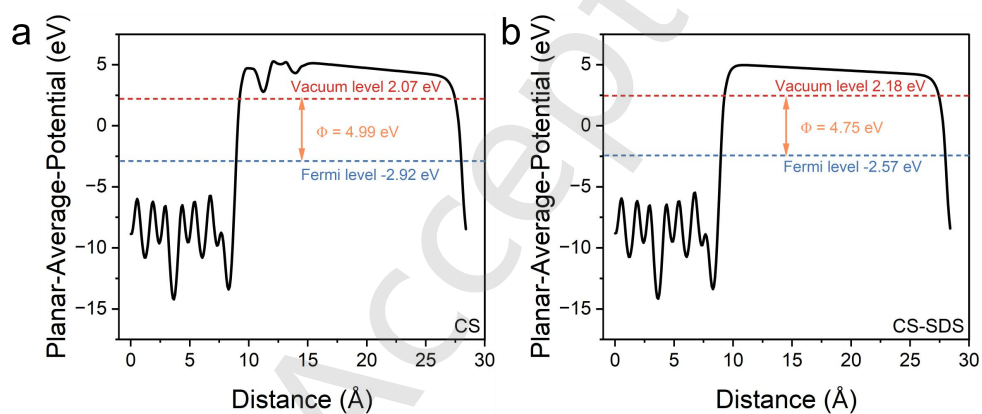


**Figure S14.** Work functions of CS and CS-SDS calculated by DFT calculation.

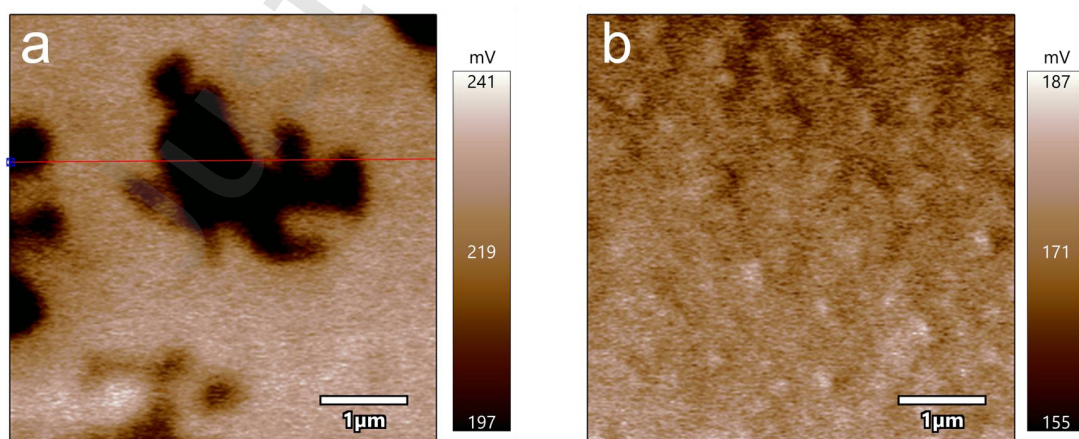


**Figure S15.** AFM and KPFM images of (a) CS and (b) CS-300.



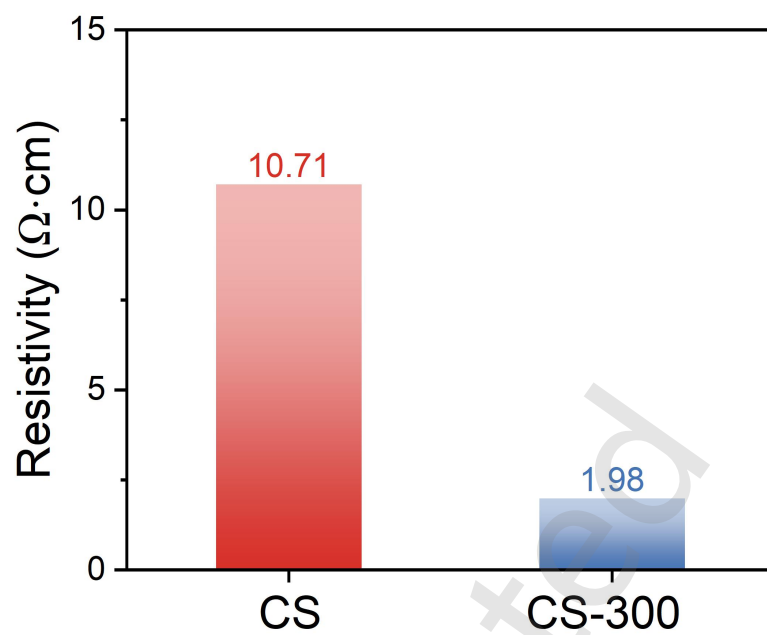


**Figure S16.** Resistivity features of CS and CS-300.

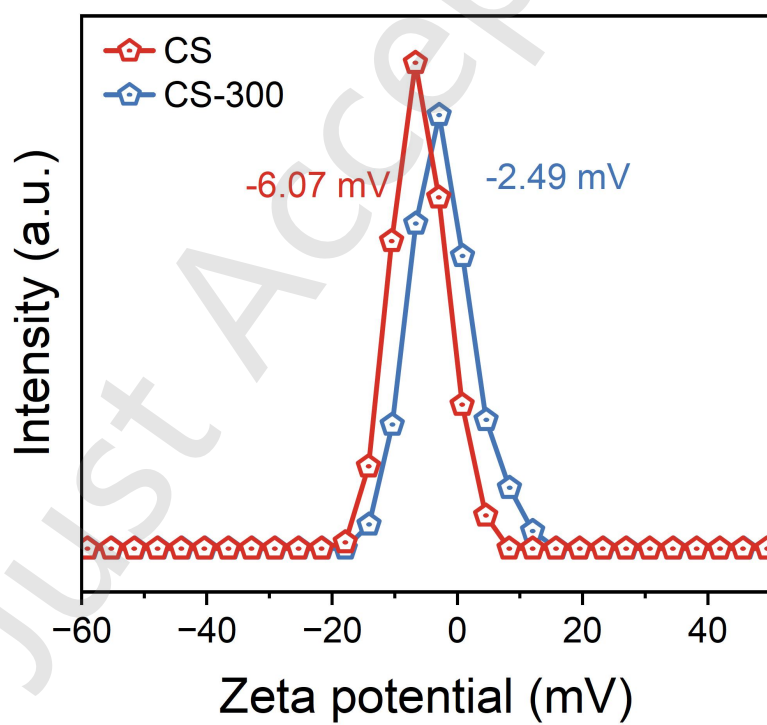


**Figure S17.** Zeta potential of CS and CS-300.

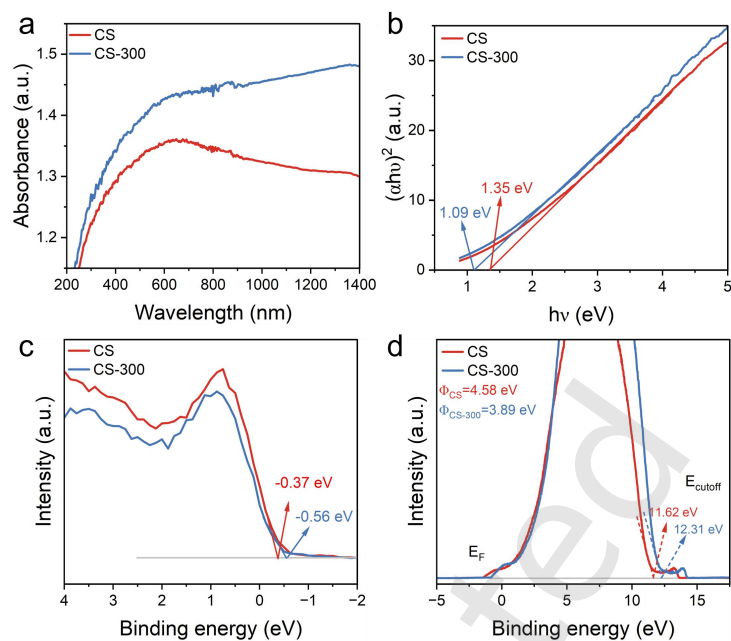


**Figure S18.** (a) UV-vis adsorption spectra, (b) Tauc plots, (c) VB spectra and (d) UPS spectra of CS and CS-300.

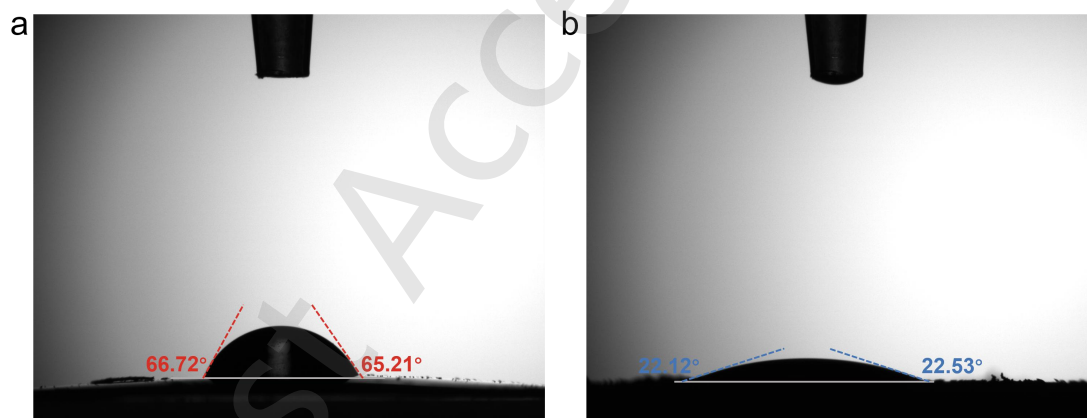


**Figure S19.** Contact angle images of (a) CS and (b) CS-300.

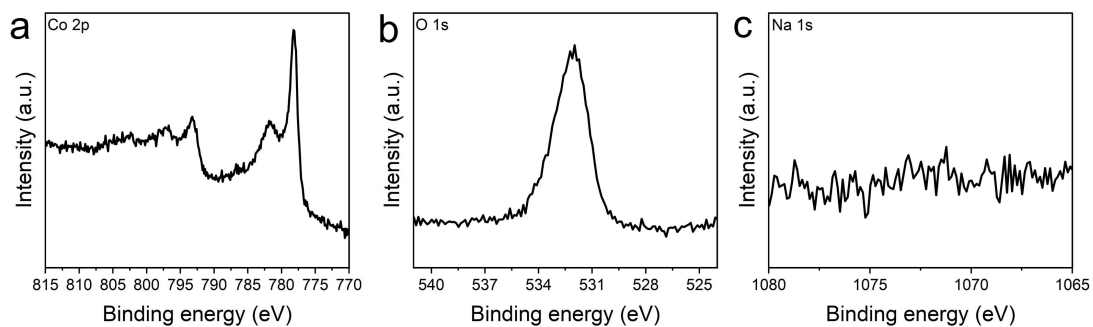


**Figure S20.** XPS spectra of (a) Co 2p, (b) O 1s, (c) Na 1s for CS-300 after CP testing.

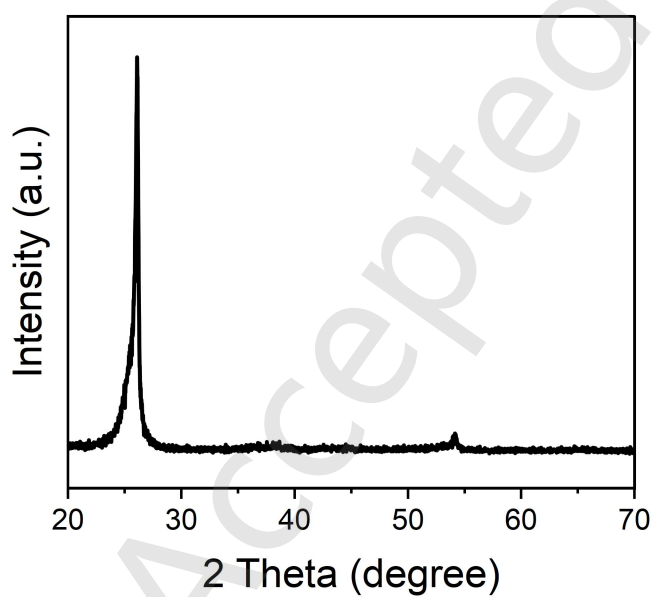


**Figure S21.** XRD pattern for CS-300 after CP testing.

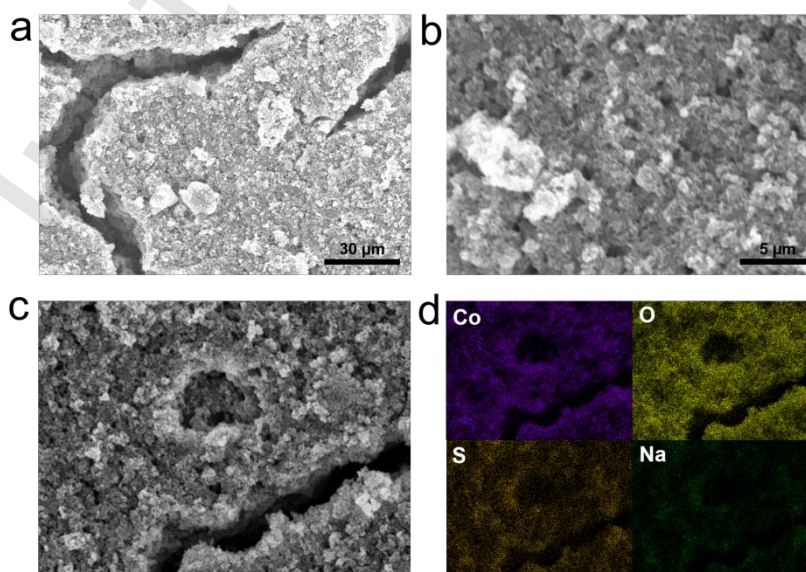


**Figure S22.** (a-c) SEM images and (d) SEM-EDX for CS-300 after CP testing.

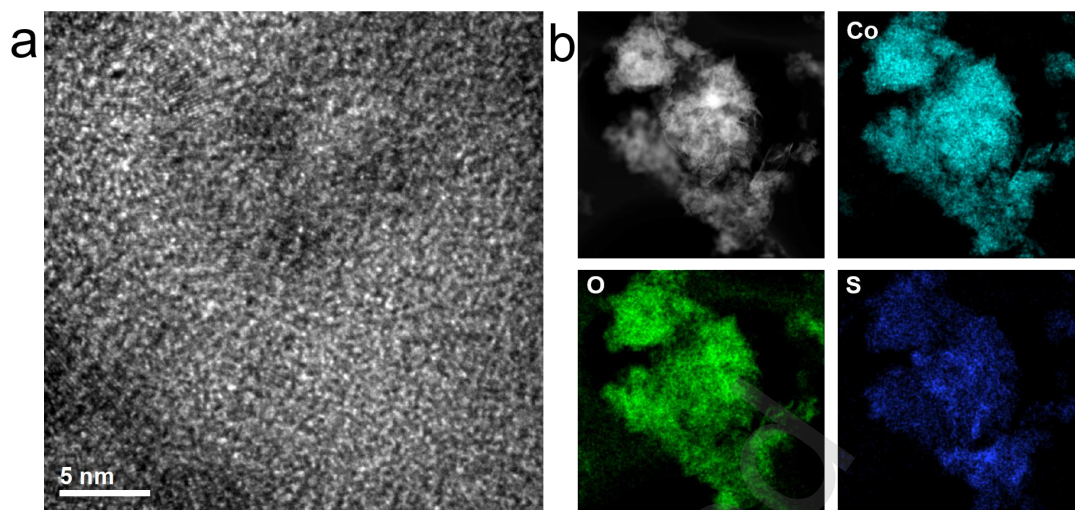


**Figure S23.** (a) HRTEM and (b) HADDF-STEM images for CS-300 after CP testing.

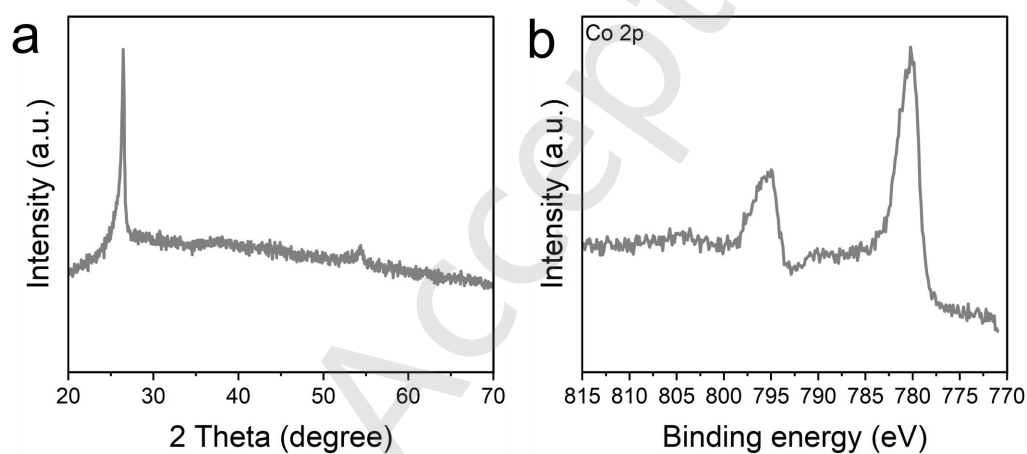


**Figure S24.** (a) XRD pattern and (b) Co 2p high resolution XPS spectra for CS after CP testing.

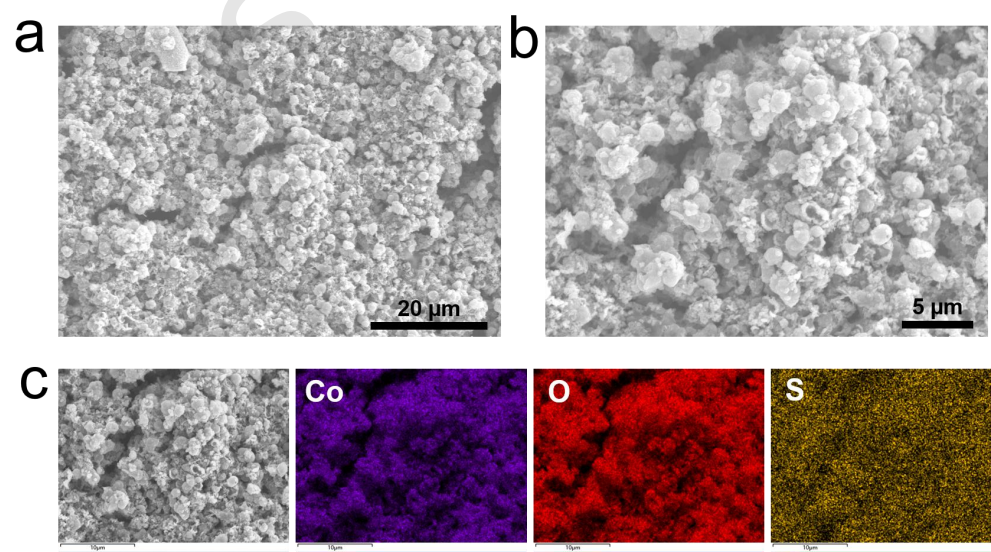


**Figure S25.** (a, b) SEM images and (c) SEM-EDX for CS after CP testing.



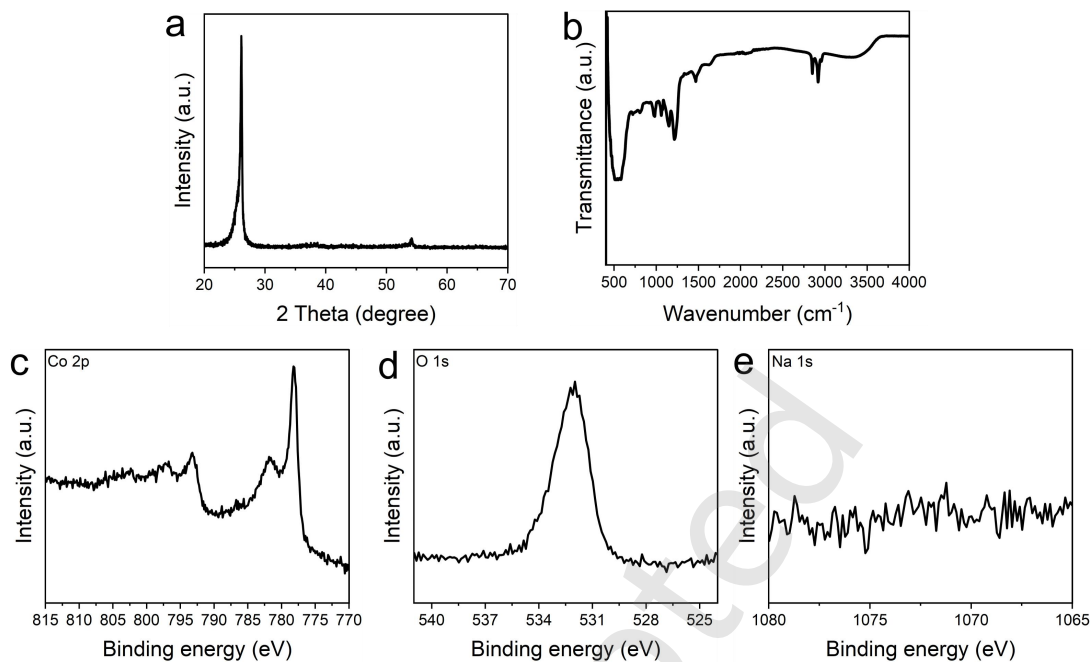


**Figure S26.** (a) XRD patterns, (b) FT-IR, (c) Co 2p, (d) O 1s and (e) Na 1s for CS after CP testing.

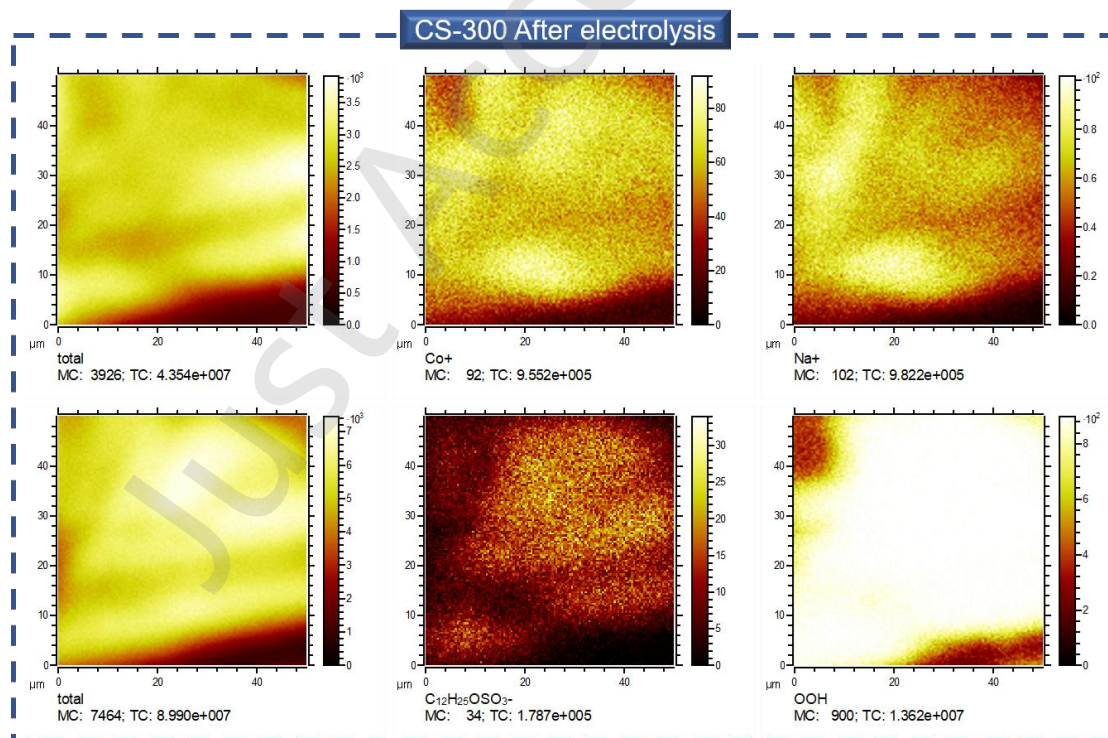


**Figure S27.** TOF-SIMS spectra for CS-300 after CP testing.



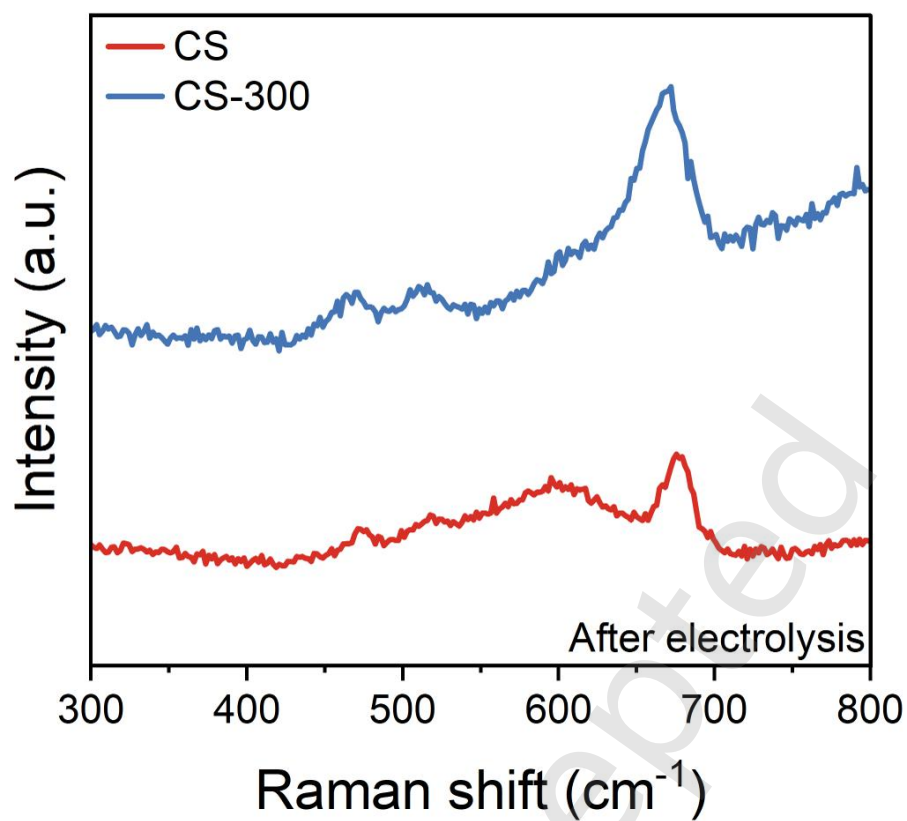


**Figure S28.** Raman spectra for CS and CS-300 after CP testing.

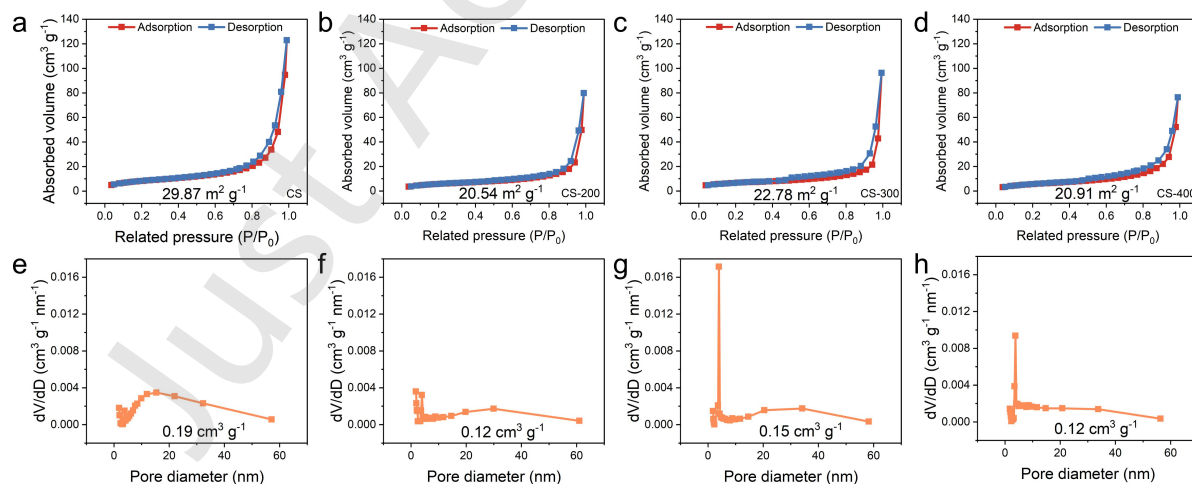


