

High-spin transition metal atoms drive acidic oxygen evolution reactions

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Synthesizing transition metal catalysts to replace precious metal ones such as IrO₂ and RuO₂, achieving efficient acidic oxygen evolution reaction while balancing intrinsic activity, stability, and cost-effectiveness always been a dream pursued by scientists and industrialists, but still remains a challenge. Here, we present an efficient catalytic system formed by graphdiyne-induced high-spin state cobalt-based oxide (HSS-CoO_x/GDY) for enhancing the activity and stability of the acidic oxygen evolution reaction. Experimental and theoretical results demonstrate that the bonding of electron-rich *sp*-hybridized carbon and Co atoms initiates the Jahn-Teller effect of CoO₆ octahedra, which regulates the occupied *d*-orbital of Co atoms and generates the high-spin Co³⁺. Such spin occupancy breaks the spin-forbidden effect and optimizes the adsorption/desorption ability of HSS-CoO_x/GDY toward key reaction intermediates, thereby promoting the coupling of O-O bonds and the evolution of oxygen gas. The proton exchange membrane water electrolyzers constructed based on this catalyst achieve a current density of 1.0 A cm⁻² at a low cell voltage of 1.80 V. This research indicates that graphdiyne has the ability to manipulate the electronic spin states of electrocatalysts.

The kinetic bottleneck of the anodic oxygen evolution reaction (OER) is reflected in proton exchange membrane water electrolyzers (PEMWEs), which is confronted with the sluggish four-electron transfer kinetics and the strong reliance on rare and precious metal catalysts such as iridium oxide (IrO₂) and ruthenium dioxide (RuO₂)^{1–4}, which have always been difficult technical issues to overcome in this field and suppressed the rapid progress of OER technology. For many years, scientists have made tremendous efforts to achieve the replacement of precious metal catalysts with transition metal (TM)-based materials, but the results have always been insignificant. The catalytic performance is fundamentally limited by the spin-forbidden effect of oxygen-containing intermediate^{5–7}. Specifically, to satisfy angular momentum conservation (spin-allowed) during the OER process, the additional energy (~1.0 eV) is required to form the oxygen molecule (O₂) with the singlet excited state (¹Δ_g), subsequently transitions to the triplet ground state O₂ (³Σ_g⁻) (Supplementary Fig. 1)⁸. Some advanced

catalysts attempted to modulate the *d*-orbital occupancy of the catalytically active centres through spin-state manipulation. An appropriate spin configuration enables a reduction in the energy barrier of O-O coupling via Hund's rule-driven parallel spin alignment, facilitating the direct coupling of O-O bond^{9–12}. However, our anxiety is that among numerous non-precious metal systems, there is still no clear roadmap for simultaneously optimizing water dissociation (H-OH cleavage) and oxygen dimerization via spin-state control.

After years of exploration, trivalent cobalt (Co³⁺), which is low-cost and abundant on Earth, has come into the view of scientists. This is because Co³⁺ has a relatively high intrinsic OER activity, and becomes a promising alternative to Ru/Ir-based oxides^{8,13–15}. Notably, elevating the spin state of Co³⁺ can effectively activate the *e_g* orbitals, thereby enhancing OER kinetics¹⁶. However, conventional strategies predominantly focus on electronic structure tuning rather than spin-state engineering. Although a few Co-based oxides with high-spin Co³⁺ have

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been reported, such metastable states are unreliable and rapidly degrade in acidic PEMWE conditions^{10,17}. To address this core issue, discovering a corrosion-resistant catalytic system that stabilizes high-spin Co^{3+} , generates strong interactions between metal and support on the interface, and preserves high-catalytic performances represents a critical pathway toward developing durable acidic OER electrocatalysts. As a novel carbon material, graphdiyne (GDY) possesses distinctive electronic and structural features, including an sp/sp^2 -hybridized carbon framework, intrinsic nanoporous architecture, high electron mobility, and a π -conjugated system with robust metal-anchoring capability^{18–21}. The electron-rich nature of GDY facilitates charge transfer through metal-carbon bonding, which modulates the d -orbital occupancy of metal atoms^{22–27}. This strong metal-GDY charge transfer might elevate e_g orbital occupancy and trigger spin-state transitions in metal centers, consequently optimizing OER performance.

Building upon these issues, we strategically employed OER-inert Co_3O_4 as a model system to demonstrate GDY's capability in stimulating and stabilizing high-spin states of Co^{3+} for enhancing acidic OER performances. Superconducting quantum interference device (SQUID) magnetometry quantified the high-spin Co^{3+} population is 58.9% in HSS- CoO_x/GDY (Total effective magnetic moment $\mu_{\text{eff}} = 5.62 \mu\text{B}$, e_g occupancy = 1.18), contrasting sharply with bulk Co_3O_4 ($\mu_{\text{eff}} = 4.35 \mu\text{B}$, e_g occupancy = 0.12). Density functional theory (DFT) calculations revealed that high-spin centres reduce the energy barrier of the rate-determining step through the optimized e_g orbital configuration, directly accelerating O-O bond formation. This spin-state modulation originates from GDY's electron-donating π -system and uneven surface charge distribution, which induces the Jahn-Teller effect and weakens crystal field splitting (Δ_{O_h} reduced by 0.247 eV), thereby forming and stabilizing the high-spin state. The spin-polarized HSS- CoO_x/GDY exhibited a high acidic OER performance with a low overpotential of 221 mV at 10 mA cm^{-2} (140 mV lower than Co_3O_4) and good stability (>400 h at 10 mA cm^{-2} , <7.1% activity decay). When integrated into a PEMWE device, the catalyst achieved industrially relevant current densities (1.0 A cm^{-2} at 1.80 V without iR -correction) with minimal voltage drift at 200 mA cm^{-2} (<2.87 mV h^{-1} over 100 h). Mechanistic studies combining pulse voltammetry and in-situ EIS analysis revealed that the enhanced OER performance, compared to its low-spin counterpart, is attributable to a spin-aligned, facilitated electron transfer process.

Results and discussion

Orbital configuration and theoretical predictions of HSS- CoO_x/GDY

The Co_3O_4 spinel consists of corner-sharing CoO_4 tetrahedra and edge-sharing CoO_6 octahedra. According to the ligand field theory, Co^{2+} ($3d^7$) in the tetrahedral field adopts a high-spin configuration ($e_g^4 t_{2g}^3$) because the ligands have relatively less shielding effect on the d -orbitals of the central Co^{2+} ion (Fig. 1a)²⁸. Therefore, it is difficult to regulate the spin configuration of the CoO_4 tetrahedra, which results in activity that cannot be modified. In contrast, Co^{3+} in octahedral structures has been widely recognized as the primary active site of the OER^{29,30}. This inference is consistent with the density functional theory (DFT) calculation results (Supplementary Fig. 2). To further increase the catalytic activity of the Co^{3+} active center, the spin configuration of Co^{3+} in the CoO_6 octahedron is manipulated by GDY. To verify this, DFT calculations were first performed to investigate the effect of GDY on the electronic and crystal configurations of Co_3O_4 . As shown in Fig. 1b and Supplementary Fig. 3, the lattice structure of the CoO_6 octahedron is distorted after loading on GDY. The structural distortion shortens the gap between the e_g orbital and t_{2g} orbital because of the Jahn-Teller effect, which favors the electron transition from the t_{2g} orbital to the e_g orbital (Fig. 1c and Supplementary Fig. 4).

To further reveal the influence of spin states on OER performance, we explored the relationships between the spin states of Co^{3+} and structural distortions, the spin channels of Co-O bonds, and the spin alignment of $^*\text{OOH}$ intermediates, respectively. Figure 1d shows that the distortion degree ($L_{\text{max}}/L_{\text{min}}$) of the crystal structure increases with increasing spin state, further demonstrating that distorting the structure of Co_3O_4 increases the probability of producing high-spin Co^{3+} . Another key change is that the magnetic moment of lattice oxygen (O_L) is positively correlated with the spin state of Co^{3+} (Fig. 1e), meaning that the O_L is magnetized by the adjacent Co^{3+} ions. This change highlights the emergence and intensification of the spin channel between Co^{3+} and O_L , which facilitates increased delocalization of electrons and charge transport during electrocatalysis^{31,32}. In addition, the average magnetization of the oxygen atoms on the adsorbed $^*\text{OOH}$ species increases as the spin state increases (Fig. 1f). As a result, the high-spin state is conducive to the spin alignment of the oxygen-containing intermediates, and enhances the reaction kinetics by breaking the spin-forbidden effect³³. On the basis of these analyses, the Gibbs free energy profiles were calculated to explore the OER performance differences between HSS- CoO_x/GDY and Co_3O_4 (Supplementary Fig. 5). As displayed in Fig. 1g, HSS- CoO_x/GDY has a lower energy demand (0.360 eV) in the rate-determining step (RDS) than Co_3O_4 does (0.453 eV) at 1.23 V. Therefore, DFT calculations have shown that engineering high-spin Co^{3+} in Co_3O_4 by GDY has the ability to enhance the OER performance of Co_3O_4 in acidic media.

