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Phase-Boundary Electronic Coupling in CoP/NiCo-LDH for High-Efficiency Electrocatalysis and Energy Storage

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ABSTRACT

Developing electrode materials with high capacity and outstanding activity is essential for energy storage and conversion technologies. However, integrating multiple functions into a single material remains challenging. Herein, we synthesized a novel CoP@NiCo layered double hydroxide (CoP@NiCo-LDH) nano-electrode using hydrothermal and electrodeposition methods. X-ray absorption spectroscopy (XAS) confirms the coexistence of Co-P, Ni-O, and Ni-O-M units in the synthesized sample as bifunctional active sites. The optimized CoP@NiCo-LDH electrode delivers a specific capacity of 892 C g⁻¹ at 1 A g⁻¹. The asymmetric supercapacitor delivers an energy density of 74.6 μWh cm⁻². Moreover, as a bifunctional electrocatalyst, CoP@NiCo-LDH requires overpotentials of 195.3 mV for the oxygen evolution reaction (OER) and 94.5 mV for the hydrogen evolution reaction (HER) at 10 mA cm⁻². Additionally, the assembled two-electrode electrolyzer requires only 1.8 V to drive overall water splitting at 50 mA cm⁻². Density functional theory (DFT) calculations indicate that the enhanced activity of the heterostructure is attributed to its modulated electronic structure and optimized adsorption energies for key reaction intermediates. This work offers opportunities for advancing energy storage and conversion technologies for further exploration and development of phosphide-based nano-electrode materials.

1 | Introduction

As countries around the world set carbon neutrality goals, energy decarbonization has become a critical agenda [1–4]. In this transition, clean and sustainable renewable energy plays a central role [5–8]. Supercapacitors (SCs), owing to their portability and excellent cycling stability, have become an attractive option for energy storage technologies [9–13]. SCs have attracted extensive attention, with electrode materials identified as key components influencing SC performance [14–17]. According to $E = 1/2CV^2$ [18–20], where E is the energy density, C is

the capacitance, and V is the operating voltage, a higher operating voltage and a larger capacitance lead to a higher energy density in SCs [21–23]. Therefore, increasing the operating voltage and capacitance is key to designing high-performance electrode materials [24–26].

Among various candidate materials, cobalt phosphide (CoP) has garnered considerable attention owing to its unique electrochemical properties. Its excellent electrical conductivity and distinctive redox activity enable CoP-based materials to deliver

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high energy output [27, 28]. Liu et al. [29] synthesized a novel core-shell nanostructure, Co(OH)F@CoP , grown on conductive carbon cloth (CC). The resulting material exhibited a specific capacity of 654 mF cm^{-2} at 1 mA cm^{-2} . In parallel, NiCo layered double hydroxides (NiCo-LDHs) are promising as electrode materials for both energy storage and electrocatalytic applications due to their unique layered structure and rich redox chemistry. The layered architecture exposes active sites and facilitate electrolyte ion diffusion, while the synergistic interaction between Ni and Co species provides multiple redox centers and enhanced electrochemical activity. In addition, the tunable composition of NiCo-LDH offers opportunities to optimize its electronic structure and reaction kinetics [30–33]. However, the relatively limited electrical conductivity of LDH-based materials may hinder their practical performance, making it highly desirable to integrate NiCo-LDH with conductive phosphide components to construct high-performance heterostructures.

Water electrolysis enables efficient hydrogen production and supports the clean energy transition [34–36]. During this process, water is electrochemically converted into hydrogen and oxygen through the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) at the electrode surface. However, the overall efficiency and energy conversion rate are largely constrained by the performance of the electrocatalysts involved. Consequently, the electrocatalysts are essential for improving the practical viability of water electrolysis. Although noble metals have demonstrated excellent catalytic performance [37–39], their limited natural abundance significantly hinders their application in large-scale industrial settings [40, 41]. Transition metal phosphides are efficient and stable catalysts [42, 43]. CoP stands out as an electrocatalyst due to its excellent conductivity and electrochemical activity [44, 45]. Duan et al. [46] synthesized the CoP-1.5 nanorod catalyst. It exhibited higher HER and OER activities. Currently, composite electrode materials offer new perspectives and solutions [47–51].

In this work, CoP was prepared by a hydrothermal method, followed by the electrodeposition of NiCo-LDH onto the CoP substrate. CoP@NiCo-LDH samples have a specific capacity of 892 C g^{-1} . The asymmetric supercapacitor (ASC) exhibits an energy density of $74.6 \text{ } \mu\text{Wh cm}^{-2}$ at 1.125 mW cm^{-2} . The overpotential was 195.3 mV (OER) and 94.5 mV (HER) at 10 mA cm^{-2} . The electrolyzer voltage for water splitting at 50 mA cm^{-2} was 1.8 V. After 12 h of water electrolysis, the system maintained excellent stability. The enhanced activity of the heterostructure arises from the tailored structure and optimized adsorption energies.

2 | Experimental

Cobalt nitrate hexahydrate, sodium hypophosphite, nickel nitrate hexahydrate, urea, ammonium fluoride, potassium hydroxide, anhydrous ethanol, hydrochloric acid (HCl), platinum on carbon (Pt/C), RuO_2 , and nickel foam were sourced from Sigma-Aldrich Chemical Company. All chemicals were utilized as received, without additional purification. Deionized water was used to prepare all aqueous solutions in this experiment.

2.1 | Preparation of Co_3O_4 Precursor

The Co_3O_4 precursor electrode was synthesized via a hydrothermal method. In a typical procedure, 3 mmol of $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 6 mmol of urea, and 2 mmol of NH_4F were dissolved in 70 mL of deionized water under continuous magnetic stirring to obtain a homogeneous solution. The solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave, and a pre-cleaned nickel foam substrate was immersed in the solution. The autoclave was sealed and maintained at 120°C for 6 h. After naturally cooling to room temperature, the obtained Co_3O_4 precursor electrode was removed, washed several times with deionized water and anhydrous ethanol, and then dried at 60°C for 12 h.