**Figure S29.** N<sub>2</sub> adsorption-desorption isotherms of (a) CS, (b) CS-200, (c) CS-300, (d) CS-400.

Pore size distribution of (e) CS, (f) CS-200, (g) CS-300, (h) CS-400.

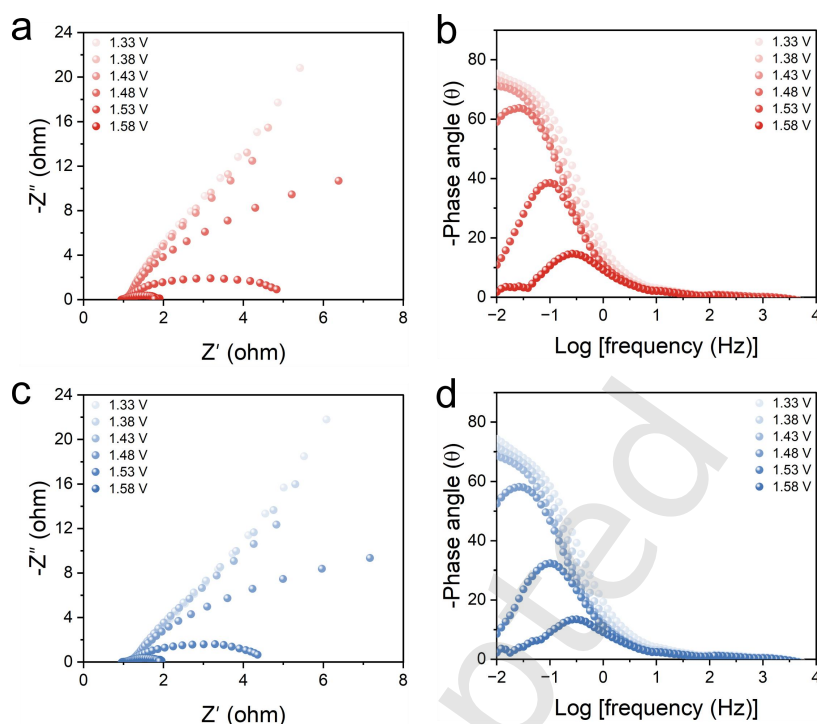


**Figure S30.** In-situ Nyquist plots of (a) CS and (c) CS-300. In-situ bode plots of (b) CS and CS-300.

When the potential rises to 1.48 V, the CS sample exhibits a large semicircle with a  $-Z''$  peak value of approximately 2  $\Omega$ . In contrast, the semicircle for CS-300 is flatter, with a peak value around 1.5  $\Omega$  and a slightly smaller intercept on the real axis, indicating reduced charge transfer resistance and diffusion impedance. Especially in the reconstruction region at 1.53 V, the diameter of the semicircle for CS-300 is significantly smaller than that of CS, demonstrating a markedly accelerated charge transfer process and decreased interfacial migration resistance between electrons and  $\text{OH}^-$  in the CS-300 system. The in situ Bode phase plots further reveal differences in interfacial kinetics (Figure S26b, d). In the potential range of 1.33–1.43 V, the CS sample maintains a phase angle above 60–70° at low frequencies, indicating pronounced capacitive behavior. When the potential increases to 1.53 V, the peak phase angle decreases to about 38.5°, corresponding to a characteristic frequency of approximately 0.1 Hz. For CS-300, the peak phase angle is even lower, at only 32.4°, with the characteristic frequency increasing to 0.3 Hz, shortening the response time constant by about three times. The higher characteristic frequency combined with the lower peak phase angle indicates that during the reconstruction process, the double-layer discharge in CS-300 occurs more rapidly, the Co–O/OH charge transfer rate is significantly enhanced, and the ionic conductivity at the solid-liquid interface is greatly improved.