Preparation and structural investigation of HSS- CoO_x/GDY and Co_3O_4

Encouraged by the theoretical predictions, we prepared HSS- CoO_x/GDY and Co_3O_4 via simple pulsed electrochemical deposition and a low-temperature thermal oxidation method. In a typical synthesis, $\text{Co}(\text{OH})_x$ precursor is first electrodeposited on GDY or a carbon cloth substrate, followed by calcination to form HSS- CoO_x/GDY or Co_3O_4 (Fig. 2a). Scanning electron microscopy (SEM) revealed that pure Co_3O_4 and HSS- CoO_x/GDY present an interconnected 3D network (Fig. 2b, c, Fig. 2f–h, and Supplementary Fig. 6a, b), meaning that HSS- CoO_x/GDY maintains the morphology of GDY after Co_3O_4 loading. Compared to HSS- CoO_x/GDY , Co_3O_4 looks much more random and thicker (Fig. 2b, c). Atomic force microscopy (AFM) measurements revealed thicknesses of 4.8 nm for the Co_3O_4 and 4.3 nm for HSS- CoO_x/GDY , respectively (Fig. 2c, 2g). Furthermore, transmission electron microscopy (TEM) image of HSS- CoO_x/GDY revealed that Co_3O_4 nanoparticles were dispersed on the GDY surface (Fig. 2i and Supplementary Fig. 7), while the Co_3O_4 samples without GDY present the structure of nanosheets (Fig. 2d). High-resolution TEM (HRTEM) images show that the lattice distance of the (311) plane (0.245 nm) in Co_3O_4 is irregularly expanded to 0.247 nm, 0.250 nm and 0.255 nm in HSS- CoO_x/GDY (Fig. 2e and 2j–2l), indicating that the degree of lattice distortion ranges from 0.8% to 4.08%. This conclusion was confirmed by the X-ray diffraction (XRD) patterns (Fig. 2m). In addition, some stepped interfaces exist in HSS- CoO_x/GDY (Fig. 2n–q), further confirming the presence of defects and distortions in the crystal structure of HSS- CoO_x/GDY . Energy-dispersive spectroscopy (EDS) elemental mapping results confirmed the distribution of the C, O, and Co elements on the entire HSS- CoO_x/GDY (Supplementary Fig. 8). From the above analysis, it is concluded that GDY plays a constructive role in constructing the expansion and stepped interfaces of the crystal structure^{34,35}. This situation destroyed the structural symmetry of Co_3O_4 and redistributed the d -orbital level of Co^{3+} , which could regulate the electronic configuration of the e_g orbital.

Characterization of the electronic structure and spin states

The electronic structure and coordination environment were analyzed via Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS). Raman spectroscopy of the pure

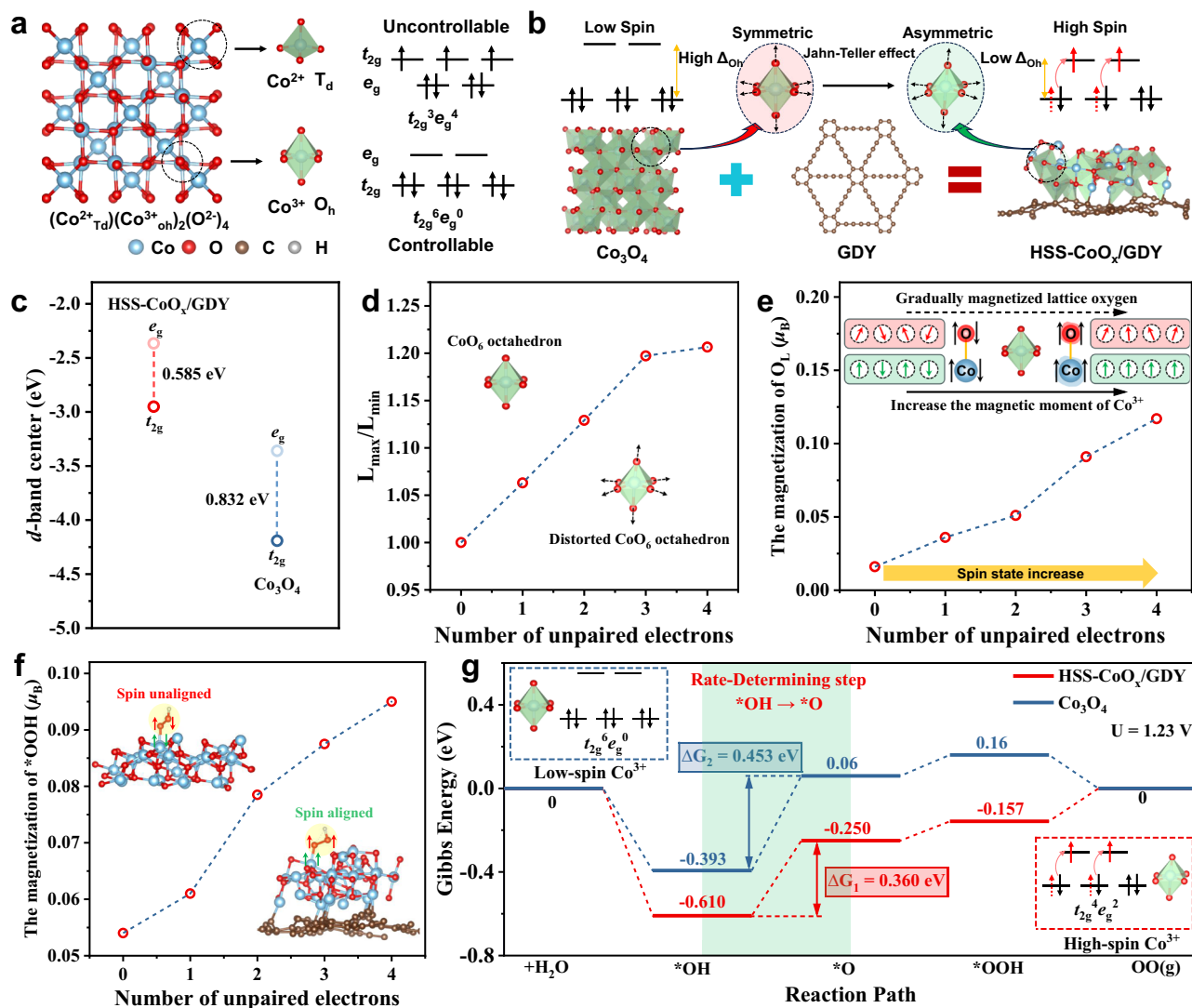


Fig. 1 | DFT calculations. **a** Structural model of Co_3O_4 . **b** Illustration of the relationship between the crystal splitting energy (Δ_{Oh}) and the structure in the octahedral field. **c** The calculated e_g and t_{2g} band centers in HSS- CoO_x/GDY and Co_3O_4 . **d** Relationship between the distortion of octahedral structures and the spin state. The insets show the structural model of standard and distorted CoO_6 octahedra. **e** The calculated lattice oxygen magnetization during the spin state increases. The

inset is a schematic illustration of a high-spin Co^{3+} atom polarizing the surrounding O atoms. **f** The magnetization of the adsorbed $^*\text{OOH}$ species during the spin state increase and the corresponding structural diagram is presented in the inset. **g** Gibbs free energy diagrams of the OER on the octahedral Co^{3+} in HSS- CoO_x/GDY and Co_3O_4 . The distribution of d -electron in t_{2g} and e_g orbitals for high and low-spin Co^{3+} is presented in the inset.