2.2 | Preparation of CoP Precursor

The CoP electrode was obtained by phosphorizing the Co_3O_4 precursor electrode in a tubular furnace. The dried Co_3O_4 precursor electrode and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ were placed at two separate positions in a porcelain boat, with $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ located upstream of the precursor electrode. The phosphorization process was conducted under a flowing Ar atmosphere at 350°C for 2 h. After naturally cooling to room temperature, the resulting electrode was collected and denoted as the CoP electrode.

2.3 | Preparation of CoP@NiCo-LDH Composite Material

The CoP@NiCo-LDH samples were prepared using an electrochemical deposition method. First, 2 mmol $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1 mmol $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 6 mmol urea, and 2 mmol NH_4F were dissolved in 70 mL of deionized water to prepare a 70 mL reaction solution. Pour the solution into a three-electrode electrolytic cell. During the experiment, a platinum electrode (Pt) was used as the counter electrode, a silver/silver chloride electrode (Ag/AgCl) was used as the reference electrode, and the synthesized CoP precursor was used as the working electrode. Then, electrochemical deposition was carried out using a constant voltage method on a CHI660E electrochemical workstation. During the electrochemical deposition process, the deposition voltage was maintained at 0.9 V, with deposition times of 200, 400, and 600 s, respectively. Based on the deposition time, the obtained electrode materials were named CoP@NiCo-LDH-200s, CoP@NiCo-LDH-400s, and CoP@NiCo-LDH-600s. After completing the electrochemical deposition, the electrodes were repeatedly washed with anhydrous ethanol and deionized water to remove surface residues, then placed in an oven at 60°C and maintained for 12 h to obtain the CoP@NiCo-LDH electrodes.

2.4 | Material Characterizations

The crystal structures and phase compositions of the samples were analyzed by X-ray diffraction (XRD) using an X-ray diffractometer (D/max-2500/PC) with $\text{Cu K}\alpha$ radiation. The XRD patterns were collected at a tube voltage of 40 kV and a tube current of 40 mA over a 2θ range of 0° – 90° . The elemental composition and chemical valence states were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250), and all binding energies were calibrated using the C 1s peak at 284.8 eV. The surface morphologies and microstructures of the

samples were examined by scanning electron microscopy (SEM; Zeiss Sigma 500). Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), selected-area electron diffraction, and energy-dispersive X-ray spectroscopy (EDS) elemental mapping were performed using a transmission electron microscope (JEM-2100F). The specific surface area and pore-size distribution were measured by the Brunauer–Emmett–Teller (BET) method using a Micromeritics TriStar II Plus analyzer. Ultraviolet photoelectron spectroscopy (UPS) measurements were carried out using an ultraviolet photoelectron spectrometer (ESCALAB Xi+). Raman and in situ Raman spectra were collected using a DXR3 Raman microscope (Thermo Fisher Scientific). The in situ Raman measurements were performed with an electrochemical in situ cell to monitor the surface reconstruction process during the oxygen evolution reaction. X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), was performed using a RapidXAFS 1M system to investigate the electronic structure and local coordination environment of the samples.

2.5 | Supercapacitor Measurements

The samples were prepared for testing in a three-electrode configuration at an electrochemical workstation (CHI660E) immersed in a 3M KOH aqueous solution. The as-prepared samples were used as the working electrode, while a platinum plate and Hg/HgO electrodes served as the counter and reference electrodes, respectively. The functionality of the supercapacitor electrodes was assessed using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Specific and areal capacitances were determined from the galvanostatic charge–discharge (GCD) curves, using the following formula:

$$C_s = \frac{I\Delta t_d}{m}, \quad (1)$$

$$C_A = \frac{I\Delta t_d}{S}, \quad (2)$$

where C_s and C_A are the specific capacitance and areal capacitance, respectively; I is the set current value; Δt_d is the discharge time; m is the mass of the active material; and S denotes the geometric area of the electrode.

2.6 | Assembly of Asymmetric Supercapacitors

An asymmetric supercapacitor (ASC) was assembled using activated carbon (AC) as the negative electrode, CoP@NiCo-LDH as the positive electrode, and polyvinyl alcohol–potassium hydroxide (PVA–KOH) gel as the electrolyte. As shown in Supporting Information S1: Figure S1, for electrolyte preparation, 2 g of PVA was introduced into 20 mL of deionized water, and 2 g of KOH was dissolved in 5 mL of deionized water. Both mixtures were stirred at 80°C in a water bath until clear, then set aside for use. To craft the AC electrode, AC, acetylene black, and polyvinylidene fluoride were mixed into a slurry with a mass ratio of 8:1:1, coated onto nickel foam, and dried at 60°C for 24 h. The durability of the electrodes and supercapacitors was evaluated using the land battery test system (CT2001A).

The energy density (E , mWh cm^{−2}) and power density (P , mW cm^{−2}) were evaluated using the following equations:

$$E = \frac{C_A \Delta V^2}{7200}, \quad (3)$$

$$P = \frac{3600E}{\Delta t}, \quad (4)$$

where C_A is the areal capacitance, ΔV is the voltage window, and Δt is the discharge time.

2.7 | Electrochemical Water Splitting Measurements

In a 1 M KOH solution (pH = 13.7), the samples' performance for both the HER and OER was evaluated using a three-electrode setup. Techniques such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), and Amperometric (I - t) curves were employed to assess the electrocatalytic activity, with CV scan rates ranging from 5 to 50 mV s^{−1}. For LSV, the rates were specifically set at 2 mV s^{−1} for OER and 5 mV s^{−1} for both HER and water splitting activities. These measurements were conducted on an electrochemical workstation equipped with automatic 90% infrared compensation. The electrodes comprised prepared samples sized 0.5 cm × 0.5 cm as the working electrodes, Hg/HgO as the reference electrode, a graphite rod for HER, and a Pt plate for OER as the counter electrodes. Potentials were standardized to the reversible hydrogen electrode (RHE) scale according to the Nernst equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.059 \times \text{pH}$. The OER overpotentials (η) were determined using the equation: $\eta = E_{\text{RHE}} - 1.23$.