The characteristic interfacial relaxation time was quantitatively estimated from the maximum phase-response frequency according to  $\tau = 1/(2\pi f_c)$  where  $f_c$  is the characteristic frequency extracted from the Bode phase response. At 1.53 V,  $f_c$  increases from approximately 0.10 Hz for CS to 0.30 Hz for CS-300, corresponding to a decrease in  $\tau$  from approximately 1.59 s to 0.53 s. Accordingly, an apparent interfacial relaxation rate was defined as  $k_{\text{relax}} = 1/\tau$ , yielding  $0.63 \text{ s}^{-1}$  for CS and  $1.88 \text{ s}^{-1}$  for CS-300. Thus, the reconstruction-associated interfacial response of CS-300 is approximately three times faster than that of CS. It should be noted that  $k_{\text{relax}}$  represents an apparent interfacial relaxation rate rather than an elementary chemical rate constant of a single reconstruction step.

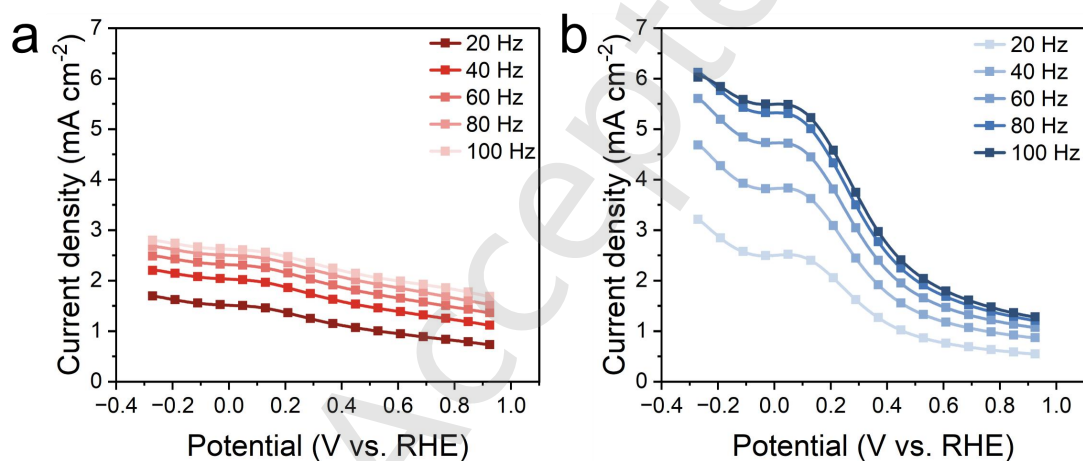


**Figure S31.** AC Voltammetry (ACV) plots of (a) CS and (b) CS-300.

Alternating current voltammetry (ACV) was employed to further monitor the electrode current response to potential changes during the reconstruction process. It was observed that, at the same potential and frequency, the total current of CS-300 was significantly higher than that of CS, indicating a substantial enhancement in the electrode's charge transfer capability and energy storage capacity. Statistical analysis showed that within the frequency range of 20 – 100 Hz, the total current of CS-300 increased by approximately 1.9 to 2.3 times compared to CS, the real part of the current increased by 1.65 to 2.10 times, and the imaginary part of the current saw an even more pronounced increase, ranging from 2.5 to 4.1 times and growing with frequency. This suggests that the SDS treatment primarily improves ion diffusion as well as the contributions from double-layer and pseudocapacitance, with more notable effects at higher frequencies. The real part of the current mainly reflects charge transfer and pseudocapacitive processes, whereas the imaginary part is mainly associated with ion diffusion and double-layer capacitance.

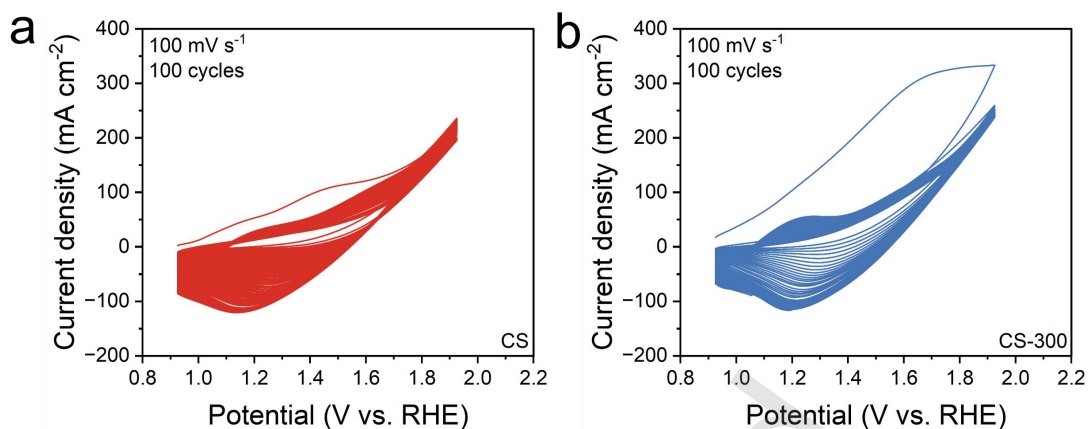


**Figure S32.** (a) CV curves of CS and (b) CS-300 recorded over 100 cycles.

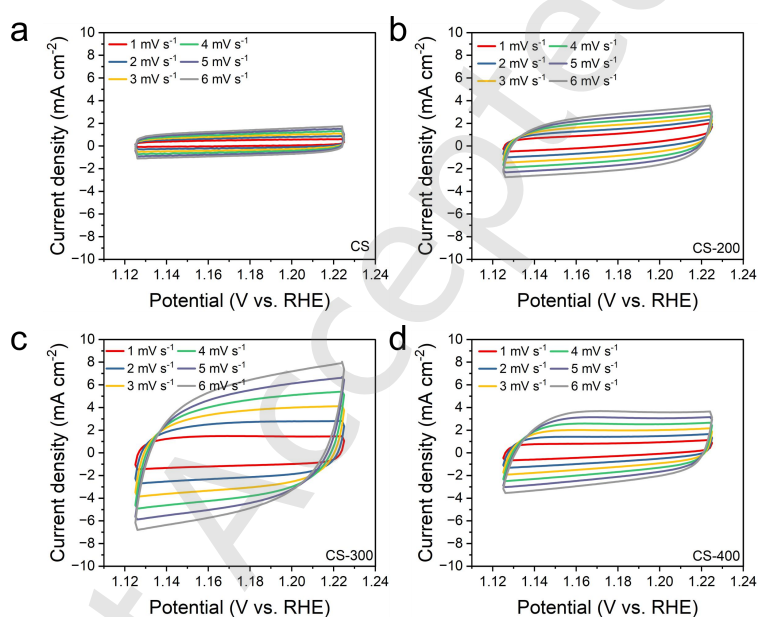


**Figure S33.** CV for  $C_{dl}$  of (a) CS, (b) CS-200, (c) CS-300, and (d) CS-400.

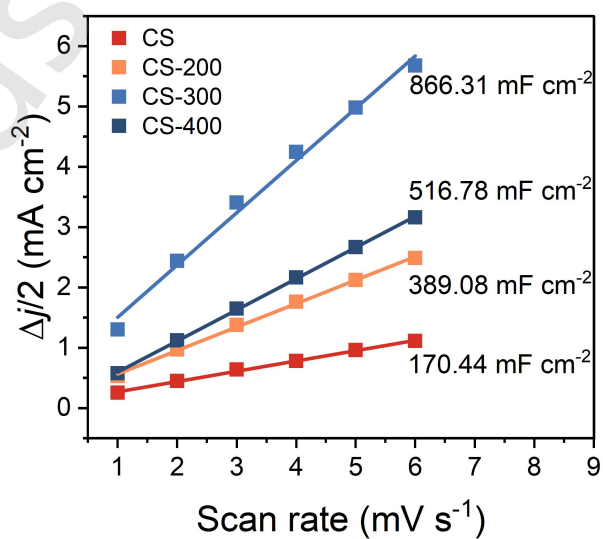


**Figure S34.**  $C_{dl}$  of CS, CS-200, CS-300, and CS-400.

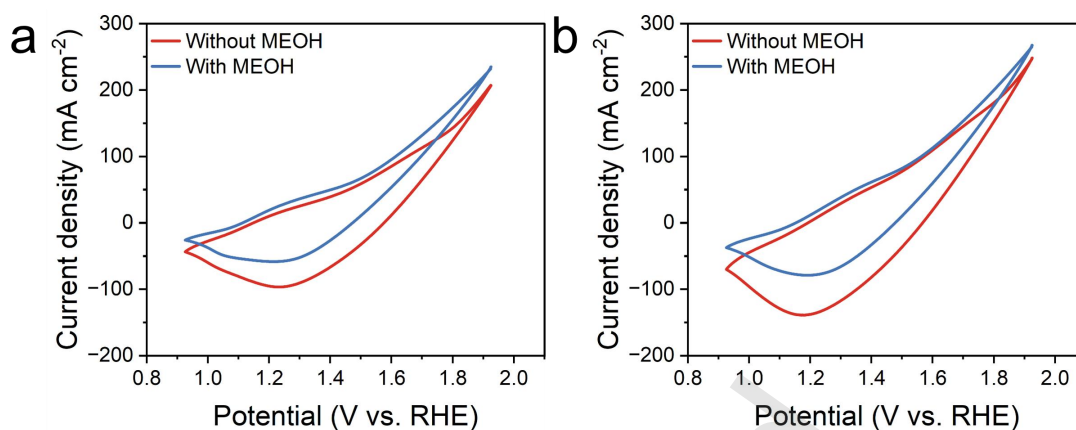


**Figure S35.** Methanol poisoning tests of (a) CS and (b) CS-300.

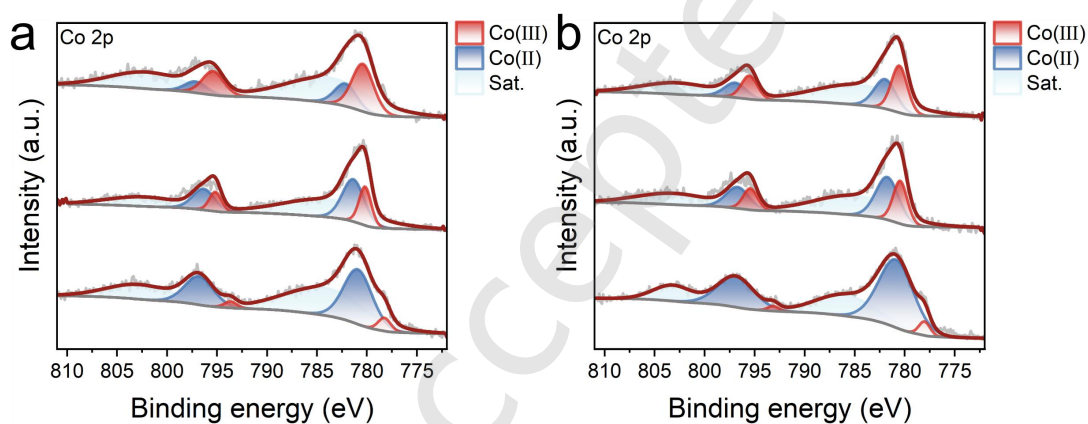


**Figure S36.** Dynamic monitoring of Co 2p dissolution during reconstruction using vacuum-integrated coupled XPS for **a** CS and **b** CS-300.

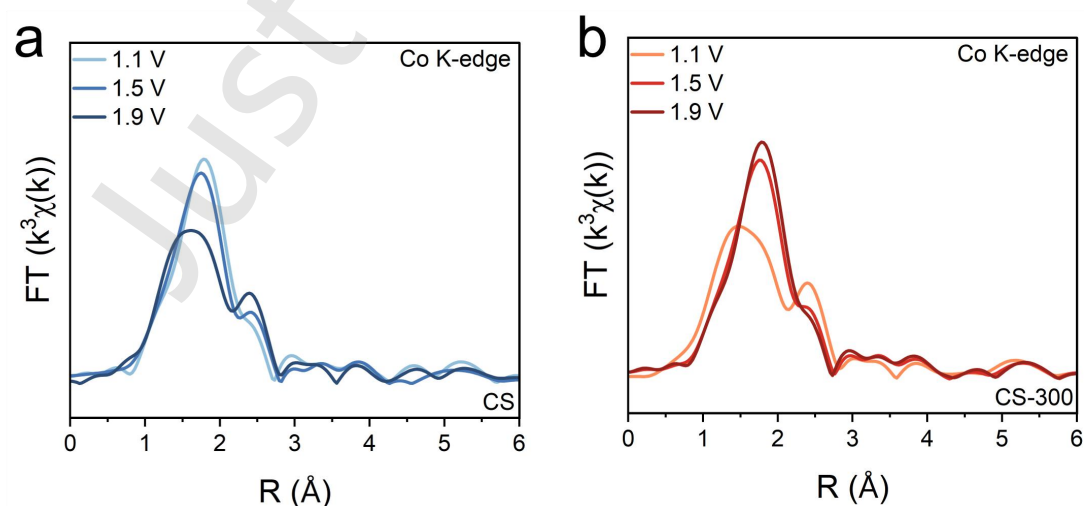


**Figure S37.** Dynamic monitoring of Co-K edge EXAFS for **a** CS and **b** CS-300 under different potentials.



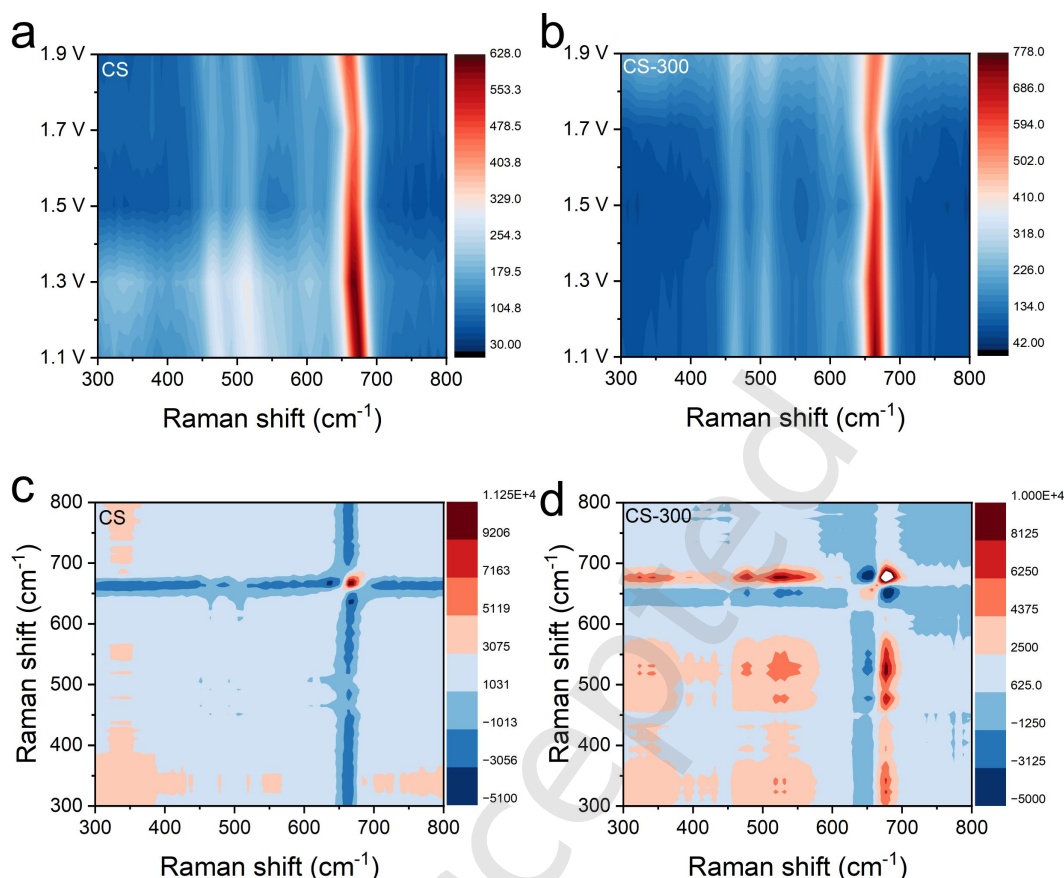


**Figure S38.** In-situ Raman spectra of **a** CS and **b** CS-300. 2D-CORs of **c** CS and **d** CS-300.

The dynamic reconstruction processes of CS and CS-300 were monitored in real-time via in situ Raman spectroscopy. Under low potential conditions (1.1 V), the spectrum of CS-300 already exhibited enhanced mid-to-high wavenumber signals in the 480–700 cm<sup>-1</sup> region, corresponding to Co–O–H stretching vibrations. In contrast, the CS sample at the same potential only showed weak Co–S vibration signals in the 150–200 cm<sup>-1</sup> and 300–400 cm<sup>-1</sup> regions. As the potential increased to 1.3–1.5 V, the high-wavenumber characteristic peaks of CS-300 significantly intensified, while the low-wavenumber signals showed only slight enhancement, indicating that surface oxidation reactions occurred earlier and more effectively on CS-300. At 1.7 V, the intensity of CS-300 remained significantly higher than that of CS within the 650–670 cm<sup>-1</sup> range, while signals in the low-wavenumber region rose sharply. This suggests a deeper, longitudinal progression of the reconstruction process accompanied by formation of defect-containing Co(OH)<sub>2-x</sub>S<sub>x</sub> intermediate phases, which introduced new vibrational modes in the 150–300 cm<sup>-1</sup> range. At 1.9 V, the integrated intensity of high-wavenumber peaks for CS-300 surpassed that of CS, along with a more pronounced enhancement of low-wavenumber signals, indicating that SDS modification