Co_3O_4 revealed that a significant A_{1g} symmetry peak at 676 cm^{-1} originating from the vibrational mode of $\text{Co}^{\text{III}}\text{O}$ in CoO_6 units (Fig. 3a). This peak blue-shifted to 698 cm^{-1} in HSS- CoO_x/GDY , confirming that the structural symmetry of the CoO_6 octahedron is broken^{36,37}. Furthermore, the peak for acetylenic bonds in pure GDY (2163 cm^{-1}) positively shifts to 2182 cm^{-1} in HSS- CoO_x/GDY , indicating the occurrence of interactions between Co_3O_4 and GDY^{38,39}. This phenomenon is also visualized by the differential charge density (Supplementary Fig. 9). To further investigate the interactions between Co_3O_4 and GDY, the C 1s and Co 2p XPS spectra of HSS- CoO_x/GDY were obtained. In the C 1s spectra (Supplementary Fig. 10a), an additional peak at 283.5 eV , which is consistent with the sp -C-Co bond appeared⁴⁰. In addition, upon composite formation with Co_3O_4 , the binding energy of the sp -C bond in GDY shows a positive shift from 285.0 eV to 285.15 eV . In return, the Co 2p XPS spectra clearly exhibited a higher $\text{Co}^{2+}/\text{Co}^{3+}$ ratio (0.75) on the surface of HSS- CoO_x/GDY than that of Co_3O_4 (0.51) (Supplementary Fig. S10b). Similarly, the Co K-edge X-ray absorption near-edge structure (XANES) revealed that a lower oxidation state (+2.53) of Co in HSS- CoO_x/GDY than in Co_3O_4 (+2.67) (Fig. 3b and

Supplementary Fig. 11). The lower Co valence state provided additional evidence for the presence of high-spin Co^{3+9} . In addition, the charge transfer between GDY and Co atoms generates a strong interaction, increases the intrinsic activity of the Co^{3+} while stabilizes catalytic active centers^{22,26,41}. Further, the pre-edges of HSS- CoO_x/GDY , attributed to the transition from the Co 1s core level to Co 3d states, are stronger than those of Co_3O_4 (Fig. 3b). This phenomenon indicates that the Co site is not centrosymmetric in HSS- CoO_x/GDY . To further investigate the local coordination environment of Co, we analyzed the Fourier transform extended X-ray absorption fine structure (FT-EXAFS) of HSS- CoO_x/GDY and Co_3O_4 (Fig. 3c). By fitting the FT-EXAFS data (Fig. 3d, Supplementary Fig. 12, and Supplementary Table 1), we find that the average coordination number (CN) of Co-O and $\text{Co}_{\text{oh}}\text{-Co}_{\text{td}}$ decreased from 5.06 and 9.73 to 4.11 and 4.97 after the introduction of the GDY substrate, respectively. In stark contrast, the average CN of $\text{Co}_{\text{oh}}\text{-Co}_{\text{oh}}$ increased from 3.94 to 6.13, indicating that GDY disrupted the symmetry of the Co_3O_4 crystal structure. Additionally, the fit results of bond length confirmed that GDY led to the elongation of the Co-O ($1.91\text{ \AA}$ to $1.94\text{ \AA}$), $\text{Co}_{\text{oh}}\text{-Co}_{\text{oh}}$ ($2.86\text{ \AA}$ to $2.89\text{ \AA}$), and $\text{Co}_{\text{oh}}\text{-Co}_{\text{td}}$

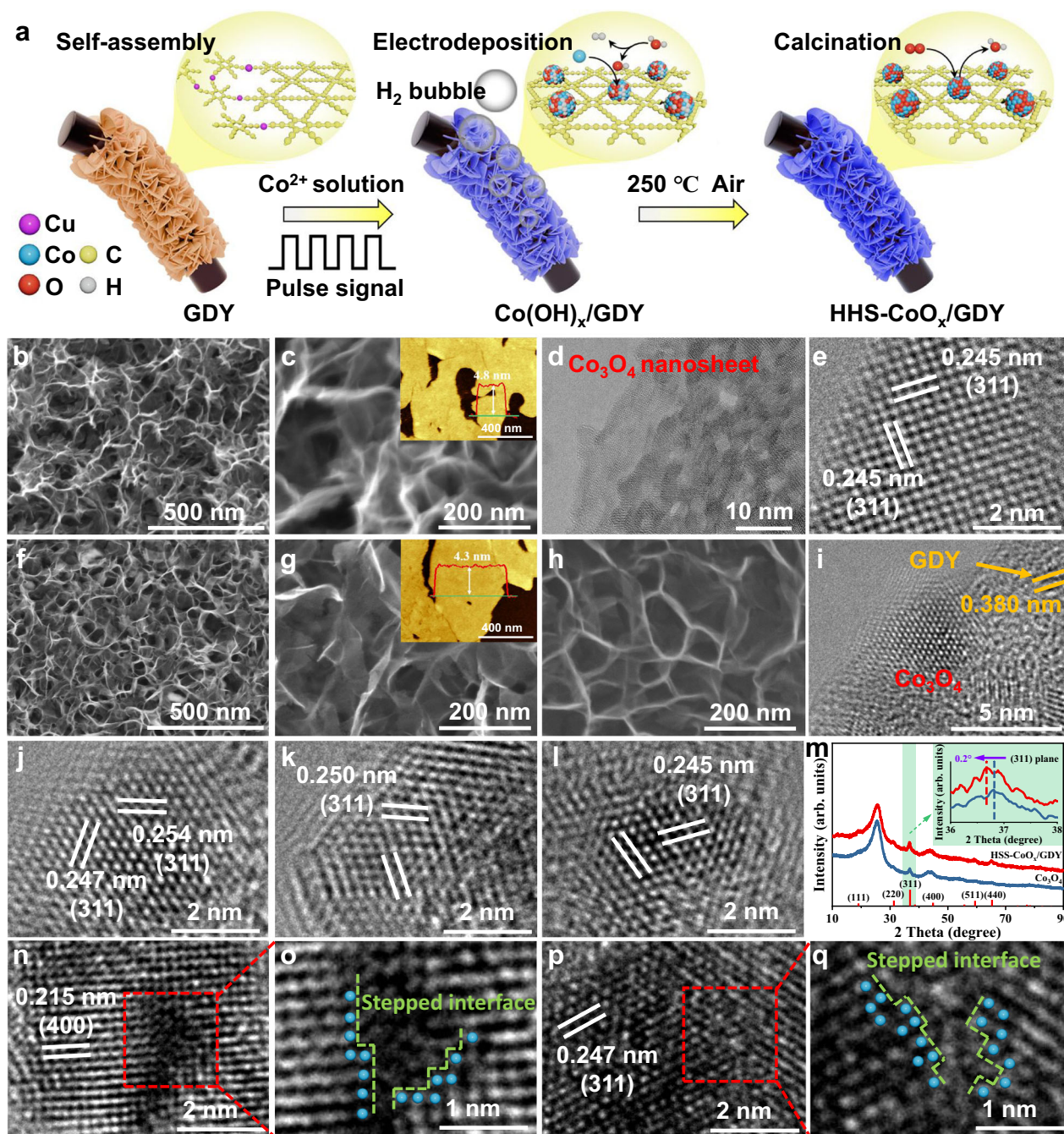


Fig. 2 | Synthesis and morphological characterization. **a** Illustration of the synthesis of HSS-CoO_x/GDY. **b, c** SEM images of Co₃O₄ (Inset: AFM image of Co₃O₄). **d** TEM image of Co₃O₄. **e** HRTEM image of Co₃O₄. **f, g** SEM images of HSS-CoO_x/GDY (Inset: AFM images of HSS-CoO_x/GDY). **h** SEM images of GDY. **i-l** HRTEM

images of HSS-CoO_x/GDY. **m** XRD patterns of HSS-CoO_x/GDY and Co₃O₄ (Inset: Magnified image of the (311) plane). **n-q** HRTEM images of HSS-CoO_x/GDY, in which some stepped interfaces exist.

(3.36 Å to 3.40 Å) bonds, the change ratio for bond length is 1.57%, 1.05%, and 1.19%, respectively, which is in good agreement with XRD and HRTEM results. The wavelet transforms of EXAFS (WT-EXAFS) analysis of the Co K-edge show that the *k* position of the Co-O/C bond in HSS-CoO_x/GDY decreases from 7.21 Å⁻¹ to 6.77 Å⁻¹ (Supplementary Fig. 12), which is attributed to the presence of the *sp*-C-Co bond. These results suggest that GDY has the ability to disrupt the symmetry of the CoO₆ octahedron and modify the local environment of Co³⁺, finally leading to the formation of high-spin Co³⁺.