3 | Results and Discussion

The CoP precursor was prepared via the hydrothermal process (Figure 1A). Subsequently, NiCo-LDH was deposited onto the CoP substrate by electrodeposition with different deposition times, yielding the CoP@NiCo-LDH composites. The phase structures were investigated by XRD (Figure 1B). Three strong diffraction peaks are attributed to Ni. The peaks of 33.0°, 38.5°, 59.0°, 62.6°, 69.8°, 72.8°, and 82.9° correspond to the NiCo-LDH (Joint Committee on Powder Diffraction Standards (JCPDS) card No. 59-0461). The peaks of 31.6°, 36.3°, 48.1°, and 89.8° correspond to CoP structure (JCPDS: 29-0497), respectively. In CoP@NiCo-LDH, the peaks of 33.0°, 38.5°, 59.0°, 62.6°, 69.8°, 72.8°, and 82.9°, correspond to the cubic planes (100), (011), (110), (111), (013), (021), and (022) of NiCo-LDH (JCPDS: 59-0461). In summary, this analysis confirms that NiCo-LDH and CoP have been successfully combined into a composite.

In the XPS survey spectrum (Figure 1C), CoP@NiCo-LDH contains Ni, Co, O, and P. The Ni 2p and Co 2p spectra (Figure 1D,E) exhibit the characteristic components. Notably, the deconvoluted Ni 2p spectra indicate the coexistence of Ni²⁺ and Ni³⁺ species in both samples. Compared with pristine NiCo-LDH, CoP@NiCo-LDH shows a relatively enhanced Ni³⁺ contribution, suggesting that CoP incorporation promotes the formation of a higher fraction of Ni³⁺ species. Meanwhile, both the Ni and Co elements peaks of CoP@NiCo-LDH shift toward higher binding energies relative to the individual components, indicating strong interfacial electronic coupling between CoP

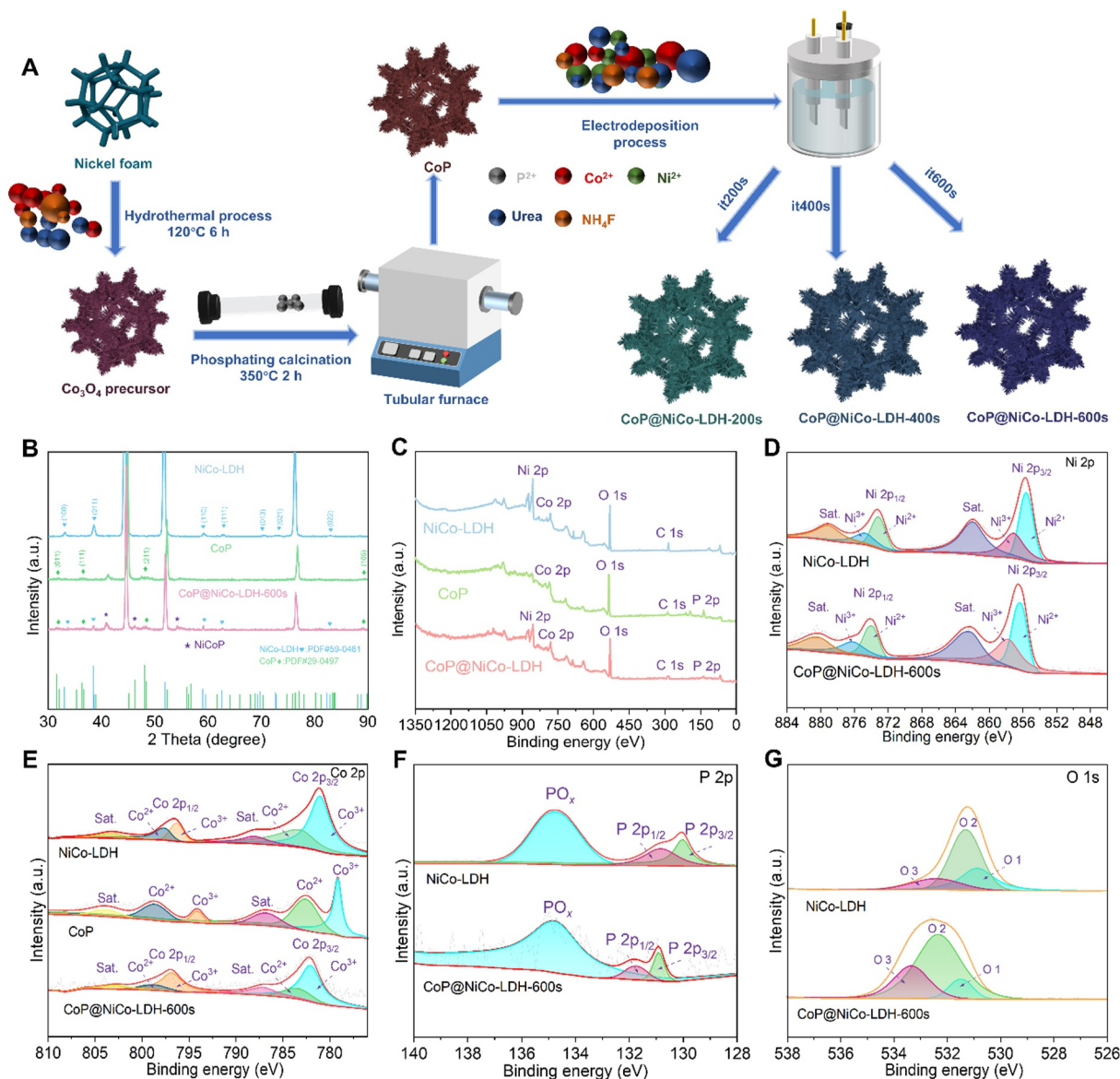


FIGURE 1 | Synthesis route and XRD/XPS analyses of CoP@NiCo-LDH. (A) Synthesis schematic of CoP@NiCo-LDH structures. (B) XRD patterns of the CoP, NiCo-LDH, and CoP@NiCo-LDH. (C) XPS full spectra of the as-prepared samples. XPS spectra of (D) Ni 2p, (E) Co 2p, (F) P 2p, and (G) O 1s.

and NiCo-LDH [52–54]. The P 2p spectrum (Figure 1F) displays Co–P bonding peaks at 129.3 and 130.3 eV. Compared with pure CoP, the P–O peak in CoP@NiCo-LDH shifts by 0.9 eV toward lower binding energy, indicating partial negative charge transfer to P induced by interfacial reconstruction. This charge redistribution is also consistent with the Co 2p evolution.