promoted a more complete reconstruction process, resulting in a thicker CoOOH active shell. Synchronous two-dimensional correlation Raman spectroscopy (2D-CORS) further confirmed the significant acceleration of the reconstruction kinetics by SDS. In the CS sample, the cross-peak intensities related to Co–S/Co–O vibrations within the 500–700  $\text{cm}^{-1}$  range were only about 1,000, whereas in CS-300, these cross-peak intensities markedly increased to 8,000–13,000, especially showing strong synchronous correlations between 676  $\text{cm}^{-1}$  and 545  $\text{cm}^{-1}$ , 490  $\text{cm}^{-1}$  and other wavenumbers. These results indicate that under the influence of SDS, the processes of Co–S bond cleavage and Co–O(H) bond formation were greatly synchronized. Notably, in the CS sample, a negative correlation appeared between 670  $\text{cm}^{-1}$  and 518  $\text{cm}^{-1}$ , which shifted to a strong positive correlation in CS-300. Combined with temperature-programmed reduction ( $\text{H}_2$ -TPR) and temperature-programmed desorption of  $\text{NH}_3$  ( $\text{NH}_3$ -TPD) results, these findings collectively demonstrate that cobalt species in the HS state induced by SDS significantly lowered the oxidation energy barrier, facilitating highly cooperative kinetics between Co–S bond breaking and Co–OH formation.

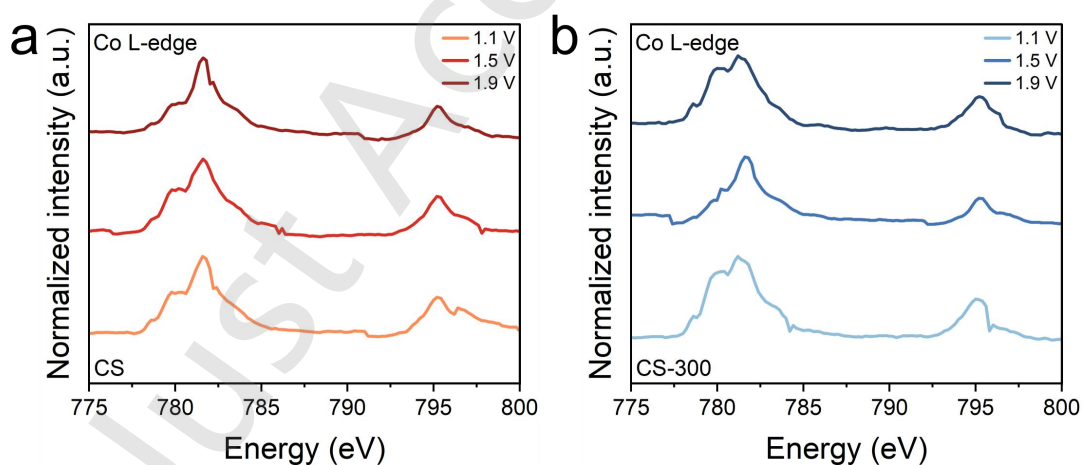


**Figure S39.** sXAS spectra of relaxed (a) CS and (b) CS-300 collected at the reconstruction potentials used for testing.

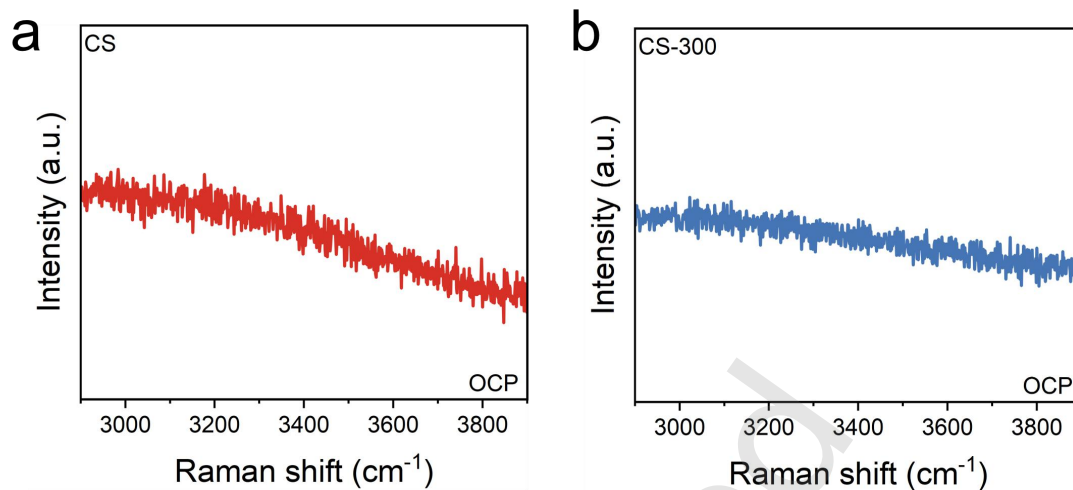


**Figure S40.** In-situ Raman spectra of (a) CS and (b) CS-300 at OCP.

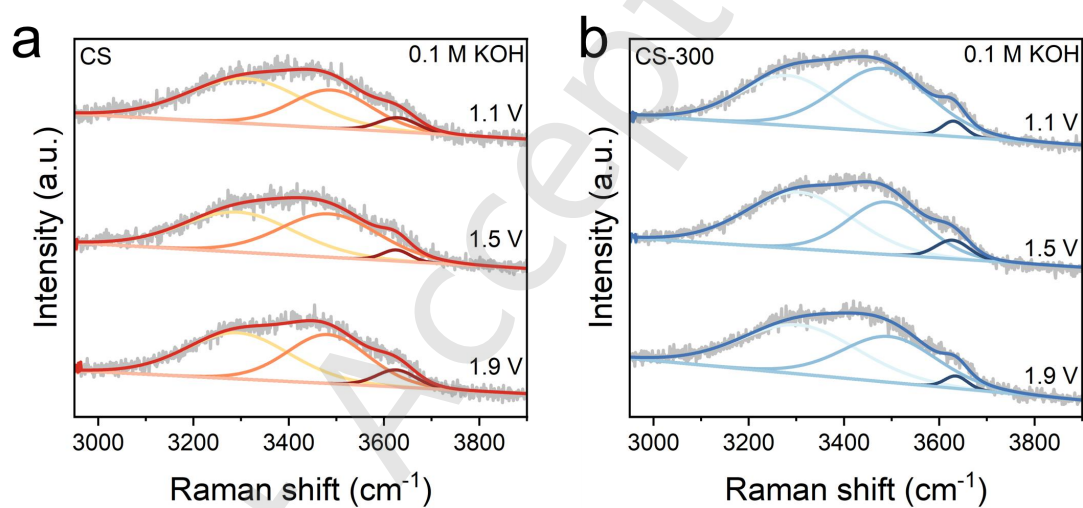


**Figure S41.** In-situ Raman spectra of interfacial water structure for (a) CS and (b) CS-300 in 0.1 M KOH.

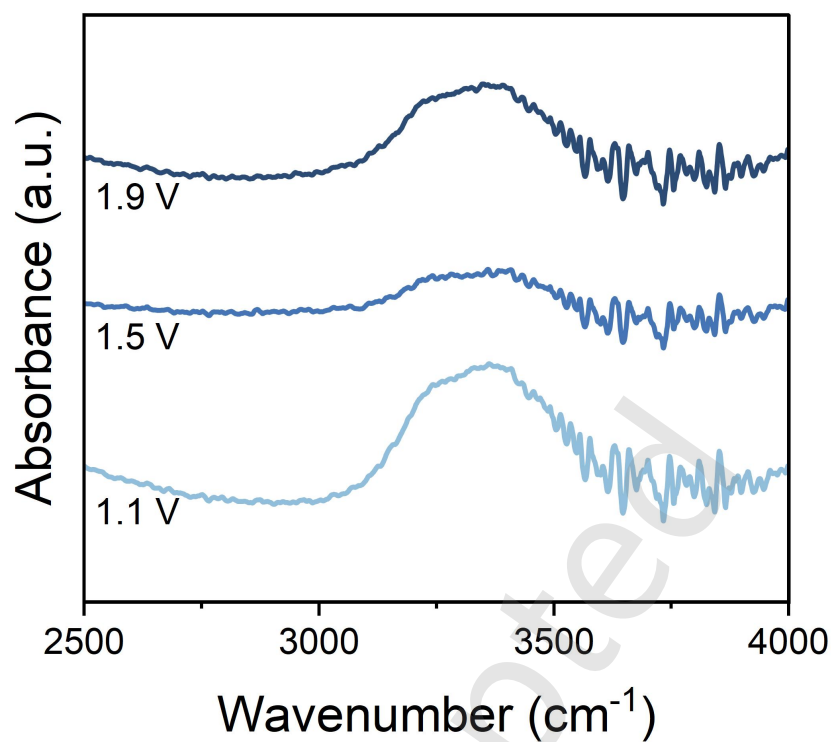


**Figure S42.** ATR-SEIRAS was measured after prolonged cycling of CS-300, during which a steady-state CoOOH layer formed on the surface.

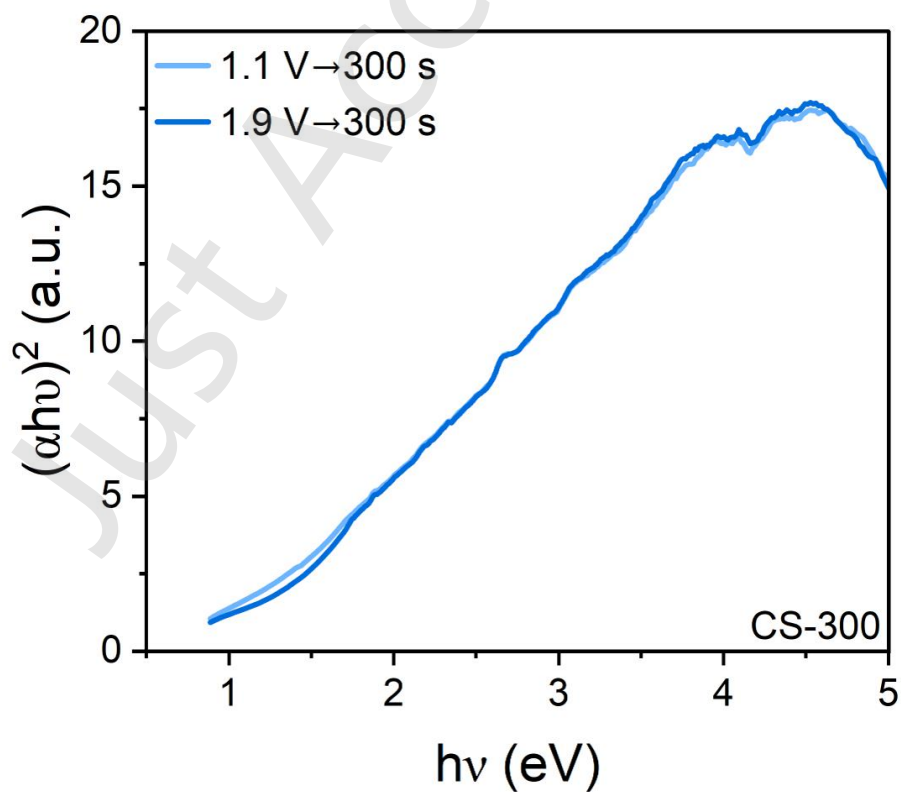


**Figure S43.** After potentiostatic relaxation at the testing potentials of 1.1 V and 1.9 V, UV-vis diffuse reflectance spectra were collected.

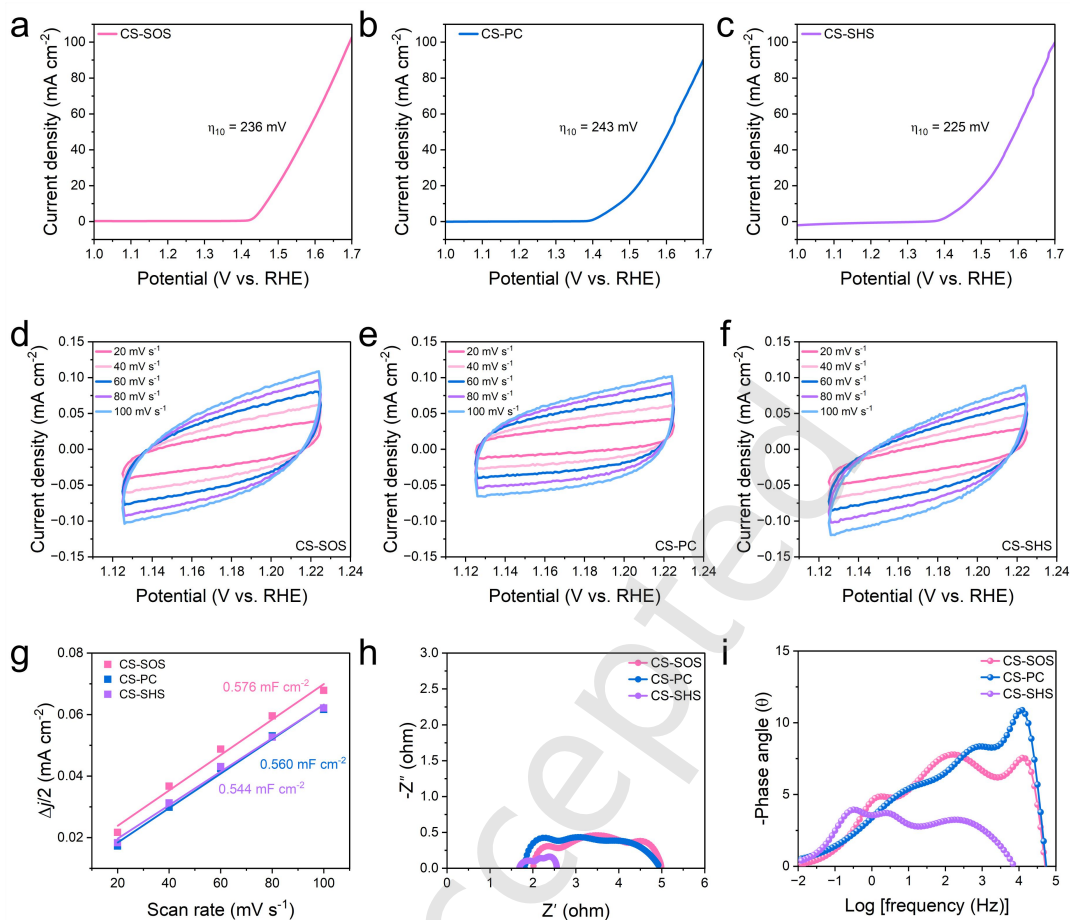


**Figure S44.** LSV curve of (a) CS-SOS, (b) CS-PC and (c) CS-SHS. CV curves of (d) CS-SOS, (e) CS-PC and (f) CS-SHS. (g) ECSA values, (h) Nyquist plots and (i) Bode plots of CS-SOS, CS-PC and CS-SHS.