In light of the above findings, the superconducting quantum interference design (SQUID) technique was used to delve into the magnetic behavior and spin configuration of HSS-CoO_x/GDY, Co₃O₄

and commercial Co₃O₄ (Com-Co₃O₄) (Fig. 3e). First, the magnetic hysteresis (**M-H**) curves of these samples were measured in a magnetic field from -50,000 Oe to 50,000 Oe under ambient conditions. The **M-H** curves of all the samples show a linear shape without a hysteresis loop and saturation magnetization (Fig. 3f), suggesting paramagnetic behavior⁴². However, the alteration in their slope signifies a change in magnetic susceptibility (χ , $\chi = \mathbf{M}/\mathbf{H}$), further implying that their spin configurations have obvious differences. To quantify the electron occupancy of *e_g* orbitals, the temperature-dependent magnetization (**M-T**) curves were recorded under zero field cooling (ZFC) and field cooling (FC) between temperatures ranging from 4 K to 300 K at **H** = 150 Oe. As shown in Fig. 3g, the Néel temperatures of HSS-CoO_x/

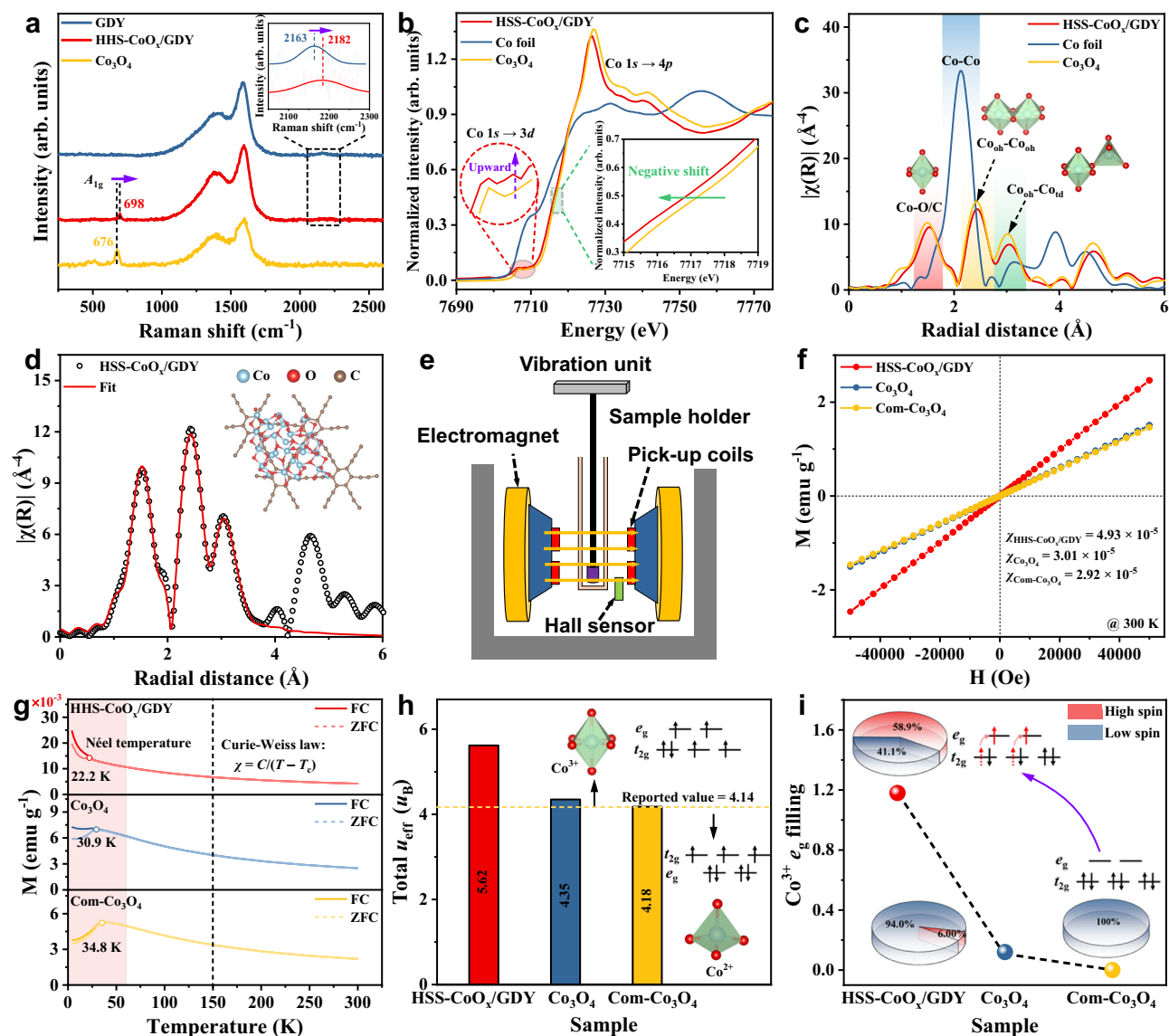


Fig. 3 | Electronic structure and spin state characterization. **a** Raman spectra of HSS-CoO_x/GDY, Co₃O₄, and GDY. The inset provides enlarged panels showing the Raman shifts in the range of 2050 cm⁻¹ to 2300 cm⁻¹ for GDY and HHS-CoO_x/GDY range. **b** Co K-edge XANES spectra of Co foil, Co₃O₄ and HSS-CoO_x/GDY (Inside: the enlarged view of the pre-edge (7705 eV to 7710 eV) and edge (7715 eV to 7719 eV) for Co K-edge). **c** Fourier transforms of k³-weighted EXAFS spectra of Co foil, Co₃O₄, and HSS-CoO_x/GDY, and the inset displays the scattering paths and structural model of Co-O, Co_{oh}-Co_{oh}, and Co_{oh}-Co_{td} local environment. **d** Fitting curve of HSS-CoO_x/GDY. Inset: The fitted structural model for HHS-CoO_x/GDY. **e** Model of

superconducting quantum interference design. **f** Magnetic hysteresis loops of HSS-CoO_x/GDY, Co₃O₄, and Com-Co₃O₄ at 300 K. **g** FC (field cooled) and ZFC (zero field cooled) magnetization curves of HSS-CoO_x/GDY, Co₃O₄, and Com-Co₃O₄ as a function of temperature at H = 150 Oe. **h** The calculated total μ_{eff} . The inset shows the contributions of Co²⁺ ($e_g^4 t_{2g}^3$) and Co³⁺ ($t_{2g}^4 e_g^2$) to the total μ_{eff} . **i** The volume fraction of Co³⁺ and corresponding e_g orbital filling of HSS-CoO_x/GDY, Co₃O₄, and Com-Co₃O₄. Inset: Schematic diagram of the transition from a low-spin state to a high-spin state.

GDY are distinctly lower than those of Co₃O₄ and Com-Co₃O₄, indicating that GDY alters the magnetic properties of Co₃O₄. Further, the Curie constant (C) value was obtained by fitting the slopes of the M-T curves above 150 K, and these values are 0.253, 0.423, and 0.458 for HSS-CoO_x/GDY, Co₃O₄, and Com-Co₃O₄, respectively (Supplementary Fig. 13)⁴³. The total effective magnetic moment (μ_{eff}) was also calculated, which was 4.35 μ_B and 4.18 μ_B for Co₃O₄ and Com-Co₃O₄, respectively (Fig. 3h). These were close to the previously reported practical measured value of Co²⁺ (4.14 μ_B) in reported previously, suggesting that almost all of Co³⁺ ions in both Co₃O₄ and Com-Co₃O₄ are in a low-spin state⁴⁴. Interestingly, the μ_{eff} value of HSS-CoO_x/GDY is 5.62 μ_B , indicating the presence of high-spin Co³⁺. The volume fraction of high-spin Co³⁺ is determined to be approximately 58.9%, and the corresponding average e_g orbital filling is 1.18 (Fig. 3i; more details

are provided in Supplementary Table 2)⁴⁵. These results provide solid evidence that GDY is capable of generating high-spin Co³⁺ in Co₃O₄. Notably, the degree of spin polarization has become an interesting descriptor of OER activity because it optimizes the adsorption capacity of reaction intermediates and accelerates charge transfer.

Catalytic performance in acidic media

To explore the influence of high-spin Co³⁺ on OER activity, the acidic OER performances of HSS-CoO_x/GDY and Co₃O₄ were first evaluated in 0.5 M H₂SO₄ solution by a traditional three-electrode system (Supplementary Fig. 14). As shown in Fig. 4a, pure Co₃O₄ has a relatively poor activity, presenting overpotentials of 361 mV and 476 mV to reach current densities of 10 mA cm⁻² and 100 mA cm⁻², respectively. After engineering the spin state of Co³⁺ in Co₃O₄ by GDY, the OER