In Figure 1G, O1 at 531.4 eV is metal–oxygen, the O2 at 532.3 eV is oxygen species on the basal planes, and O3 at 533.3 eV is associated with oxygen atoms at defect sites [55]. This multi-peak fitting reveals the rich diversity in the surface and local coordination environment of the composite material. The electrodeposition of NiCo-LDH under alkaline conditions is accompanied by partial surface oxidation/reconstruction of CoP at the outer surface/interfacial region, while the CoP phase is retained in the bulk. The resulting oxidized/hydroxylated surface species serve as favorable nucleation sites for NiCo-LDH

nanosheet growth, thereby promoting the formation of a chemically coupled heterointerface. In addition, the heterointerface formation alters the local oxygen/hydroxyl defect environment in NiCo-LDH. The defect-related O 1s feature, together with the energy shifts of Co 2p/Ni 2p and the variation of P–O species, indicates interfacial defect/environment modulation and electronic redistribution. Such structural evolution is consistent with a more defect-rich and low-coordinated oxygen/hydroxyl environment and with hydroxyl-vacancy-related defect modulation.

To further probe the interfacial electronic interaction, UPS measurements were performed for the samples. The secondary electron cutoff and valence-band edge positions indicate that CoP and NiCo-LDH possess different surface electronic structures and work functions. After coupling, the UPS features of CoP@NiCo-LDH are located between those of the two

individual components, indicating pronounced interfacial electronic coupling and charge redistribution. Based on the work–function difference, electrons tend to transfer from NiCo-LDH to CoP until Fermi-level equilibrium is established, resulting in interfacial energy-level realignment and the formation of a built-in electric field at the heterointerface. As schematically illustrated in Supporting Information S1: Figures S2 and S3, such interfacial electronic reconstruction is expected to facilitate directional charge transport. The subsequent X-ray absorption spectroscopy (XAS) analysis further supports this interpretation and suggests that the heterointerface formation is also accompanied by local coordination distortion at the phase boundary.

XANES spectroscopy was performed to investigate the Ni electronic structure (Figure 2A). Analysis of the pre-edge region reveals that the CoP@NiCo-LDH sample exhibits features similar to those of NiO, indicating that the Ni is close to Ni²⁺. Further examination of the edge position shows that the absorption edge of CoP@NiCo-LDH is shifted toward higher energies compared to NiO. This shift suggests that, under the influence of CoP, the content of Ni³⁺ in NiCo-LDH increases, resulting in a slightly elevated average oxidation state. Analysis of the white line indicates that the CoP@NiCo-LDH sample exhibits the highest white line intensity with a broader peak shape, implying that the incorporation of CoP not only increases the density of unoccupied states for Ni but also enhances the splitting of the Ni 4p orbitals, thereby producing a broader transition energy range.

Through Co K-edge XANES analysis (Figure 2B), the coordination environment of CoP@NiCo-LDH differs significantly from those in Co foil and CoO. The onset of the absorption edge

in CoP@NiCo-LDH is red-shifted relative to Co foil and CoO, indicating that the oxidation state of Co is lower in CoP@NiCo-LDH. In addition, compared to CoO, the relative content of Co²⁺ may be increased, which is corroborated by the changes in peak intensities observed in XPS. The white line intensity in CoP@NiCo-LDH is significantly reduced, suggesting that CoP modification decreases the density of unoccupied states around the Co atoms, while the energy levels of these states remain essentially unchanged. This implies that the electronic structure of Co has been reconstructed after the introduction of CoP.

In the pre-edge region, CoP@NiCo-LDH exhibits very distinct features: within the energy range of 7710–7720 eV, its absorption values are noticeably lower than those of the other samples, and the absorption edge is steeper; in contrast, within the range of 7720–7740 eV, its absorption values are higher than those of the other samples, forming a pronounced peak. These characteristics indicate that the Co atoms in CoP@NiCo-LDH possess a unique coordination environment, forming new Co–P bonds that alter the transition characteristics within this energy range.

EXAFS analysis (Figure 2C) further corroborates the alteration in the nickel coordination environment due to CoP loading. In *k*-space, the $k^3\chi(k)$ oscillation pattern of CoP@NiCo-LDH differs markedly from those of NiO and Ni foil. Specifically, in the high *k* region ($k > \sim 6 \text{ \AA}^{-1}$), the oscillation amplitude is significantly reduced while the oscillation frequency is slightly increased. This observation suggests that CoP modification alters the local coordination environment around Ni, leading to reduced contributions from the original Ni–O/Ni–O–M framework and a more heterogeneous local structure. In R-space (Figure 2C), the Ni–O and Ni–O–Ni coordination peaks of CoP@NiCo-LDH are substantially weakened, accompanied by obvious peak