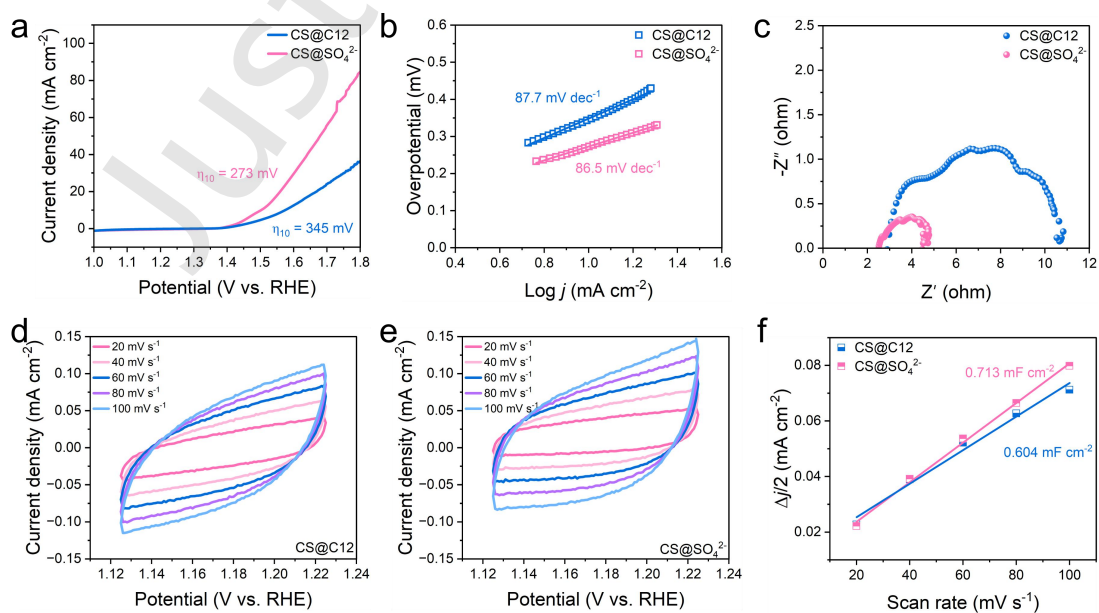


**Figure S45.** (a) LSV curves, (b) Tafel slope, (c) Nyquist plots of CS-C12 and CS-SO<sub>4</sub><sup>2-</sup>. CV



curves of (d) CS-C12 and (e) CS-SO<sub>4</sub><sup>2-</sup>. (f) ECSA of CS-C12 and CS-SO<sub>4</sub><sup>2-</sup>.

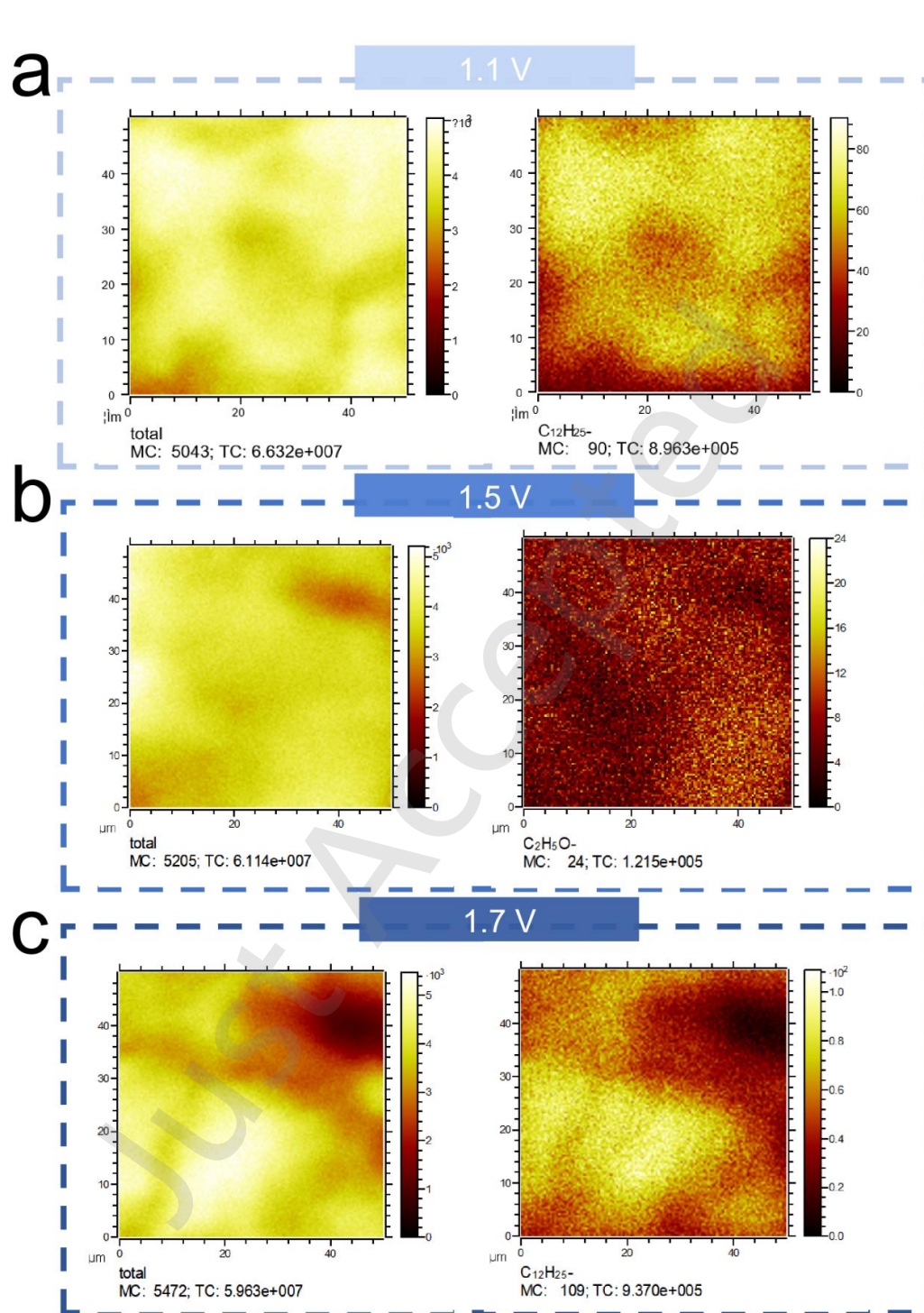


**Figure S46.** TOF-SIMS two-dimensional distribution and concentration maps of the C12 fragments in CS-C12 obtained from point measurements at different reconstruction potentials.

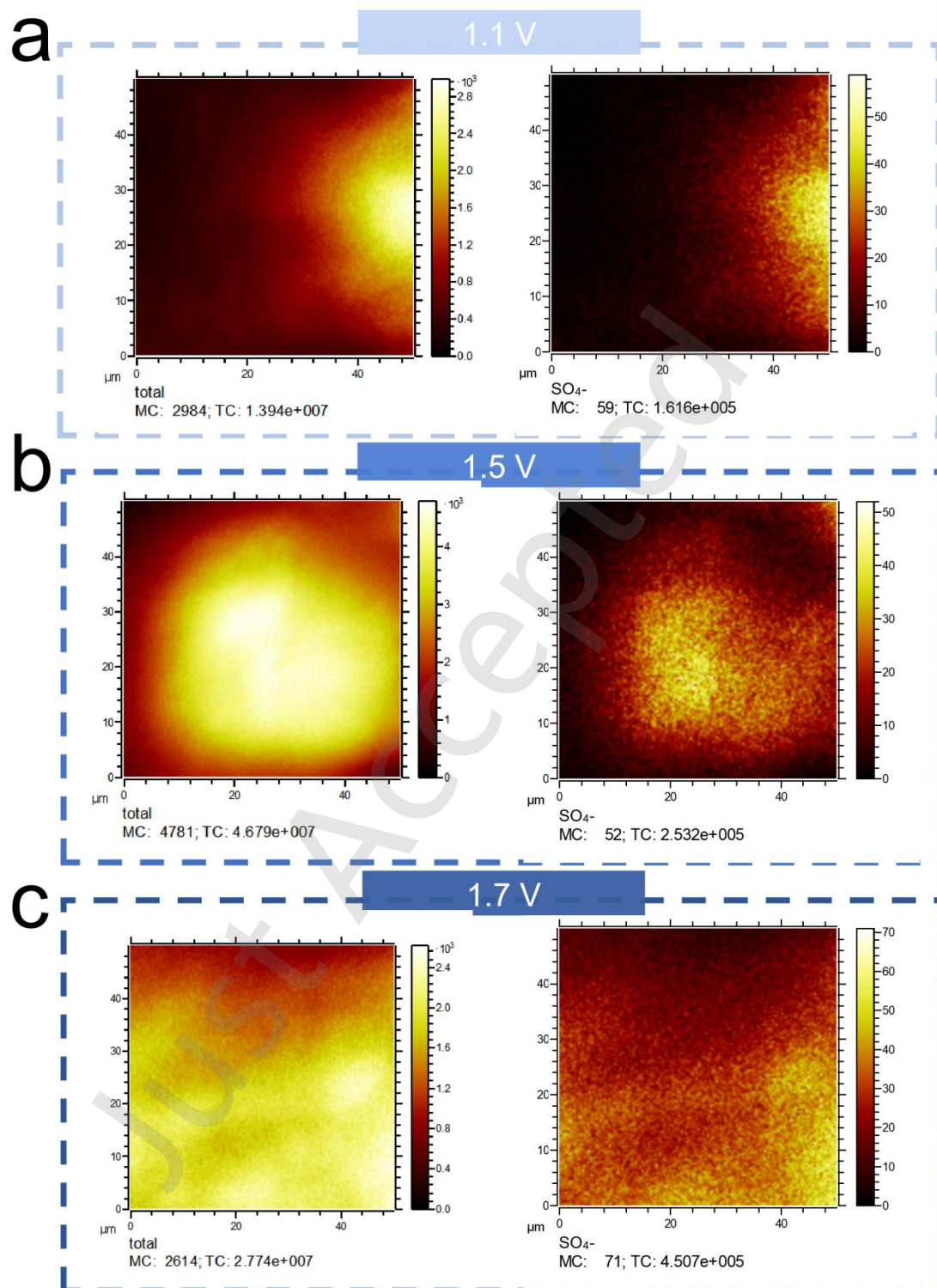


**Figure S47.** TOF-SIMS two-dimensional distribution and concentration maps of the SO<sub>4</sub><sup>2-</sup> fragments in CS-SO<sub>4</sub><sup>2-</sup> obtained from point measurements at different reconstruction potentials.

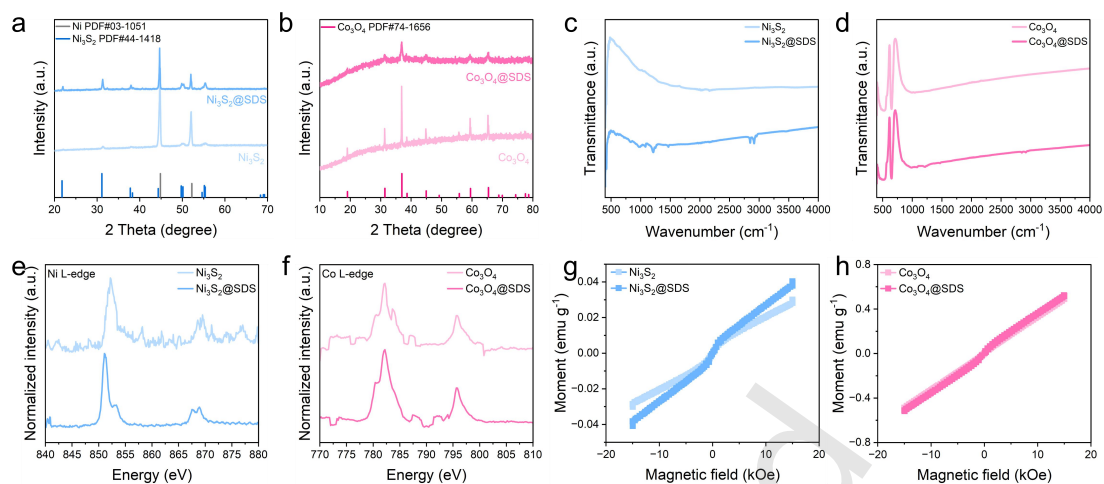


**Figure S48.** XRD patterns of (a)  $\text{Ni}_3\text{S}_2$ ,  $\text{Ni}_3\text{S}_2\text{-SDS}$  and (b)  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4\text{-SDS}$ . FT-IR spectra of (c)  $\text{Ni}_3\text{S}_2$ ,  $\text{Ni}_3\text{S}_2\text{-SDS}$  and (d)  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4\text{-SDS}$ . sXAS of (e)  $\text{Ni}_3\text{S}_2$ ,  $\text{Ni}_3\text{S}_2\text{-SDS}$  and (f)  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4\text{-SDS}$ . M-H curves of (g)  $\text{Ni}_3\text{S}_2$ ,  $\text{Ni}_3\text{S}_2\text{-SDS}$  and (h)  $\text{Co}_3\text{O}_4$ ,  $\text{Co}_3\text{O}_4\text{-SDS}$ .