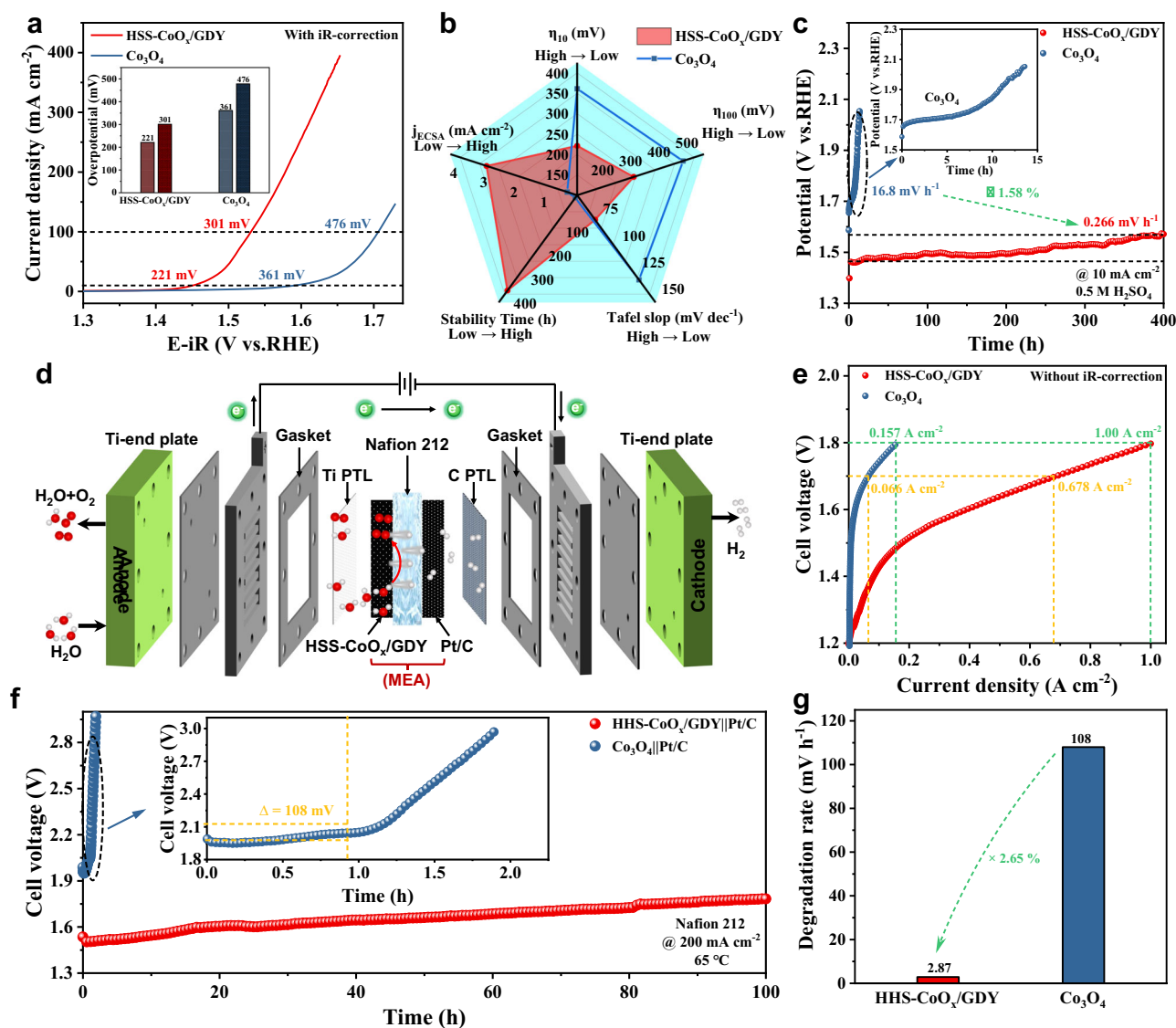


Fig. 4 | Evaluation of the electrochemical OER performance in acidic media.

a LSV curves with *iR*-correction of HSS-CoO_x/GDY and Co₃O₄ in 0.5 M H₂SO₄ solution (pH = 0 ± 0.02) at a scan rate of 5 mV s⁻¹, where R_{sol} was measured to be $4.0 \pm 0.1 \Omega$ for HSS-CoO_x/GDY and $5.0 \pm 0.1 \Omega$ for Co₃O₄. The inset shows the overpotential of HSS-CoO_x/GDY and Co₃O₄ at 10 mA cm⁻² and 100 mA cm⁻², respectively. **b** Comparison of the OER performances of HSS-CoO_x/GDY and Co₃O₄.

c Chronopotentiometry tests of HSS-CoO_x/GDY and Co₃O₄ at 10 mA cm⁻² (Inset: the enlarged E-t curve for Co₃O₄ in the three-electrode system). **d** Structural model of the PEMWE setup. **e** Polarization curves for HSS-CoO_x/GDY and Co₃O₄ anode-based electrolyzers at 65 °C at a flow rate of 30 mL min⁻¹. **f** Stability curves and **g** degradation rate of HSS-CoO_x/GDY || Pt/C and Co₃O₄ || Pt/C at a current density of 200 mA cm⁻² (Inset: the enlarged E-t curve for Co₃O₄ in the PEMWE device).

activity was increased. Specifically, HSS-CoO_x/GDY only required low overpotentials of 221 mV and 301 mV at 10 mA cm⁻² and 100 mA cm⁻², respectively. The corresponding Tafel slope for HSS-CoO_x/GDY (72.9 mV dec⁻¹) is smaller than that of Co₃O₄ (128.9 mV dec⁻¹), indicating the fast reaction kinetics (Fig. 4b and Supplementary Fig. 15). In addition, the electrochemical surface area (ECSA) values were extracted by measuring the cyclic voltammetry (CV) curves with different scan rates (Supplementary Fig. 16a-b). The calculated ECSA value for HSS-CoO_x/GDY is 8.00 cm², which is 3.94 times greater than that of Co₃O₄ (2.03 cm²), indicating that the more active sites are exposed at the reaction interface (Supplementary Fig. 16c). To compare their intrinsic OER activity, the polarization curves were normalized by the ECSA values. As shown in Fig. 4b and Supplementary Fig. 16d, the intrinsic activity of HSS-CoO_x/GDY (3.00 mA cm⁻²) was still higher than that of pure Co₃O₄ (0.33 mA cm⁻²) at 1.65 V. Furthermore, the catalytic stability of HSS-CoO_x/GDY was examined via CV and chronopotentiometry (CP) protocol. As illustrated in Fig. 4c and

Supplementary Fig. 17, HSS-CoO_x/GDY maintained almost constant activity over 400 h at 10 mA cm⁻², and maintained an unattenuated LSV curve after 10,000 cycles of CV testing. Such high stability has also been verified through ¹⁸O-labeled in-situ differential electrochemical mass spectrometry (DEMS) measurement (Supplementary Fig. 18) and in-situ XAS (Supplementary Fig. 20). As presented in Supplementary Fig. 19, the ratio of ³⁴O₂ to ³²O₂ and ³⁶O₂ to ³²O₂ in HSS-CoO_x/GDY is consistently lower than that of Co₃O₄, reflecting that the adsorption evolution mechanism dominated the OER process for HSS-CoO_x/GDY, thereby enhancing the stability⁴⁶. In-situ XAS also confirmed that the local environment and valence of Co in HSS-CoO_x/GDY undergo slight changes with potential variation, while a severe oscillation occurs in Co₃O₄ (Supplementary Fig. 21). Furthermore, the characterization of spent HSS-CoO_x/GDY after the OER test by TEM-EDS, XPS, and SQUID revealed that no obvious changes in morphology and electronic structure (Supplementary Figs. 22, 23 and Supplementary Table 2), further highlighting that HSS-CoO_x/GDY has a high catalytic activity

and structural stability. In terms of activity and stability, HSS-CoO_x/GDY is competitive with most previously reported Co-based oxide catalysts in acidic media (Supplementary Fig. 24 and Supplementary Table 3).

Motivated by the above results of the three-electrode test, HSS-CoO_x/GDY was assembled as an OER catalyst in a real PEMWE system to evaluate its performance (Fig. 4d). The steady-state polarization curves (without *iR*-correction) revealed much higher PEMWE activity when HSS-CoO_x/GDY was used as the anode catalyst than when pure Co₃O₄ was used (Fig. 4e). Specifically, a cell voltage of 1.80 V delivers a current density of 1.0 A cm⁻², which is higher than that of pure Co₃O₄ (157 mA cm⁻²). The PEMWE device efficiency reaches 68.3% at 1.0 A cm⁻², and the corresponding energy consumption is 4.31 kWh Nm⁻³ H₂, which is comparable with that of the previously reported most noble metal-free OER catalysts (Supplementary Table 4). The durability of the PEMWE cell was determined to be 100 h at 200 mA cm⁻² and 130 h at 1.0 A cm⁻² (Fig. 4f and Supplementary Fig. 25). However, pure Co₃O₄ only ran 1.8 h at 200 mA cm⁻², and lost all its activity. The degradation rate of HSS-CoO_x/GDY||Pt/C PEMWE device is 2.87 mV h⁻¹, which is 2.65% of pure Co₃O₄ (108 mV h⁻¹), confirming that the stability of HSS-CoO_x/GDY was better than that of pure Co₃O₄ (Fig. 4g). These results indicate that GDY ultimately underpinned the performance of Co₃O₄ by producing the high-spin Co³⁺, suggesting the promise of using noble metal-free anode catalysts for practical applications in PEMWE setups.

Charge transfer and storage mechanism

Charge transfer and storage on the catalyst surface directly affect the cleavage and formation of chemical bonds, further leading to differences in their performance. On the basis of this premise, it is crucial to understand the transfer and storage mechanism of charge on the catalyst surface to explain the root of catalytic performance. To this end, in-situ electrochemical impedance spectroscopy (EIS) measurements were conducted at various voltages to probe the charge transfer ability at the electrolyte-catalyst interface (Fig. 5a). Compared to Co₃O₄, HSS-CoO_x/GDY shows a more rapid decrease in phase angle in the Bode phase plots (Fig. 5b, Supplementary Fig. 26, and Fig. 5c), indicating that more electrons are used to trigger the OER process rather than being stored.