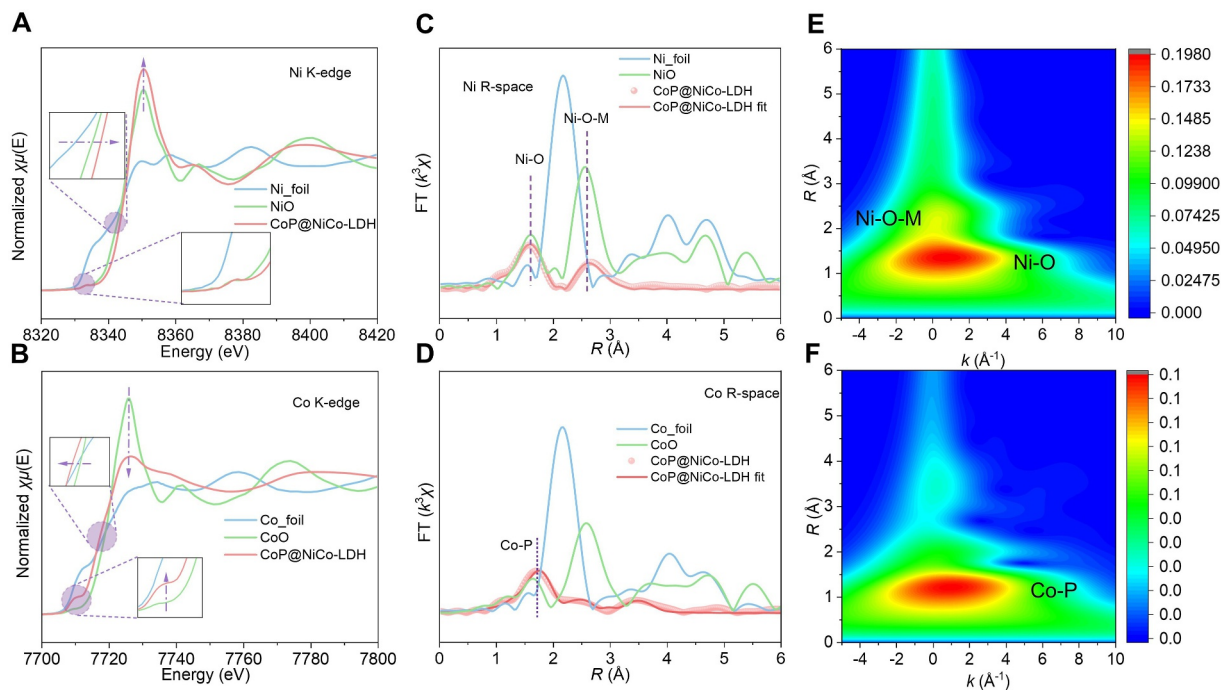


FIGURE 2 | XANES curves of CoP@NiCo-LDH-600s. (A) Ni K-edge XANES spectra. (B) Co K-edge XANES spectra. (C) The magnitude of k^3 -weighted FT of the Ni K-edge extended EXAFS spectra. (D) The magnitude of k^3 -weighted FT of the Co K-edge extended EXAFS spectra. Wavelet transforms of the k^3 -weighted EXAFS signals for a (E) Ni K edge spectra and (F) Co K edge spectra.

broadening and the loss of long-range order. Supporting Information S1: Table S1 further proves that the CoP modification leads to a reduction in the coordination number of the nickel atoms, rendering the coordination environment more complex and heterogeneous, and exhibiting structural disorder. Beyond the interfacial electronic redistribution revealed by XPS and XANES, the above EXAFS results also suggest local structural distortion at the CoP/NiCo-LDH phase boundary. Considering the distinct crystal structures and coordination characteristics of CoP and NiCo-LDH, the heterointerface formation is expected to introduce a certain degree of interfacial strain/local distortion. This interpretation is consistent with the weakened Ni–O/Ni–O–M coordination peaks, broadened EXAFS features, reduced coordination number, and diminished long-range order, all of which indicate a more distorted and heterogeneous local environment after coupling. Similar cooperative effects of electronic modulation and strain/local distortion have been reported in related LDH-based systems and heterostructures, where phase-boundary perturbation plays an important role in tuning the local coordination environment and improving electrocatalytic activity [56–59].

The R-space spectra (Figure 2D) and Supporting Information S1: Table S2 further show that, compared with CoO, the characteristic peak intensity of Co–O–Co bonds in CoP@NiCo-LDH is significantly reduced and nearly disappears. This indicates that CoP modification alters the oxidation state of Co and reconstructs its coordination environment. The atomic configuration of the Co and Ni species was further investigated through the wavelet transform analysis of the K-edge EXAFS spectra (Figure 2E,F). The wavelet transform contour plots further confirm the simultaneous presence of Ni–O, Ni–O–M, and Co–P units in the samples.

The microstructure of the prepared electrodes was observed using SEM. Figure 3A shows the flower-like CoP composed of interwoven nanowires, and the locally magnified SEM image is shown in the top left corner. After electrodeposition for different durations, NiCo-LDH were gradually grown on CoP, as shown in Figure 3B–D. Figure 3B displays SEM image of CoP@NiCo-LDH-200s, where the initial formation of NiCo-LDH nanosheets can be observed. These nanosheets, characterized by their layered structure, are dispersed on CoP nanowires. Although the coverage is relatively uniform, the NiCo-LDH layer is relatively thin, indicating the direct influence of the short electrodeposition time on the morphology. The locally magnified image reveals the interaction between NiCo-LDH and CoP nanowires, which may facilitate potential synergistic electrochemical reactions between the two. When the electrodeposition time is increased to 400 s, Figure 3C shows a denser distribution of NiCo-LDH nanosheets adhering to the CoP nanowires, with a more pronounced layered structure. This dense distribution of nanosheets increases the effective contact area of the electrode, potentially contributing positively to the enhancement of its pseudocapacitive performance. Finally, in Figure 3D, the SEM image of CoP@NiCo-LDH-600s reveals the most optimized microstructure. The density and thickness of the NiCo-LDH nanosheets have significantly increased, forming a more compact and multilayered structure with the CoP nanowires. This structure not only provides more active sites and pathways to facilitate rapid charge transfer and ion

transport but also enhances the structural integrity, thereby improving its stability during electrochemical cycling.

TEM characterization was further performed to verify the microstructure of the prepared samples, as shown in Figure 4A, CoP is composed of interlaced nanorods with uniformly distributed Co and P elements. The distribution of these elements is clearly visible in the figure. In the HRTEM image shown in Figure 4B, the (011) and (201) lattice fringes of CoP can be clearly observed, and the spacings of 0.1767 and 0.2164 nm, respectively, confirm its crystal structure. The structure of the CoP@NiCo-LDH composite possesses unique characteristics. As shown in Figure 4C, NiCo-LDH nanosheets are attached to the surface of CoP nanorods, indicating effective integration of the two components. Figure 4D,E further reveals the uniform distribution of Ni, Co, P, and O throughout the composite, demonstrating its compositional homogeneity and structural complexity. Furthermore, in the HRTEM image (Figure 4F), the (011) plane of CoP (0.1767 nm) and the (100) plane of NiCo-LDH (0.1845 nm) can be clearly observed, respectively. These observations are in complete agreement with the previous XRD data. In addition, the N₂ adsorption/desorption curves of CoP and CoP@NiCo-LDH-600s were analyzed to further evaluate the structural accessibility of the composite (Supporting Information S1: Figure S4). Both samples display typical mesoporous adsorption behavior. Compared with pure CoP, CoP@NiCo-LDH-600s exhibits a higher N₂ uptake over the whole relative pressure range, especially at medium-to-high P/P_0 values, indicating a more open porous architecture and increased accessible surface exposure after the growth of NiCo-LDH nanosheets. This hierarchical core-shell structure provides abundant interfacial void space.