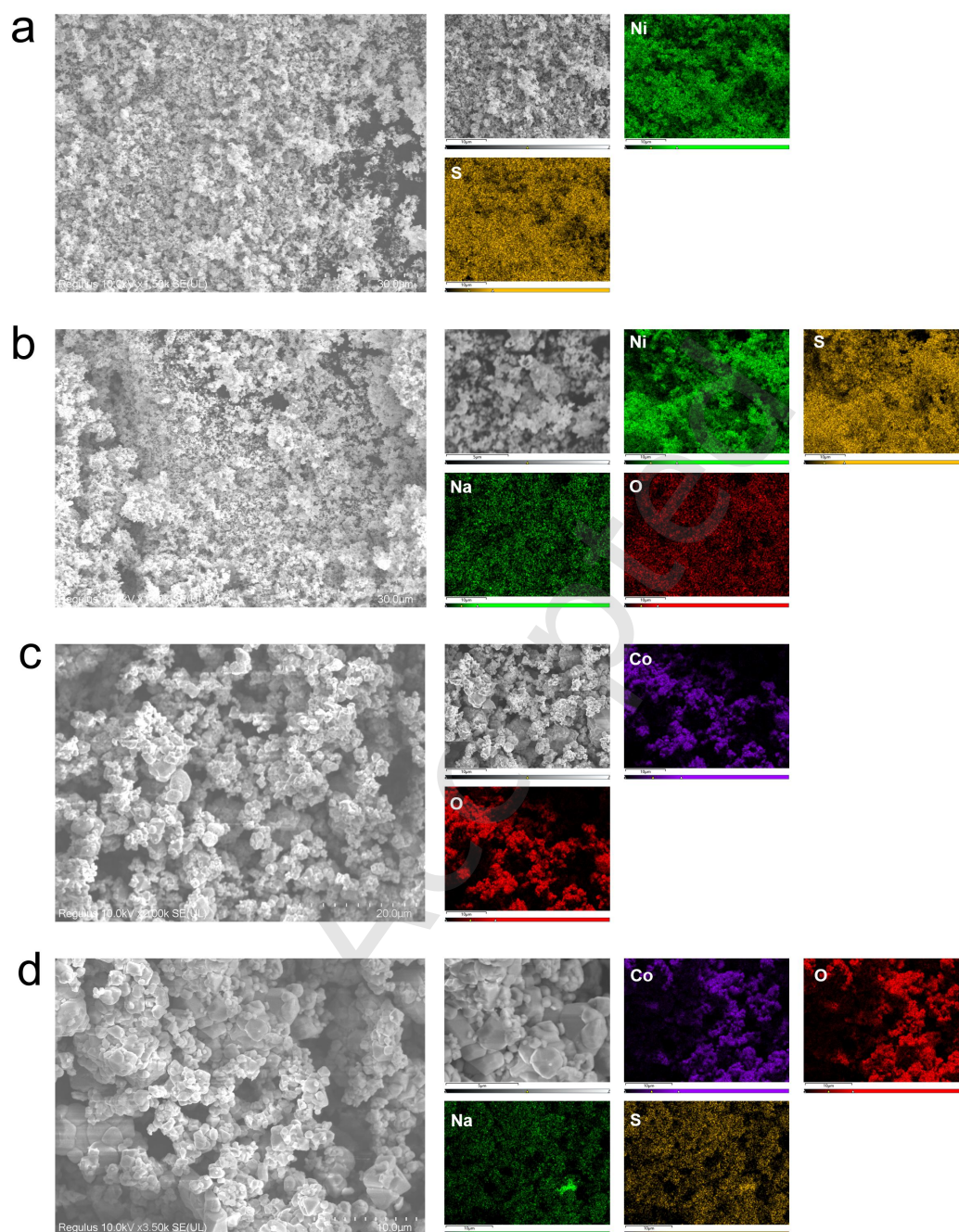


**Figure S49.** SEM and SEM-EDX images of (a)  $\text{Ni}_3\text{S}_2$ , (b)  $\text{Ni}_3\text{S}_2$ -SDS, (c)  $\text{Co}_3\text{O}_4$  and (d)  $\text{Co}_3\text{O}_4$ -SDS.

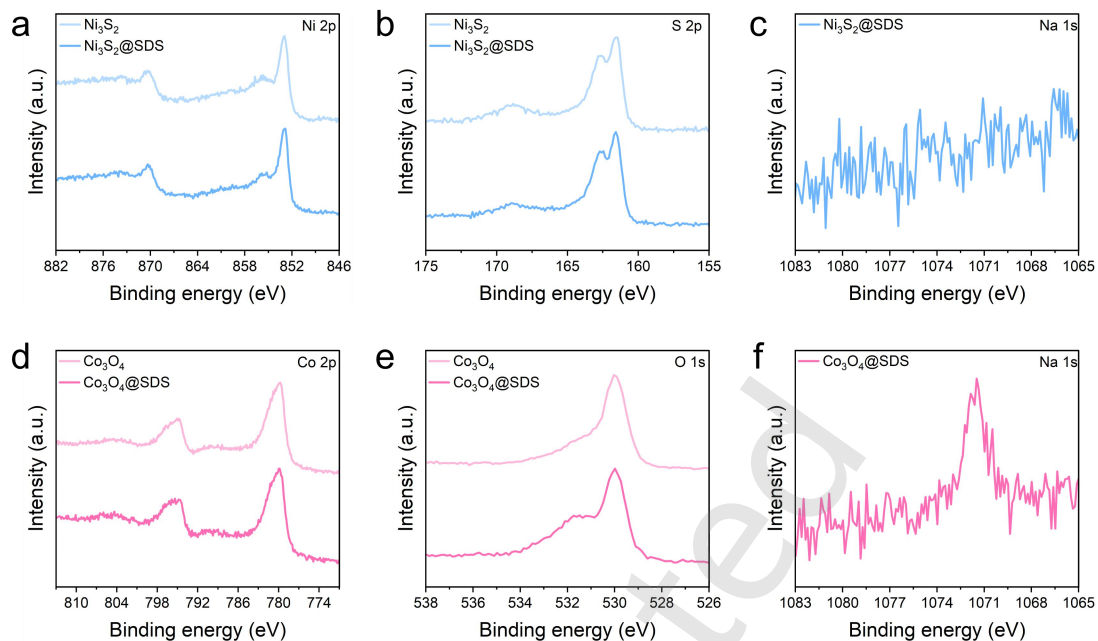


**Figure S50.** XPS spectra of (a) Ni 2p, (b) S 2p for  $\text{Ni}_3\text{S}_2$  and  $\text{Ni}_3\text{S}_2\text{-SDS}$ , (c) Na 1s for  $\text{Ni}_3\text{S}_2\text{-SDS}$ . (d) Co 2p, (e) O 1s for  $\text{Co}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4\text{-SDS}$ . (f) Na 1s for  $\text{Co}_3\text{O}_4\text{-SDS}$ .

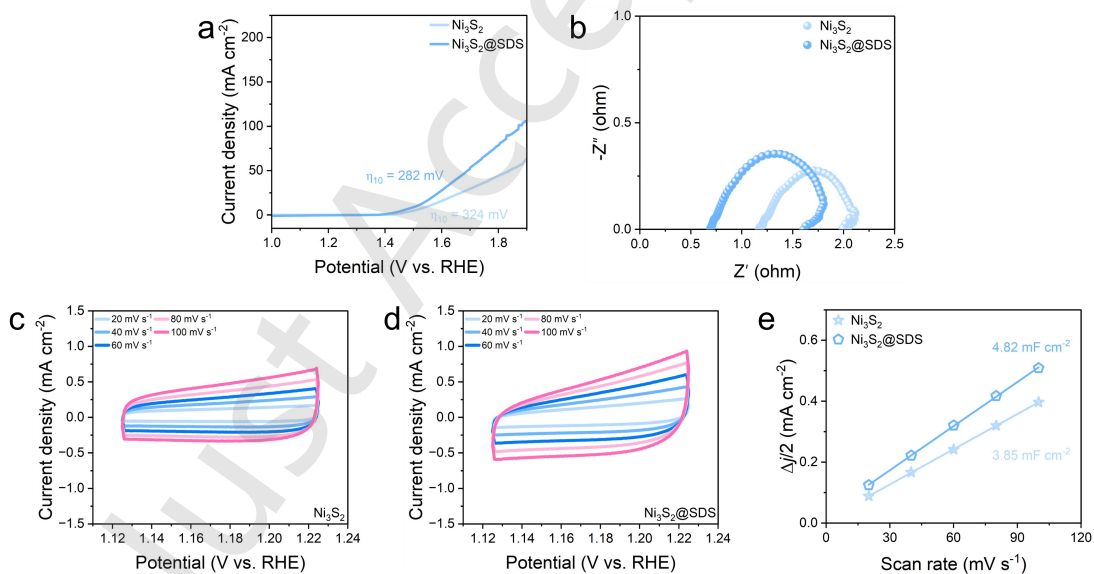


**Figure S51.** (a) LSV curves, (b) Nyquist plots of  $\text{Ni}_3\text{S}_2$  and  $\text{Ni}_3\text{S}_2\text{-SDS}$ . CV curves of (c)  $\text{Ni}_3\text{S}_2$ , (d)  $\text{Ni}_3\text{S}_2\text{-SDS}$ . ECSA of  $\text{Ni}_3\text{S}_2$  and  $\text{Ni}_3\text{S}_2\text{-SDS}$ .



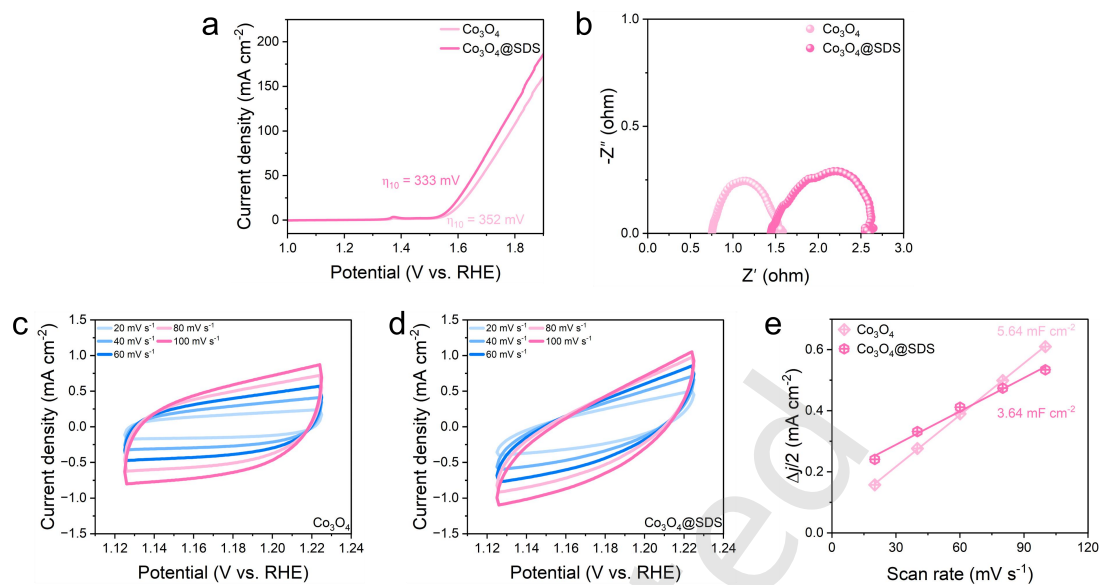


**Figure S52.** (a) LSV curves, (b) Nyquist plots of  $\text{Co}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4@\text{SDS}$ . CV curves of (c)  $\text{Co}_3\text{O}_4$ , (d)  $\text{Co}_3\text{O}_4@\text{SDS}$ . ECSA of  $\text{Co}_3\text{O}_4$  and  $\text{Co}_3\text{O}_4@\text{SDS}$ .

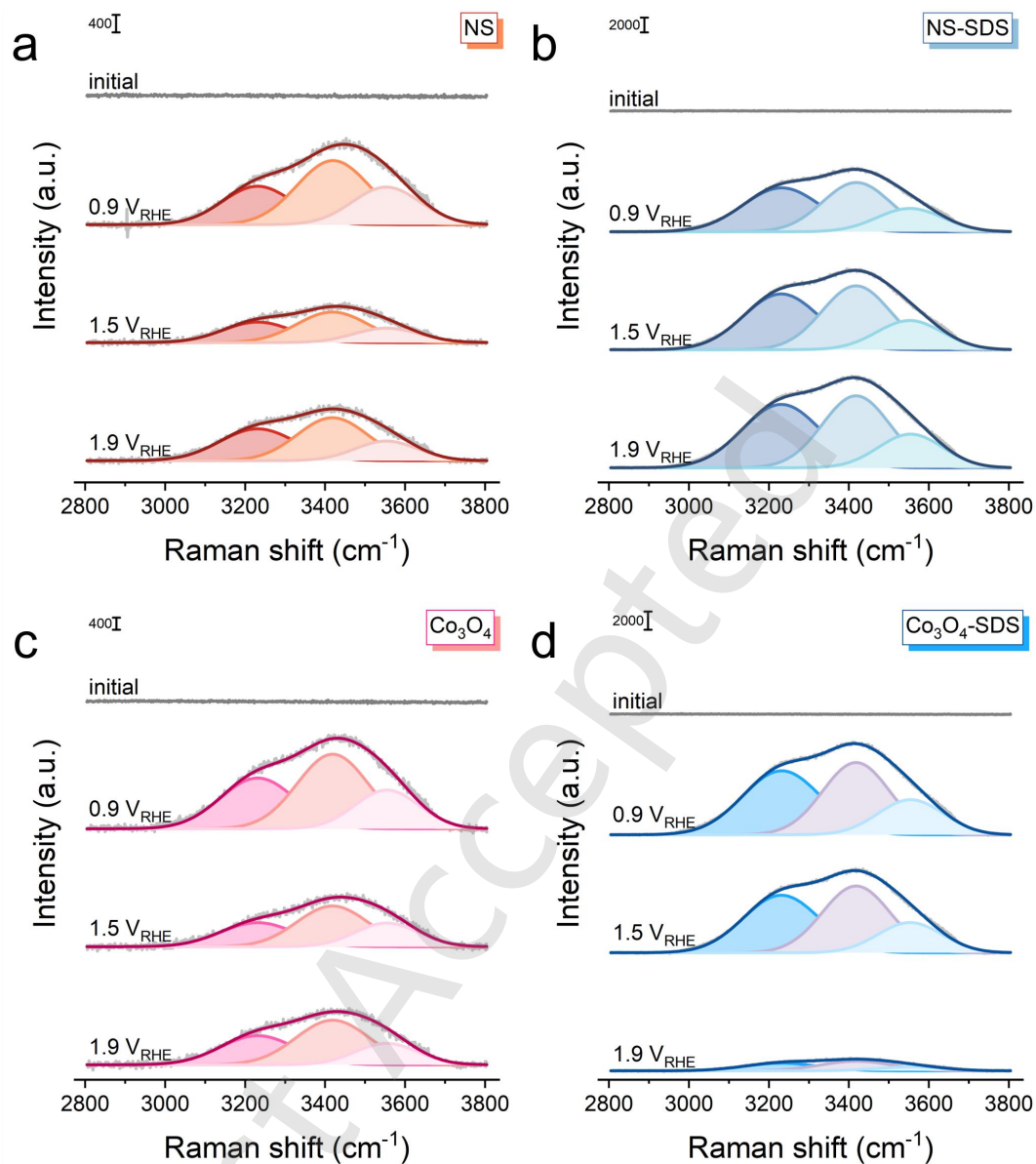


**Figure S53.** In-situ Raman spectra of interfacial water structure for (a) NS, (b) NS-SDS, (c)  $\text{Co}_3\text{O}_4$ , (d)  $\text{Co}_3\text{O}_4$ -SDS.

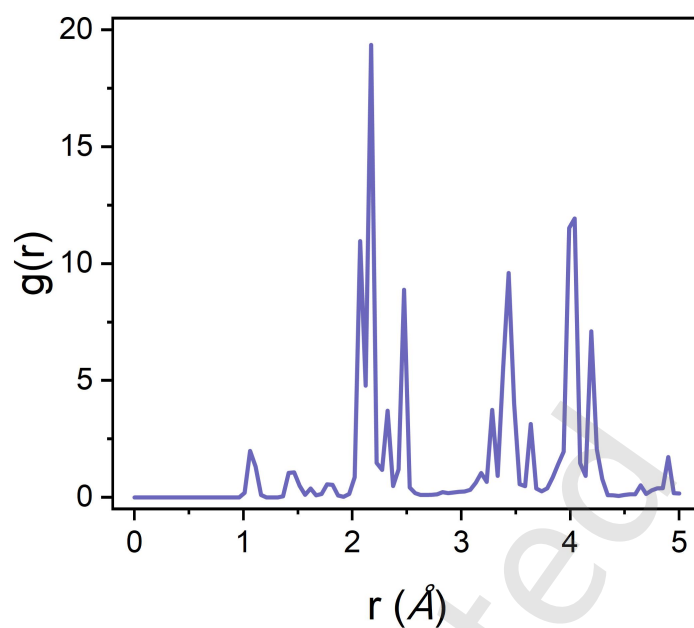


**Figure S54.** Radial distribution function (RDF) of the SDS tail chain after standing upright on CS.

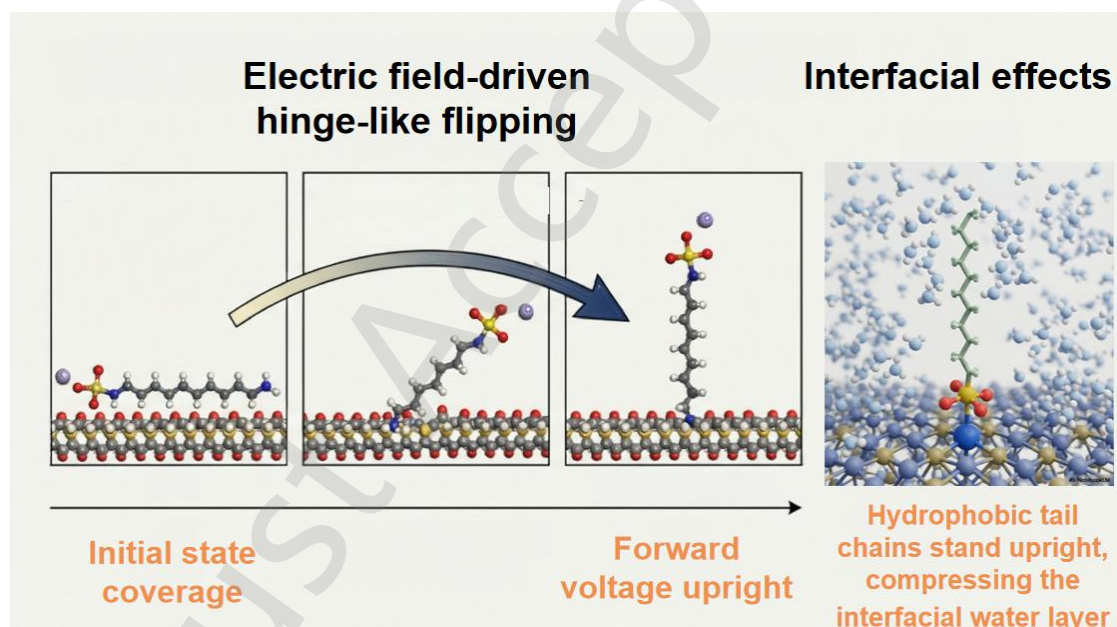


**Figure S55.** Schematic diagram of the process illustrating interfacial water structure changes caused by SDS conformational changes.