A pulse voltammetry (PV) protocol was also employed to investigate the dynamic evolution of intermediates on electrocatalysts during the OER process (Fig. 5d)^{47,48}. The applied pulse voltage can directly affect the accumulation and release of charge on the catalyst surface, resulting in a change in current. The obtained current response curve is primarily composed of the transient process corresponding to the evolution of intermediates and the steady-state process of kinetic equilibrium, which includes information on the double layer capacitance (*C_{dl}*) and diffusion process⁴⁹. First, the total charge was obtained by integrating the cathodic charge from the current profile. As displayed in Fig. 5e, the total charge in HSS-CoO_x/GDY is linear in potential. Moreover, that of Co₃O₄ can be divided into three parts: Co²⁺→Co³⁺, OER, and Co³⁺→Co⁴⁺. In addition, the slope of the total charge relative to the potential in HSS-CoO_x/GDY is 8.30 mC V⁻¹, which is lower than that of Co₃O₄ (24.99 mC V⁻¹, 206.8 mC V⁻¹, 92.70 mC V⁻¹), indicating that the charge transfer in HSS-CoO_x/GDY is faster than that in Co₃O₄, which is in agreement with the EIS results. To acquire the *C_{dl}*-type capacitance and charge, the Dupont and Donne model was subsequently used to fit the transient current response curves. Both the anodic *C_{dl}*-type capacitance and charge for HSS-CoO_x/GDY first rise rapidly and then begin to decrease after reaching 1.45 V (Fig. 5a, 5f and Supplementary Fig. 27). This phenomenon means that the charge on the HSS-CoO_x/GDY surface is sufficient to initiate the OER at 1.45 V, which is consistent with the LSV curve results. However, the anodic *C_{dl}*-type capacitance and charge for Co₃O₄ undergo three processes, including an increase (1.30 to 1.55 V), a decrease (1.55 to 1.68 V), and another increase (1.68 to

1.80 V), which are attributed to the processes of Co²⁺→Co³⁺, OER and Co³⁺→Co⁴⁺ (Supplementary Fig. 28). The lifetime of the charge was calculated by dividing the total charge by the OER current (Fig. 5g). Compared with Co₃O₄, HSS-CoO_x/GDY has a shorter charge lifetime and a faster decay, demonstrating that the charges on the HSS-CoO_x/GDY surface are difficult to accumulate due to the parallel spin alignment of the reaction intermediate⁵⁰. These results indicate that HSS-CoO_x/GDY with high-spin Co³⁺ accelerates charge transfer during the reaction process, not only increasing the catalytic reaction activity but also improving the stability by rapid charge transfer (Fig. 5h).

In summary, we demonstrate that Co₃O₄ anchored on GDY has the comprehensive ability to serve as an alternative to noble metal catalysts, representing the beginning of the challenge from non-noble metals to noble metal OER catalysts in acidic media because of the abundance of high-spin Co³⁺ in the CoO₆ octahedron. The existence of GDY successfully leads to the imbalance of the symmetry of the CoO₆ octahedron, causing a decrease in the crystal field splitting energy and promoting the transition of *t_{2g}* electrons to *e_g* orbitals of Co³⁺. This transition reconfigures octahedral Co³⁺ ions from a low-spin state (*t_{2g}⁶e_g⁰*) in Co₃O₄ to a favorable high-spin state (*t_{2g}^{5.188}e_g^{0.812}*) in HSS-CoO_x/GDY. High-spin Co³⁺ possesses high electron delocalization ability and fast charge transfer kinetics, enabling high acidic OER performance. Our research results indicate that the activity and performance of spin-engineered HSS-CoO_x/GDY have undergone favorable changes compared to the activity of Co₃O₄ without a spintronic structure. This work has encouraged us to construct high-performance OER catalysts by manipulating the spin states of earth-abundant metals, which is expected to replace expensive precious metal catalysts for PEMWE setups in the future.

Methods

Materials

Cobalt (II) acetate tetrahydrate (Co(CH₃COO)₂·4H₂O, ≥99.5 %), carbon cloth (CC), copper foil (Cu, 0.1 mm thick), hydrochloric acid (HCl, 1.19 g mL⁻¹), nitric acid (HNO₃, 1.40 g mL⁻¹), sulfuric acid (H₂SO₄, 1.84 g mL⁻¹), acetone (CH₃COCH₃, ≥99.7 %), dichloromethane (CH₂Cl₂, ≥99.5 %) and pyridine (C₅H₅N, ≥99.9 %), hydrogen peroxide (H₂O₂, 30 wt%), heavy-oxygen water (H₂¹⁸O, ≥99.9%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Before the experiment, the CC was activated in 8 M HNO₃ at 100 °C for 48 h, and then rinsed by deionized water (DI) and CH₃COCH₃, finally dried at 60 °C for 12 h.

Preparation of porous GDY nanosheet

30 mL of CH₂Cl₂ and 2 mL of C₅H₅N containing 20 mg of hexaethynylbenzene (HEB) were injected into a petri dish (Φ7.0 cm × H 3.5 cm). Then, the cleaned Cu foil (4.5 cm × 4.5 cm, two pieces) clamps the activated CC (3.0 cm × 2.0 cm, two pieces), which were placed together in the above petri dish and kept for 2 days in the dark and at 25 °C. After the reaction was completed, the CC with GDY was cleaned several times with CH₃COCH₃ and DI water. Subsequently, the CC with GDY was placed in a tube furnace and annealed under Ar atmosphere at 200 °C for 2 h. Cu species in GDY/CC were removed in 1.0 M HCl solution at 80 °C for 2 h, which was followed by drying in a vacuum oven at 60 °C for 12 h, finally obtained the GDY nanosheet.

Preparation of HSS-CoO_x/GDY electrode

The HSS-CoO_x/GDY electrode was prepared by the pulse electro-deposition method on a CHI660E electrochemical workstation. Firstly, a piece of GDY with 3 cm² was used as work electrode (WE), graphite plate as counter electrode (CE, Φ 0.6 cm × H 10.0 cm) and Ag/AgCl as a reference electrode (RE, 3.5 M KCl-saturated), immersed 20 mL of Co(CH₃COO)₂·4H₂O solution (0.02 mmol mL⁻¹, 498 mg of Co(CH₃COO)₂·4H₂O was dissolved in 50 mL DI water and titrated into a 100 mL volumetric flask. The solution was prepared fresh for immediate use.). Next, a constant voltage pulse is applied to the GDY.