In Figure 5A, the CV curves of the three electrode materials recorded at 10 mV s^{−1} are presented. Distinct peaks indicate the typical pseudocapacitive behavior of these materials. Among them, the specific capacities of CoP@NiCo-LDH-600s, CoP@NiCo-LDH-400s, CoP@NiCo-LDH-200s, CoP, Co₃O₄, and NiCo-LDH are 892, 551, 474.8, 437, 192, and 400.2 C g^{−1} at 1 A g^{−1}, respectively (Figure 5B). In addition, the GCD curves in Supporting Information S1: Figure S5 show that CoP@NiCo-LDH-600s exhibits a longer discharge time than the other two electrode materials, further confirming its superior charge-storage performance. To further assess the charge performance of the CoP@NiCo-LDH-600s, its specific capacity was compared with those of several recently reported cobalt-based phosphide electrodes, as summarized in Supporting Information S1: Table S3. The CoP@NiCo-LDH-600s possesses a higher specific capacity than CuCoP@Ni₃Se₂/CC [60] (666.4 C g^{−1}) and NCP/MX-20/CC [61] (848.83 C g^{−1}), and also markedly outperforms Mn-CoP/NF [62] (456 C g^{−1}). The CoP@NiCo-LDH-600s heterostructure exhibits competitive charge-storage capability among recently reported phosphide-based electrodes. The enhanced electrochemical performance can be attributed to the synergistic integration of conductive CoP and redox-active NiCo-LDH, which provides abundant electroactive sites and facilitates both electron transfer and ion diffusion.

The charge-transfer behavior and resistance characteristics of the electrode materials were evaluated by EIS. Figure 5C

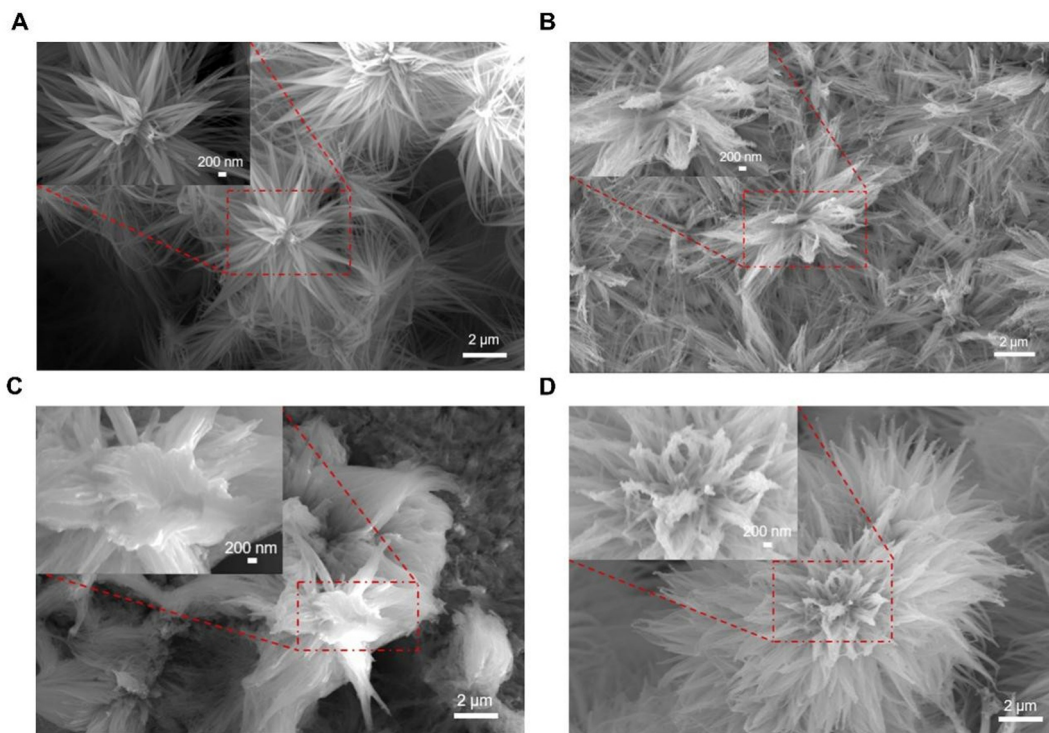


FIGURE 3 | SEM images of CoP, CoP@NiCo-LDH-200s, CoP@NiCo-LDH-400s, and CoP@NiCo-LDH-600s. (A) SEM images of CoP. (B) SEM images of CoP@NiCo-LDH-200s. (C) SEM images of CoP@NiCo-LDH-400s. (D) SEM images of CoP@NiCo-LDH-600s.