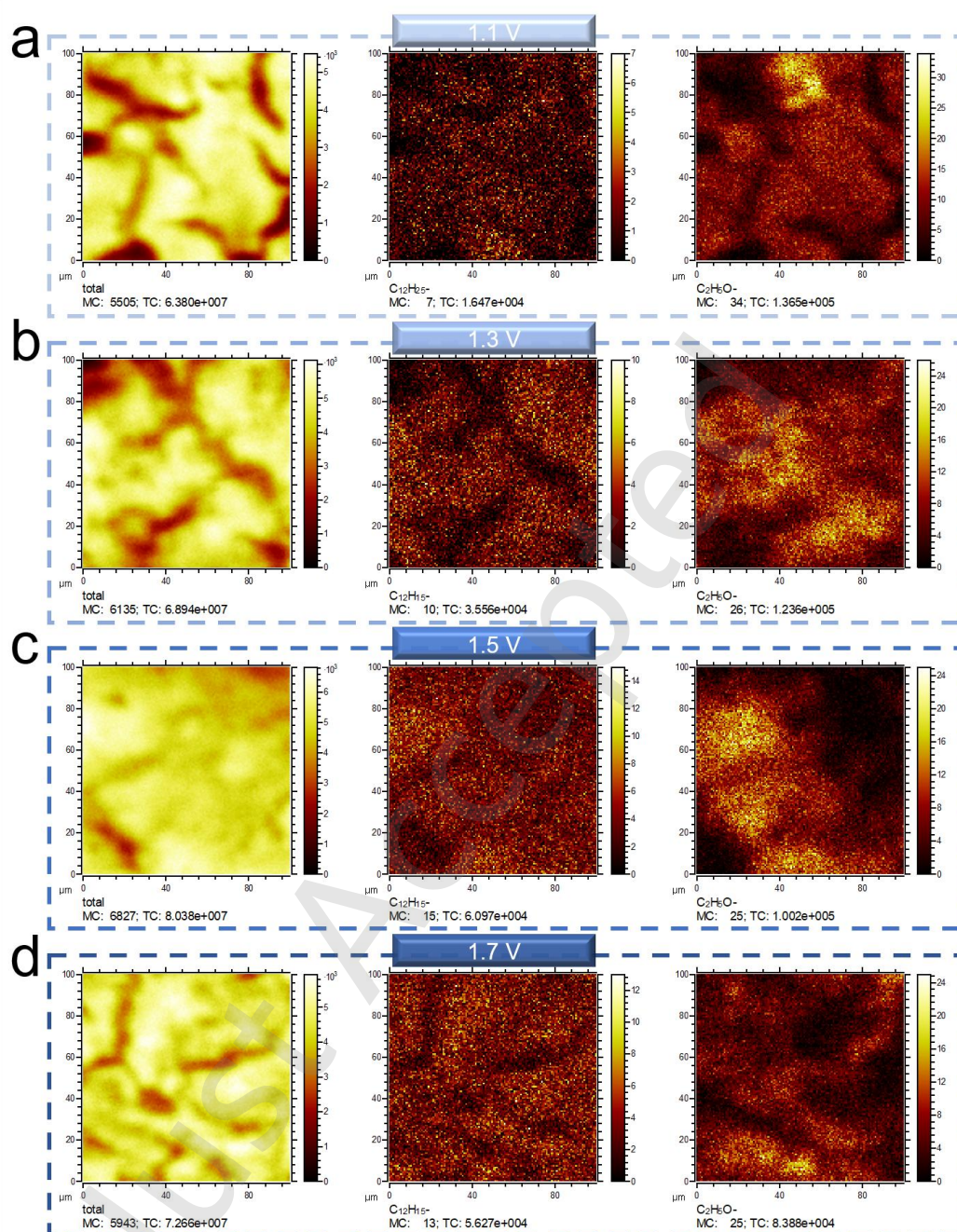


**Figure S56.** TOF-SIMS two-dimensional distribution and concentration maps of head-group and tail-chain fragments obtained from point measurements at different reconstruction potentials.



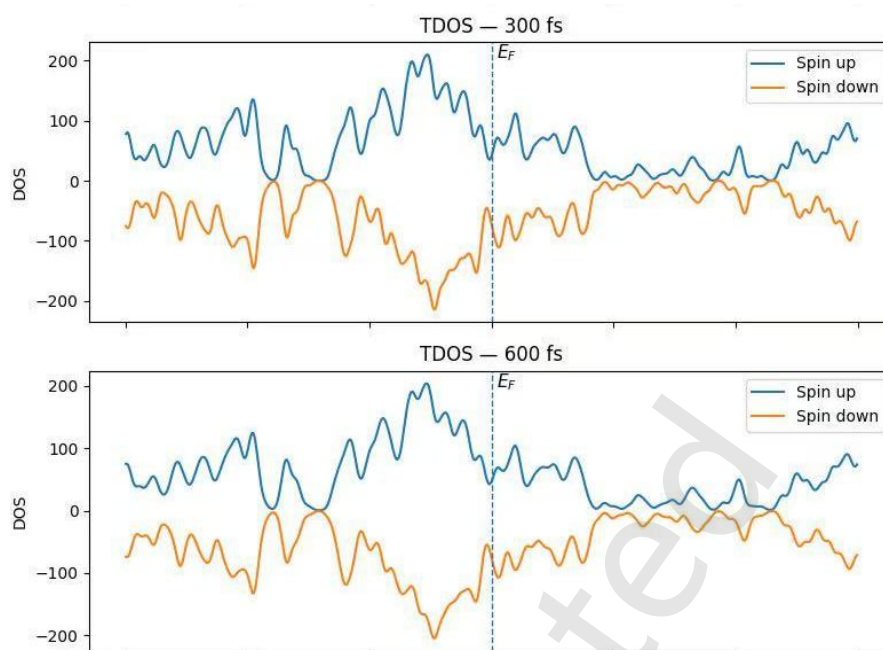


**Figure S57.** Comparison of DOS at 300 and 600 fs.

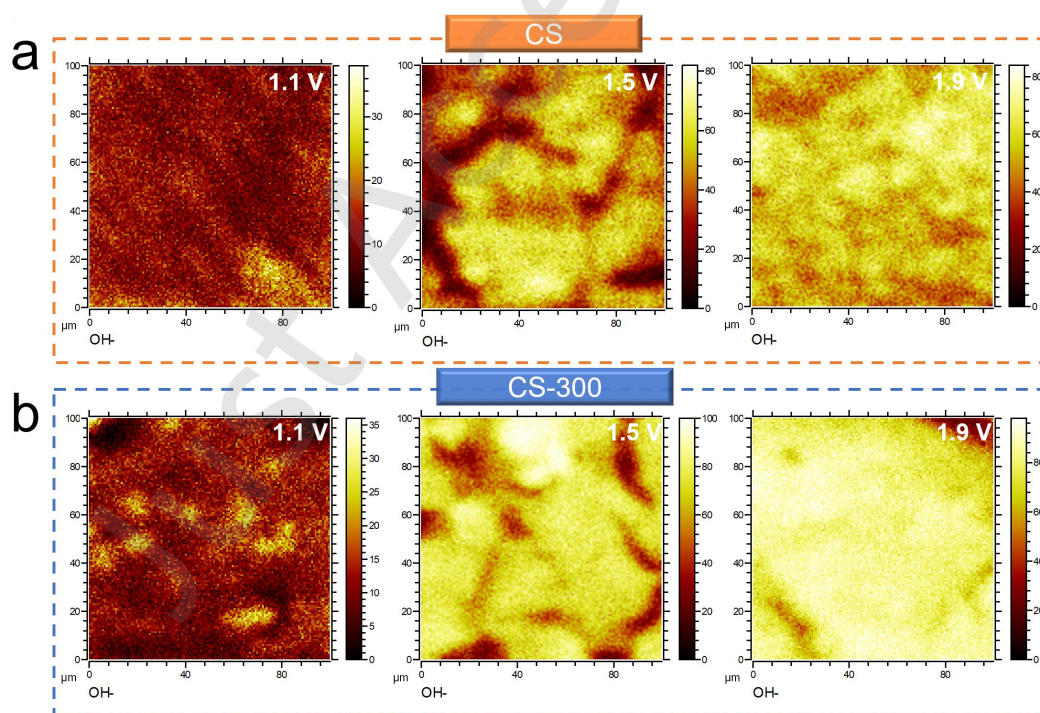


**Figure S58.** Visualization of TOF-SIMS images showing the variation of OH<sup>-</sup> content over time during reconstruction of **a** CS and **b** CS-300.