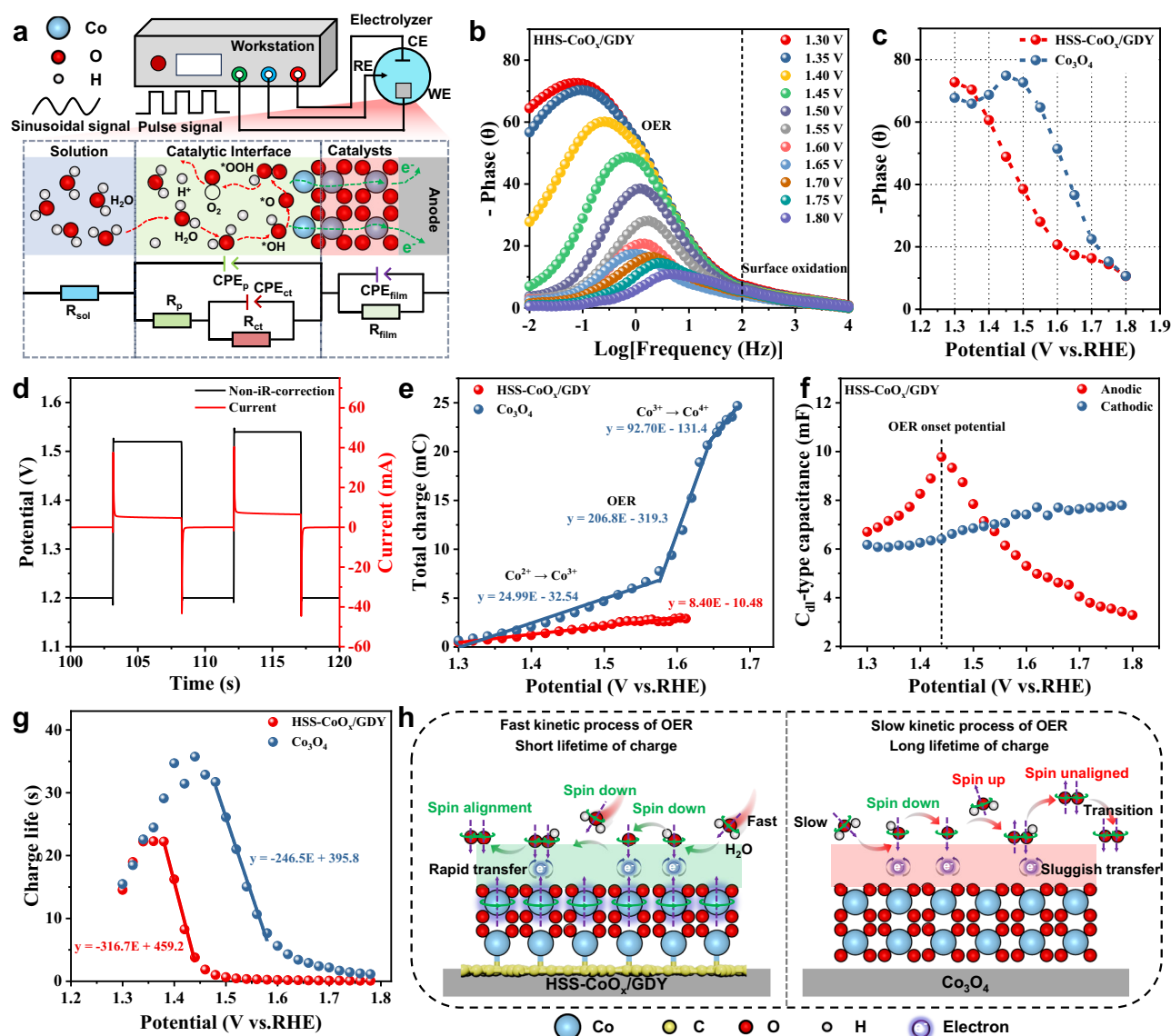


Fig. 5 | Charge transfer and storage mechanism. **a** Illustration of the equivalent circuit model of the electrode surface during the reaction process (R_{sol}: Electrolyte resistance; R_p: Interface resistance; CPE_p: Interface capacitance; R_{ct}: Charge transfer resistance; CPE_{ct}: Charge transfer capacitance; R_{film}: Catalyst's resistance; CPE_{film}: Catalyst's capacitance). **b** Bode phase plots of HSS-CoO_x/GDY. **c** Summarized phase

peak angles of HSS-CoO_x/GDY and Co₃O₄. **d** Pulse voltammetry protocol and corresponding current response. **e** Total charge versus potential from pulse voltammetry. **f** C_{dl}-type capacitance of HSS-CoO_x/GDY. **g** Charge lifetime as a function of the potential. **h** Schematic diagram of the mass transfer process on the HSS-CoO_x/GDY and Co₃O₄ surfaces.

The voltage was kept at -1.0 V for 20 s, then switched to open-circuit voltage (OCV) for 40 s. This cycle was repeated 60 times. The resulting Co(OH)₂/GDY electrode was annealed at 250 °C in air for 2 h, and finally formed the HSS-CoO_x/GDY electrode.

Preparation of Co₃O₄ electrode

The same preparation process with the HSS-CoO_x/GDY electrode was used to produce the Co₃O₄ electrode, which only employed bare CC as the substrate.

Material characterizations

The powder X-ray diffraction patterns of HSS-CoO_x/GDY and Co₃O₄ were collected on a PANalytical X'pert with Cu Kα radiation (λ = 1.542 Å) at the ambient temperature. The morphological and structural information of HSS-CoO_x/GDY and Co₃O₄ were investigated by a field emission scanning electron microscope (SEM, Hitachi SU-4800), a transmission electron microscope (TEM), and high-resolution TEM (HRTEM, JEM-2100) at an acceleration voltage of 200 kV. The

corresponding energy dispersive X-ray spectrum (EDS) was recorded to detect the species and distribution of elements. The Raman spectroscopy of HSS-CoO_x/GDY, Co₃O₄, and GDY was recorded at a Renishaw-2000 Raman spectrometer with 473 nm excitation laser. XPS measurements were conducted on a Thermo Scientific ESCALab 250Xi instrument with Al Kα light source to uncover the chemical states. The thickness of the samples was determined by an AFM device on a Bruker FASTSCANBIO in non-contact mode. The K-edge X-ray absorption spectra (XAS) of Co were recorded at the 1W1B beamline of the Beijing Synchrotron Radiation Facility in Beijing, China.

Magnetic measurements

The magnetic properties of the samples were studied by a SQUID magnetometer (MPMS3, Quantum Design, America). The M-H curves were recorded at 300 K in fields between -50,000 Oe and +50,000 Oe. The susceptibilities (χ) were obtained by calculating the slope of M-H plots (χ = M/H). Further, the M-T plots were collected by measuring the variation of magnetization with temperature (4 K to 300 K) with a

constant external magnetic field ($H = 150$ Oe). The Curie constant (C) value was extracted by fitting the **M-T** curves above 150 K based on the Curie-Weiss law: $\chi = C/(T - T_c)$, where T_c is the Curie-Weiss temperature. The effective magnetic moments (μ_{eff}) for these samples were subsequently obtained from the expression: $\mu_{\text{eff}} = (8C)^{1/2}\mu_B$. Further, the total μ_{eff} of samples includes contributions from both magnetic ions, i.e., Co^{2+} ($3d^7$) in a tetrahedral field and Co^{3+} ($3d^6$) in an octahedral field, and obeys Eq. (1):

$$\mu_{\text{eff}}^2 = \mu_{\text{eff, Co}^{3+}}^2 + \mu_{\text{eff, Co}^{2+}}^2 \quad (1)$$

The volume fractions of Co^{3+} in high-spin (HS) and low-spin (LS) derived from the following Eq. (2)¹⁰:

$$\mu_{\text{eff, Co}^{3+}} = g \sqrt{S_{\text{LS}}(S_{\text{LS}} + 1)V_{\text{LS}} + S_{\text{HS}}(S_{\text{HS}} + 1)V_{\text{HS}}}\mu_B \quad (2)$$

Where S_{LS} and S_{HS} are the unpaired eg electrons number of Co^{3+} for the LS and HS states, their values are 0 and 2 for S_{LS} and S_{HS} , respectively; V_{LS} and V_{HS} ($V_{\text{LS}} + V_{\text{HS}} = 1$) represents the volume fractions of Co^{3+} ions in LS and HS states, respectively; g is the Lande g -factor, its value is 2 for electrons.

The e_g filling can be further calculated by Eq. (3):

$$x = 2V_{\text{HS}} \quad (3)$$

Electrochemical measurements

All electrochemical studies were performed on a CHI660E electrochemical workstation by a three-electrode system with HSS-CoO_x/GDY or Co₃O₄ as a WE (0.3 cm × 0.3 cm), Ag/AgCl as a RE (3.5 M KCl-saturated) and graphite plate as a CE (Φ 0.6 cm × H 10.0 cm), cylindrical glass vessels (Φ3.5 cm × H 7.0 cm) as an electrolytic cell, respectively. All the potentials were converted to a reversible hydrogen electrode (RHE) through the following Eq. (4):

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \times \text{pH} \quad (4)$$

Where $E_{\text{Ag/AgCl}}$ is the potential relative to the Ag/AgCl electrode, 0.197 V is the potential of the Ag/AgCl electrode against the standard hydrogen electrode (SHE). All tests were conducted in 20 mL of 0.5 M H₂SO₄ solution (pH = 0 ± 0.02, 27.76 mL of concentrated H₂SO₄ was gradually diluted with DI water. After cooling, the solution was made up to 1.0 L in a volumetric flask with DI water, and stored in a sealed and dark environment, unless otherwise specified. The linear sweep voltammetry (LSV) curves were collected once at a scan rate of 5 mV s⁻¹ from 1.0 V to 1.8 V (without iR -correction) at room temperature (25 °C). The LSV curves were compensated by iR -correction for eliminating the effect of solution resistance, according to Eq. (5):

$$E_{\text{IR-correction}} = E_{\text{RHE}} - I_{\text{mea}} \times R_{\text{sol}} \quad (5)$$

Where I_{mea} is the measured polarization current, R_{sol} is the solution resistance, obtained by electrochemical impedance spectroscopy (EIS). The electrochemically active surface area (ECSA) values were estimated by the cyclic voltammetry (CV) method in a non-Faradaic area (1.10 V – 1.30 V vs. RHE without iR -correction) with different scan rates (10 mV s⁻¹, 20 mV s⁻¹, 30 mV s⁻¹, 40 mV s⁻¹ and 50 mV s⁻¹). The electrochemical double-layer capacitance (C_{DL}) was calculated by plotting the corresponding current density difference ($\Delta j = (j_+ - j_-)/2$) at 1.20 V (vs. RHE without iR -correction) against the scan rate, then linear fitting this curve, the slope of this curve is the C_{DL} value. The ECSA value was estimated using the following Eq. (6):

$$\text{ECSA} = C_{\text{DL}}/C_s \quad (6)$$

Where C_s represents the ideally flat electrode, $C_s = 0.035$ mF cm⁻². In-situ EIS was carried out in the frequency range from 10⁶ Hz to 10⁻² Hz at a voltage range of 1.3 V – 1.8 V (vs. RHE without iR -correction) with a 10 mV amplitude. Stability tests were conducted by chronopotentiometry (CP) and the CV method.