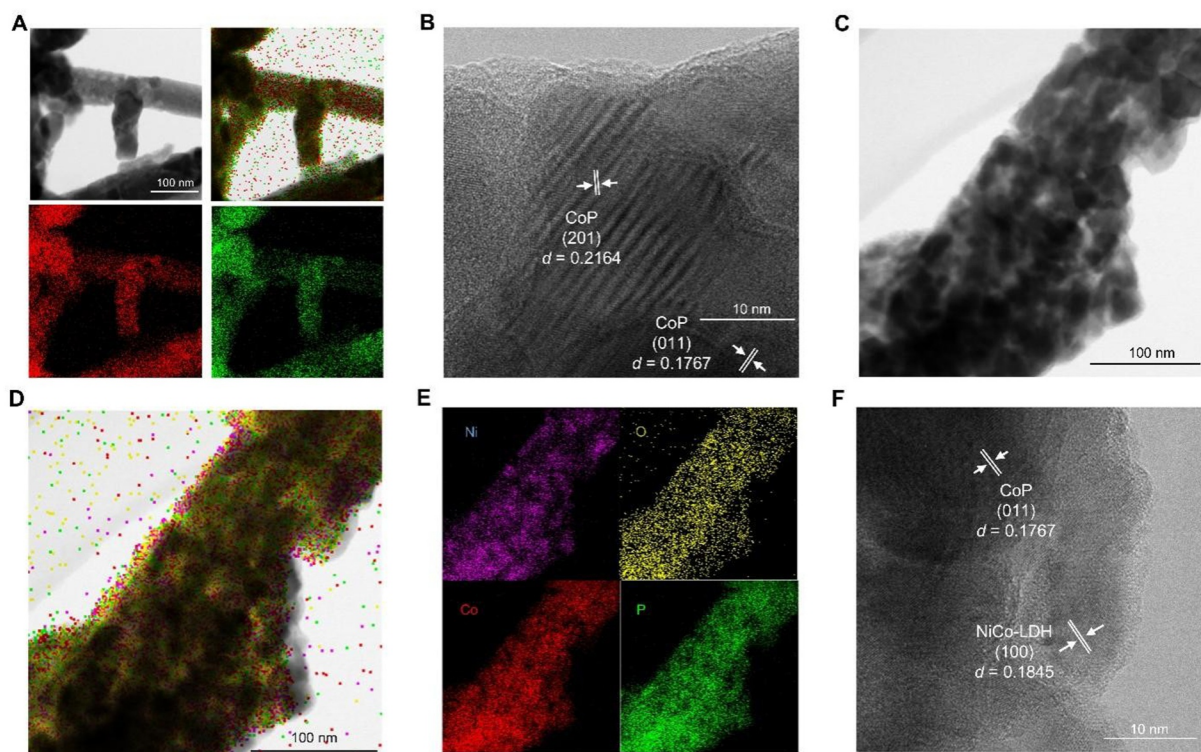


FIGURE 4 | TEM images of CoP and CoP@NiCo-LDH. (A) TEM images of CoP. (B) HRTEM image of CoP. (C) TEM image of CoP@NiCo-LDH. (D) Mapping images of CoP@NiCo-LDH. (E) EDS images of CoP@NiCo-LDH. (F) HRTEM image of CoP@NiCo-LDH.

displays the EIS curves. Figure 5C highlights the high-frequency region with a purple dashed line. CoP@NiCo-LDH-600s exhibits the lowest solution resistance (R_s) and the charge-transfer resistance (R_{ct}), indicating fast charge transfer and low

internal resistance. In Figure 5D, the relationship between the i and v is given as follows [63]:

$$i = av^b, \quad (5)$$

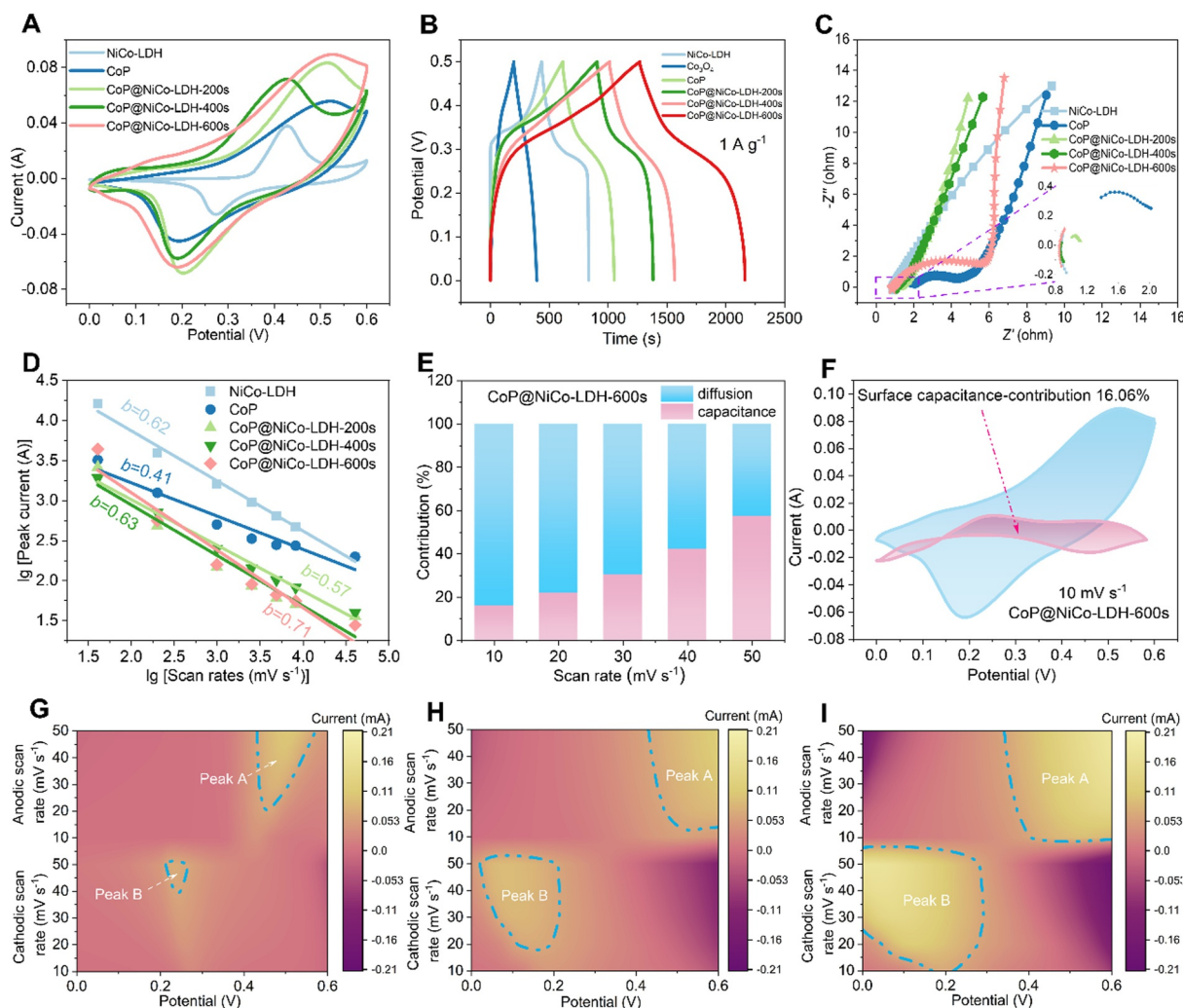


FIGURE 5 | Electrochemical performance of the as-prepared electrodes. (A) CV curves at 10 mV s⁻¹. (B) GCD curves at 1 A g⁻¹. (C) Electrochemical impedance plots (inset shows the high frequency region). (D) *b*-values of three electrodes. (E) Contribution ratio between capacitive (calculated one) and diffusion-controlled capacity. (F) Composite surface capacitance ratio. Contour CV plots of (G) NiCo-LDH, (H) CoP, and (I) CoP@NiCo-LDH.