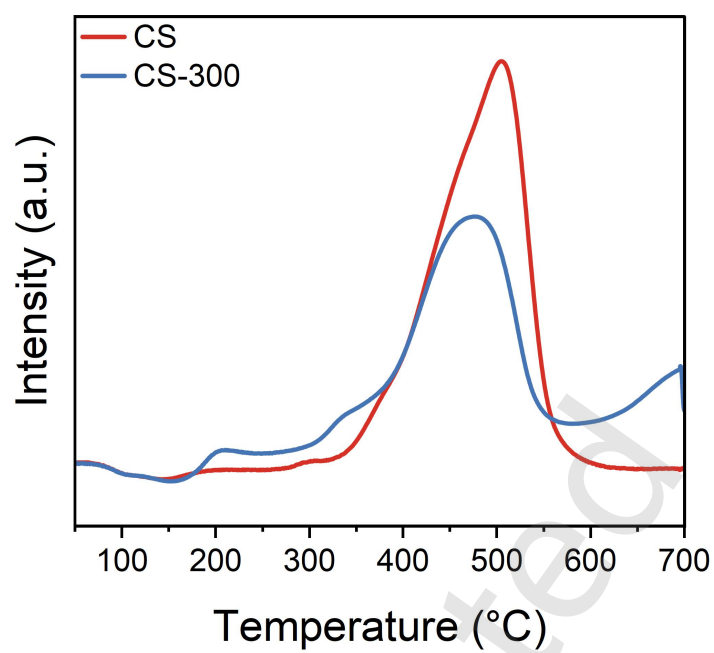


**Figure S59.** H<sub>2</sub>-TPR curves of CS and CS-300.

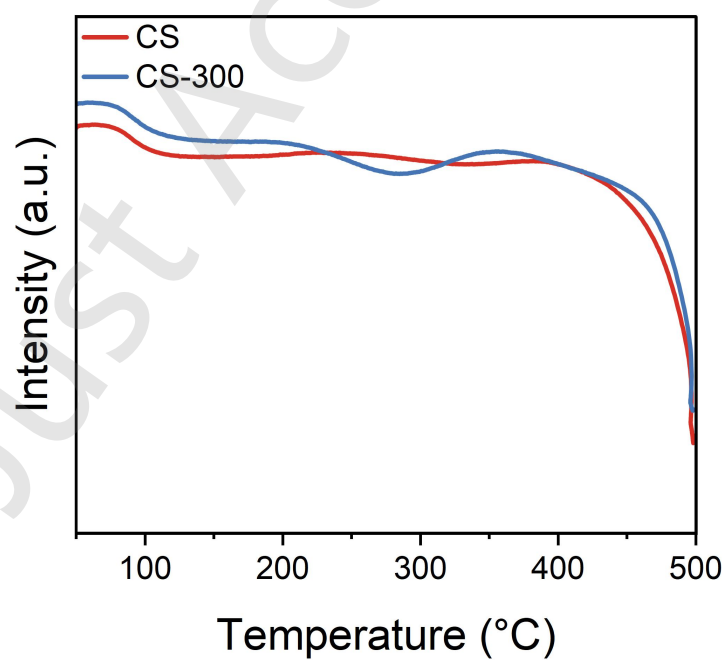


**Figure S60.** NH<sub>3</sub>-TPD curves of CS and CS-300.

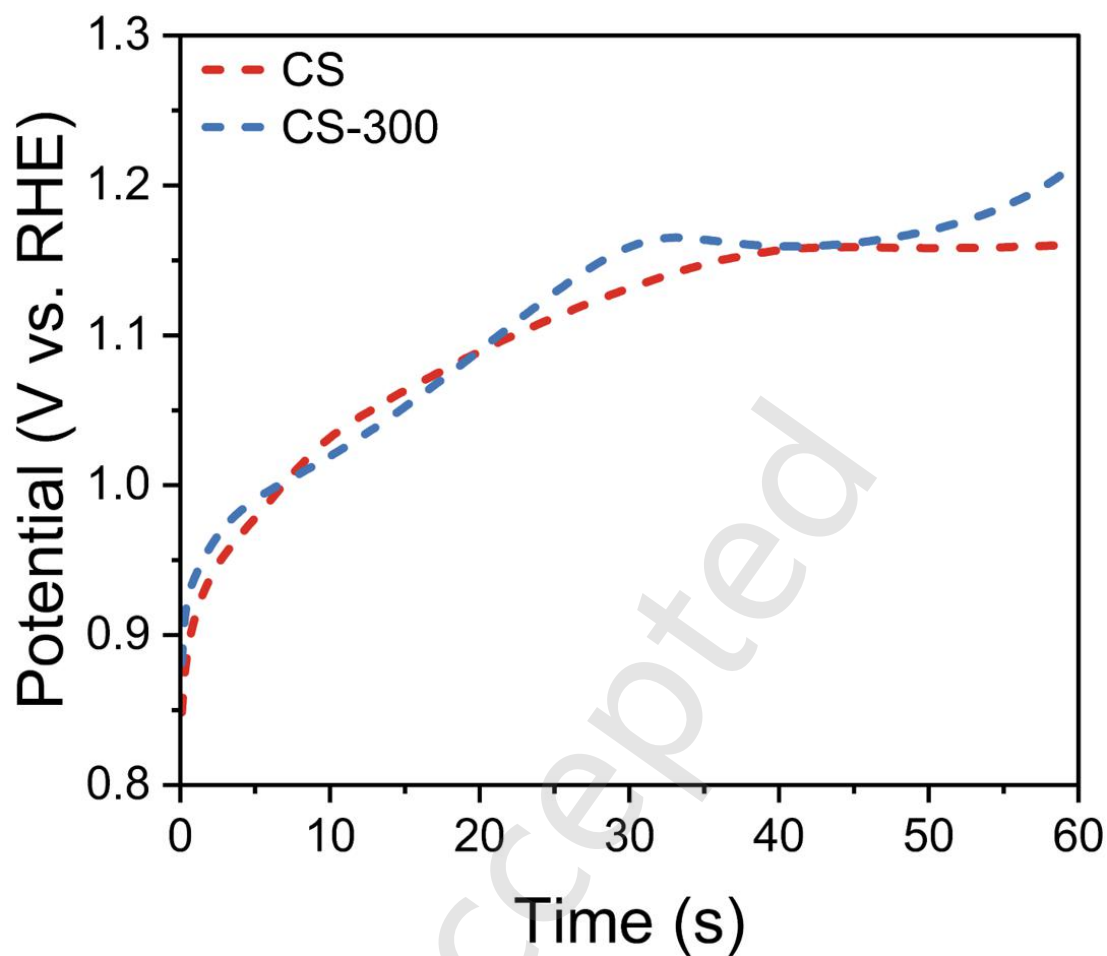


**Figure S61.** Kinetic process of the reconstruction reaction during constant current testing.

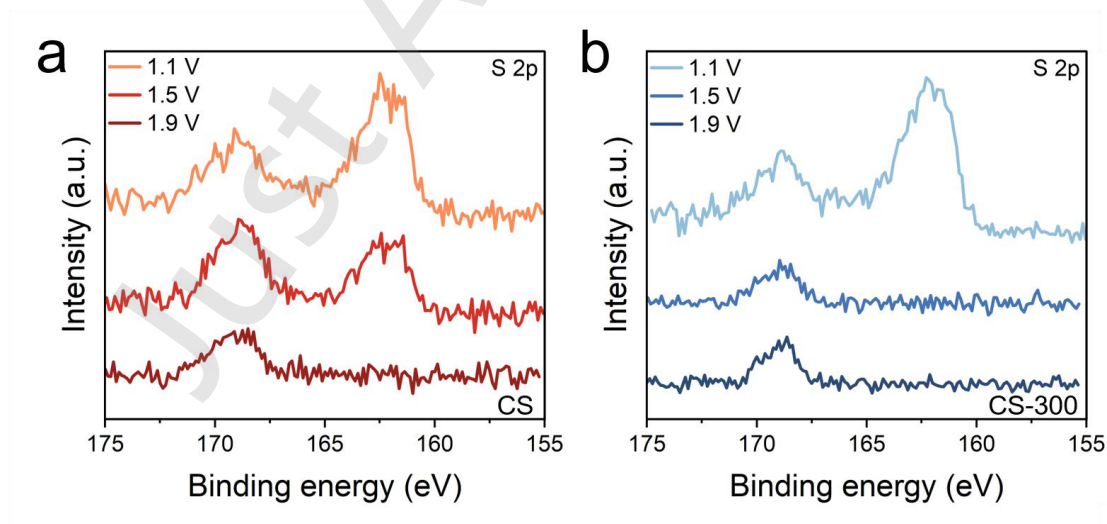


**Figure S62.** Dynamic monitoring of  $\text{S}^{2-}$  dissolution during reconstruction using vacuum-integrated coupled XPS for **a** CS and **b** CS-300.

Combining vacuum interconnection XPS for dynamic monitoring of elemental chemical states under the same potential, it is observed that as the potential increases, the attenuation rate of the  $\text{S}^{2-}$  signal in CS-300 is significantly faster than in CS. This indicates that the surface sulfur

species in CS-300 desorb more rapidly and thoroughly, clearing structural barriers for the large-scale and deep insertion of  $\text{OH}^-$ , and providing the necessary space and sites.

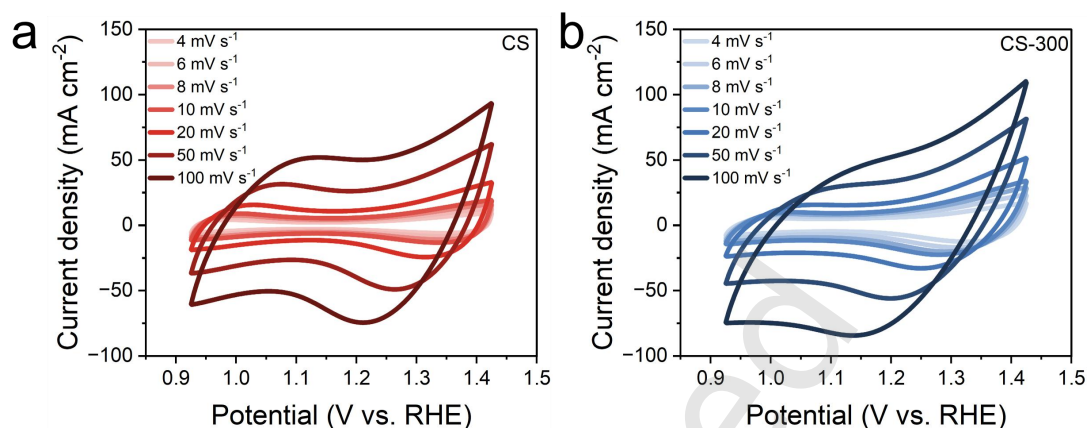


**Figure S63.** CV curves of (a) CS and (b) CS-300.

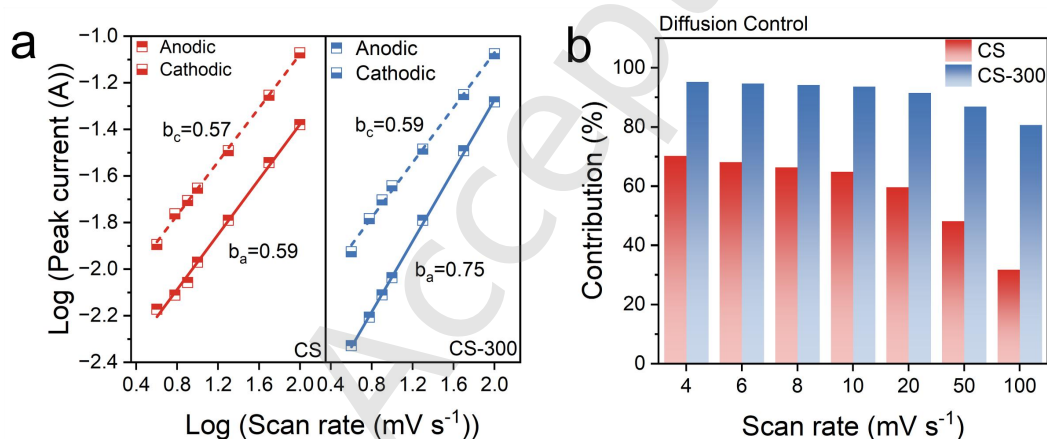


**Figure S64.** **a** Proportion of the  $\text{OH}^-$  diffusion process in CS and CS-300. **b** Intensity of the  $\text{OH}^-$  diffusion process in CS and CS-300.

The scan-rate dependence of the reconstruction-associated redox current was first analyzed using the power-law relation  $i = av^b$  where  $i$  is the peak current and  $v$  is the scan rate.  $b$  value approaching 1 indicates a stronger surface-controlled contribution, whereas a value approaching 0.5 reflects an increasing diffusion limitation. The anodic  $b$  value increases from approximately 0.59 for CS to 0.75 for CS-300, demonstrating accelerated surface-controlled reconstruction initiation.

The current response was further separated according to  $i(V) = k_1v + k_2v^{1/2}$ , where  $k_1v$  and  $k_2v^{1/2}$  represent the surface-controlled and diffusion-associated contributions, respectively. CS-300 exhibits a consistently larger diffusion-associated contribution than CS over the investigated scan-rate range, indicating enhanced  $\text{OH}^-$  transport during reconstruction propagation. These  $b$ ,

$k_1$ , and  $k_2$  parameters describe the kinetic mode and relative contributions of surface and diffusion processes and are not treated as elementary reconstruction rate constants.

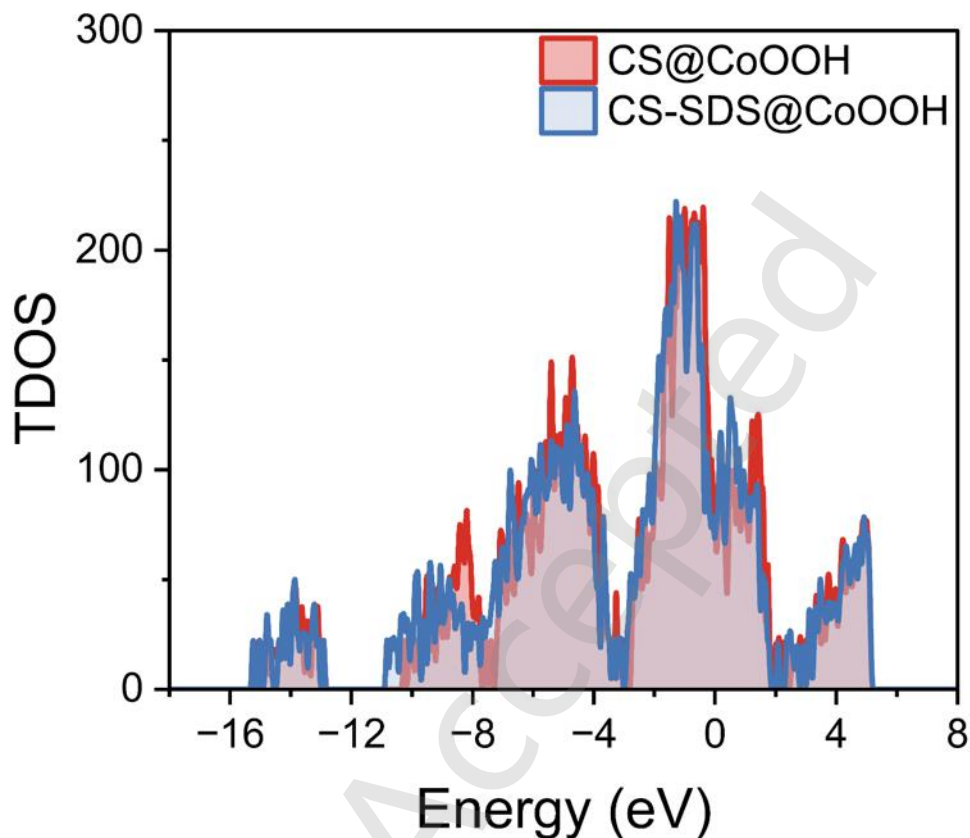


**Figure S65.** TDOS plots of CS and CS-SDS after reconstruction.

**Table S1.** Quantitative evaluation of the normalized entropy–energy competition ratio ( $\xi_{\text{rel}}$ ) for different amphiphilic molecular regulators.

| Sample | Headgroup | Alkyl tail | $N_{\text{conf}}$ | $\Delta S_{\text{rel}}$ | $\Delta E_{\text{rel}}$ | $\xi_{\text{rel}}$ | $M_s(\text{emu})$ |
|--------|-----------|------------|-------------------|-------------------------|-------------------------|--------------------|-------------------|
| CS-SOS | Sulfate   | C8         | 5                 | 0.556                   | 1                       | 0.556              | 0.237             |
| CS-300 | Sulfate   | C12        | 9                 | 1                       | 1                       | 1                  | 0.265             |
| CS-SHS | Sulfate   | C16        | 13                | 1.444                   | 1                       | 1.444              | 0.269             |
| CS-PC  | Phosphate | C12        | 9                 | 1                       | 1.46                    | 0.685              | 0.214             |

Here,  $N_{\text{conf}}$  denotes the number of conformational dihedral angles, defined as  $N_{\text{conf}} = n_C - 3$ , which represents the conformational degrees of freedom. Using  $C_{12}$  as the reference,  $\Delta S_{\text{rel}} = N_{\text{conf}}/N_{\text{conf}, C_{12}}$ . Because CS-SOS, CS-SDS and CS-SHS possess the same sulfate headgroup, their headgroup-controlled ligand-field energy terms were normalized to  $\Delta E_{\text{rel}}$ . The stronger ligand-field

contribution of the phosphate headgroup in CS-PC was quantified from the Co L-edge spectral response, giving  $\Delta E_{\text{rel}}=1.46$ . The normalized descriptor was calculated as  $\xi_{\text{rel}}=\Delta S_{\text{rel}}/\Delta E_{\text{rel}}/(\Delta S_{\text{rel,SDS}}/\Delta E_{\text{rel,SDS}})$ .

**Table S2.** Relative amounts of cobalt in different oxidation states obtained by linear component fitting of CS and CS-300.

|        | Co <sup>2+</sup> | Co <sup>3+</sup> |
|--------|------------------|------------------|
| CS     | 0.876            | 0.124            |
| CS-300 | 0.782            | 0.218            |

**Table S3.** Comparison of OER performance of recently reported OER electrocatalysts in alkaline electrolytes.

| Catalysts                             | $\eta_{10}$<br>(mV) | Ref.      |
|---------------------------------------|---------------------|-----------|
| CS-300                                | 227                 | This work |
| NiFeS-2                               | 286                 | [1]       |
| Ni <sub>3</sub> S <sub>2</sub> @Ni/NF | 310                 | [2]       |
| Ni-Fe-S/3NCQDs                        | 295                 | [3]       |
| Fe-NiO/NiS <sub>2</sub>               | 270                 | [4]       |
| FeNi <sub>3</sub> @NCNT               | 264                 | [5]       |

**Table S4.** Co ion concentration in the solution after cycling tested by ICP.

|         | CS                       | CS-300                   |
|---------|--------------------------|--------------------------|
| Content | 0.025 mg L <sup>-1</sup> | 0.013 mg L <sup>-1</sup> |

**Table S5.** Specific surface area and pore diameter values of different samples.



| Sample | $S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ ) | $V_p$ ( $\text{cm}^3 \text{g}^{-1}$ ) |
|--------|-------------------------------------------------|---------------------------------------|
| CS     | 29.87                                           | 0.19                                  |
| CS-200 | 20.54                                           | 0.12                                  |
| CS-300 | 22.78                                           | 0.15                                  |
| CS-400 | 20.91                                           | 0.12                                  |

**Table S6.** EIS data of CS and CS-X (X = 200, 300, 400).

| Sample | $R_s$ ( $\Omega$ ) | $R_{\text{ct}}$ ( $\Omega$ ) |
|--------|--------------------|------------------------------|
| CS     | 2.58               | 42.45                        |
| CS-200 | 1.43               | 5.05                         |
| CS-300 | 1.05               | 4.38                         |
| CS-400 | 2.97               | 12.83                        |

**Table S7.** The calculation process of the electrochemical active surface area (ECSA) after the same testing conditions.

| Sample | $C_{\text{dl}}$ ( $\text{mF cm}^{-2}$ ) | $C_s$ ( $\text{mF cm}^{-2}$ ) | ECSA  |
|--------|-----------------------------------------|-------------------------------|-------|
| CS     | 170.44                                  | 0.04                          | 4261  |
| CS-200 | 389.08                                  | 0.04                          | 9727  |
| CS-300 | 866.31                                  | 0.04                          | 21658 |
| CS-400 | 516.78                                  | 0.04                          | 12920 |

**Table S8.** The area and peak intensity ratios of weak hydrogen-bonded water to strong hydrogen-bonded water for CS and CS-300 under different potentials.

| Potential | CS     | CS-300 |
|-----------|--------|--------|
| 0.2 V     | 0.8254 | 0.6855 |
| 0.4 V     | 0.8076 | 0.6681 |
| 0.6 V     | 0.7787 | 0.7935 |
| 0.8 V     | 0.7315 | 0.7893 |
| 1.0 V     | 0.7102 | 0.7790 |

**Table S9.** Adsorption energies of  $^*\text{OH}$  and  $^*\text{O}$  on snapshot structures of CS-SDS at different

simulation times.

|        |     | 0 fs     | 300 fs   | 600 fs   | 1000 fs  |
|--------|-----|----------|----------|----------|----------|
| CS-SDS | *OH | -2.02 eV | -2.09 eV | -2.14 eV | -2.17 eV |
|        | *O  | -2.25 eV | -2.33 eV | -2.37 eV | -2.43 eV |

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