Pulse voltammetry (PV) tests

PV tests were performed on a CS310X electrochemical workstation at a low potential ($E_1 = 1.20$ V vs. RHE) for 4 s and a high potential (E_2) for 5 s, and then returned to E_1 for 4 s. This process was cycled while increasing the potential from 1.20 to 1.80 (V vs. RHE) in 0.02 V/step, and recording the current response. The total charge was obtained by integrating the cathodic charge. The Dupont and Donne model was used to fit the temporal decay profile based on Eq. (7)^{47–49}:

$$i_{\text{dl}} = \frac{E}{R_s} \exp\left(-\frac{t}{R_s C_{\text{dl}}}\right) \quad (7)$$

Where the i_{dl} is the decaying current; R_s is the electrolyte resistance (Ω); C_{dl} is the C_{dl} -type capacitance (F); t is the time (s); E is the potential (V vs. RHE).

The lifetime of the charge was calculated by dividing the total charge by the OER current.

PEMWE tests

The membrane electrode assembly (MEA) was firstly prepared, using Nafion 212 membrane (thickness: 50.8 μm, area: 3.0 cm × 3.0 cm) as solid polymer electrolytes, HSS-CoO_x/GDY or Co₃O₄ as anode catalysts (~4.0 mg cm⁻²), and Pt/C (40 wt.%) as cathode catalyst (~0.4 mg cm⁻²), Ti fiber with Pt layer and carbon paper as anode and cathode porous transport layer (PTL), respectively. The Nafion 212 membrane was sequentially treated with 3 wt% H₂O₂ and 0.5 M H₂SO₄ at 80 °C for 1 h, and stored in DI water. HSS-CoO_x/GDY catalyst was collected by the ultrasonic method. The anode (4.0 mg) and cathode (1.0 mg) catalyst ink were separately prepared by dispersing the catalyst in a mixture of 0.055 mL of Nafion (5 wt%), 1.6 mL of isopropanol, and 0.4 mL of DI water. The catalyst ink was sprayed onto both sides of a Nafion 212 membrane with an active area of 1.0 cm × 1.0 cm. Then, the MEA electrode was assembled into a PEMWE device, and DI water was injected as the electrolyte solution at a flow rate of 30 mL min⁻¹. Finally, the PEMWE setup was run at the temperature of 65 °C, and polarization curves were collected between 0.8 V and 1.8 V in the CS310X electrochemical workstation. The stability was also measured by recording the cell voltage change under a constant current of 200 mA cm⁻² and 1.0 A cm⁻².

The energy efficiency, hydrogen production cost, and energy consumption of the PEMWE setup were evaluated.

Energy consumption calculation: The energy consumption of a PEMWE setup is calculated based on Eq. (8):

$$\text{Energy consumption} = \frac{U_{\text{cell}} \times z \times F}{3600 \times V_m} \quad (8)$$

Where U_{cell} is cell voltage (V) when a current density reaches 1.0 A cm⁻²; z is the number of electrons transfers for generating one hydrogen molecule, its value is 2; F represents Faraday's constant (96484 C mol⁻¹); V_m is the molar volume of gas under standard conditions (22.4 L mol⁻¹).

Energy efficiency calculation: The energy efficiency of a PEMWE setup is evaluated by the following Eq. (9):

$$\text{Energy efficiency} = \frac{1.23}{U_{\text{cell}}} \quad (9)$$

where 1.23 V is the theoretical thermodynamic voltage for water splitting.

In-situ XAS measurements

In-situ XAS spectroscopy for Co under different potentials (OCP, 1.4 V, 1.5 V, 1.6 V and 1.7 V (vs. RHE) without *iR*-correction) in flow cell with three-electrode were carried out using the Rapid XAFS 2 M (Anhui Absorption Spectroscopy Analysis Instrument Co., Ltd.) by transmission mode at 20 kV and 20 mA, and the Si (533) spherically bent crystal analyzer with a radius of curvature of 500 mm was used for Co. Electrochemical signals are driven by CHI660E electrochemical workstation.

DEMS measurements

To elucidate the OER mechanism, differential electrochemical mass spectrometry (DEMS) measurements were conducted using heavy-oxygen water (H_2^{18}O) in a CIS-DEMS-DM-C device (Hefei in situ technology Co., Ltd., China) with AOEPF-TB002HS-T membrane (pore size: 0.2 μm). The catalyst ink was prepared by dispersing 1.0 mg of HHS- CoO_x/GDY or Co_3O_4 in a mixture solution with 0.8 mL of isopropanol, 0.2 mL of DI water, and 0.027 mL of Nafion solution (5 wt%). Subsequently, 0.3 mL of the ink was drop-cast onto a porous gold (Au) electrode, yielding a catalyst loading of 0.3 mg cm^{-2} . A three-electrode configuration was employed, with the catalyst-modified porous Au, an Ag/AgCl electrode, and a pure Pt mesh as WE, RE, and CE, respectively.

Prior to DEMS detection, the catalysts were isotopically labeled with ^{18}O at 1.5 V (vs. Ag/AgCl) for 10 min in 0.5 M H_2SO_4 containing H_2^{18}O by CHI660E electrochemical workstation. After labeling, the electrodes were thoroughly rinsed with DI water (H_2^{16}O) to remove residual H_2^{18}O . The electrodes were then transferred to a fresh 0.5 M H_2SO_4 electrolyte with DI water. To ensure comparable current density between HHS- CoO_x/GDY and Co_3O_4 , the LSV potential windows were adjusted to 1.0 V–1.4 V (vs. Ag/AgCl) for HHS- CoO_x/GDY and 1.0 V–1.9 V (vs. Ag/AgCl) for Co_3O_4 . Throughout the LSV process, the evolved oxygen was monitored in real time using mass spectrometry.

Theoretical calculations

All calculations were performed using spin-polarized density functional theory (DFT) with the projector augmented plane-wave (PAW) method, as implemented in the Vienna Ab Initio Simulation Package (VASP). The exchange-correlation potential was modeled using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA). Long-range van der Waals interactions were accounted for by employing the DFT-D3 correction. A plane-wave cutoff energy of 480 eV was used for all calculations. The energy convergence criterion was set to 10^{-5} eV for the iterative solution of the Kohn-Sham equations.

A unit cell of pristine Co_3O_4 was constructed by 48 Co atoms and 64 O atoms, and the most stable (311) plane was exposed at the terminal. The slab model of HHS- CoO_x/GDY , it contained 72 C atoms, 28 Co atoms, and 44 O atoms. C atoms were used to form the skeleton of GDY. Co and O atoms were applied to build the model of Co_3O_4 , and the Co atoms were connected to the *sp*-C atoms in the GDY model. During the structural optimization process, Brillouin zone integration was carried out using $3 \times 3 \times 4$ gamma k-point sampling, and all atoms were fully relaxed until the residual forces reached below 0.02 eV/Å to form the most stable structure (Supplementary Data 1). Data analysis and visualization were performed using the VASPKIT and VESTA software packages⁵¹. A 20 Å vacuum layer was introduced normal to the slab surface to eliminate interlayer interactions.

Free energy changes (ΔG) were computed via the computational hydrogen electrode (CHE) approach, with potentials referenced to the standard hydrogen electrode by Eq. (10):

$$\Delta G = \Delta E_{\text{ZPE}} + \Delta E - T \times \Delta S + \Delta G_U \quad (10)$$

Where ΔE is the binding energy of the intermediates; ΔE_{ZPE} is the zero-point energy at 298.15 K; T is the experimental temperature (298.15 K);

ΔS is the entropy change; ΔG_U is the free energy correction term for the electrode potential, which can be obtained by: $\Delta G_U = -eU$, in which U refers to the electrode potential with respect to the standard hydrogen electrode, and e is the transferred charge number.

Data availability

The source data generated in this study are provided in the Source Data file. Source data are provided with this paper.

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Author contributions

Y. L. and Y. X. conceived the project and directed the main experimental works. Y. X. and X. P. analyzed the experimental data. X. P. carried out the sample synthesis, characterization, and electrochemical measurements. S. C. (Siyi Chen), Y. Z., S. C. (Siao Chen), and Y. G. provided useful help during the experiments. Y. L., Y. X., and X. P. wrote the manuscript together.

Competing interests

The authors declare no competing interests.

Additional information

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