where i is the peak current, v is the scan rate, and a and b are adjustable parameters. The calculated b values for NiCo-LDH, CoP, CoP@NiCo-LDH-200s, CoP@NiCo-LDH-400s, and CoP@NiCo-LDH-600s are 0.62, 0.41, 0.57, 0.63, and 0.71, respectively. It is noteworthy that b close to 0.5 usually indicates that the electrochemical process is diffusion-controlled, while a b near 1 suggests that it was capacitive control. For the CoP@NiCo-LDH composites with different reaction times (200, 400, and 600 s), the b -values are 0.57, 0.63, and 0.71, respectively. This trend indicates that with the increase in reaction time, the electrochemical performance improves, and the reaction kinetics gradually shift toward surface capacitive control. This change is likely due to the longer deposition time, which leads to a more uniform and dense growth of NiCo-LDH on the CoP nanorods, thereby enhancing conductivity and electrochemical activity. The pseudocapacitance contribution ratio is calculated as follows [64]:

$$i = k_1 v + k_2 v^{1/2}, \quad (6)$$

In this equation, i is the current at a given potential, v is the scan rate, k_1 and k_2 are constants used to distinguish the capacitive and diffusion-controlled contributions. Figure 5E further illustrates the variation of pseudocapacitance and diffusion-controlled capacity. These results show that, as the scan rate increases, the diffusion-controlled contribution decreases, highlighting the effectiveness of the electrode materials in accelerating the diffusion of hydroxide ions. Figure 5F shows that the capacitive contribution of the composite is 16.06% at 10 mV s⁻¹.

Figure 5G-I shows CV contour plots. The color variation spectrum on the right side represents the intensity of the current density, with the areas enclosed by the blue dashed lines corresponding to the anodic and cathodic reactions. By comparing the color intensity in these images, it is evident that the regions enclosed by the blue dashed lines are lighter for NiCo-LDH and CoP than for the composite under the same potential, indicating lower peak currents and weaker electrochemical activity of the individual components. In contrast, the composite material

exhibits a stronger current response within this range, suggesting better electrochemical activity.

Additionally, the color intensity of CoP@NiCo-LDH-600s changes only slightly as the scan rate decreases, indicating a relatively stable current response over a wide scan-rate range. The material can maintain a high current response at lower scan rates. This demonstrates that the electrode material can effectively perform electrochemical reactions over a wide range of scan rates, showcasing excellent stability and reaction activity.

To explore the application of the composite material, it was used to construct an asymmetric supercapacitor. Figure 6A shows that under a 1.5 V voltage window, the shape of CV curves of the device remains unchanged as the scan rate increases, whereas the integrated area expands, indicating that the device possesses excellent capacitive performance. Figure 6B displays CV curves at 100 mV s⁻¹ as voltage varies from 1.1 to 1.6 V, with the shape remaining consistent. This demonstrates that the asymmetric supercapacitor exhibits good operational stability across multiple voltage ranges. The specific capacity of the device reaches 238.8, 105.8, 44.7, 25.8, 17.1, and 12.2 C cm⁻² from 1 to 10 mA cm⁻² (Figure 6C). These data provide insight into the performance under various load conditions. Figure 6D displays EIS results, showing that after 2500 cycles, R_s ranged from 1.3 to 2.8 Ω , and the shape of the impedance curve remained essentially unchanged. The CoP@NiCo-LDH//AC device retains 88% of its initial capacitance after 10,000 charge–discharge cycles (Figure 6E), demonstrating its excellent cycling stability. Finally, the device achieves a high energy density of 74.6 $\mu\text{Wh cm}^{-2}$ at 1.125 mW cm^{-2} (Figure 6F). Compared to previous studies, this result represents a significant improvement, highlighting the great potential of this material in high-efficiency energy storage devices [65–71].

HER and OER performance were evaluated in 1 M KOH. CoP@NiCo-LDH-600s presents the LSV curves of the different catalysts for evaluating their HER and OER activities (Figure 7A). For HER, CoP@NiCo-LDH-600s catalyst requires an overpotential of 94.5 mV at 10 mA cm⁻², which is lower than NiCo-LDH (174.5 mV), CoP (133.6 mV), CoP@NiCo-LDH-200s (124.2 mV), and CoP@NiCo-LDH-400s (110.2 mV) (Figure 7B). For OER, In Figure 7C, the CoP@NiCo-LDH-600s catalyst also delivers the overpotential of 195.3 mV at 10 mA cm⁻², outperforming NiCo-LDH (323.6 mV), CoP (254.9 mV), CoP@NiCo-LDH-200s (244.6 mV), and CoP@NiCo-LDH-400s (205.6 mV). Figure 7D,E demonstrates that the CoP@NiCo-LDH-600s composite exhibits superior HER and OER activities to other catalysts. It achieves a HER Tafel slope of 22.67 mV dec⁻¹, which is significantly lower than the other materials. In OER process, the CoP@NiCo-LDH-600s composite also shows a lower Tafel slope of just 18.85 mV dec⁻¹, again surpassing the performance of other materials. A lower Tafel slope indicates that the CoP@NiCo-LDH-600s composite has a lower overpotential, faster reaction rates, and outstanding catalytic efficiency in both processes, attributed to its unique nanostructure and synergistic effects. Figure 7F provides a comprehensive comparison of the HER and OER performance. This comparison demonstrates that the unique nanostructure effects of the composite material significantly enhance its HER and OER performance.

To further clarify the structural evolution of the catalyst under OER operating conditions, in situ Raman measurements were performed (Figure 7G,H). At relatively low applied potentials, both samples exhibit weak Raman responses without obvious oxyhydroxide-related characteristic bands. With increasing potential, a broad Raman feature gradually emerges and intensifies in the range of approximately 500–560 cm⁻¹, indicating the

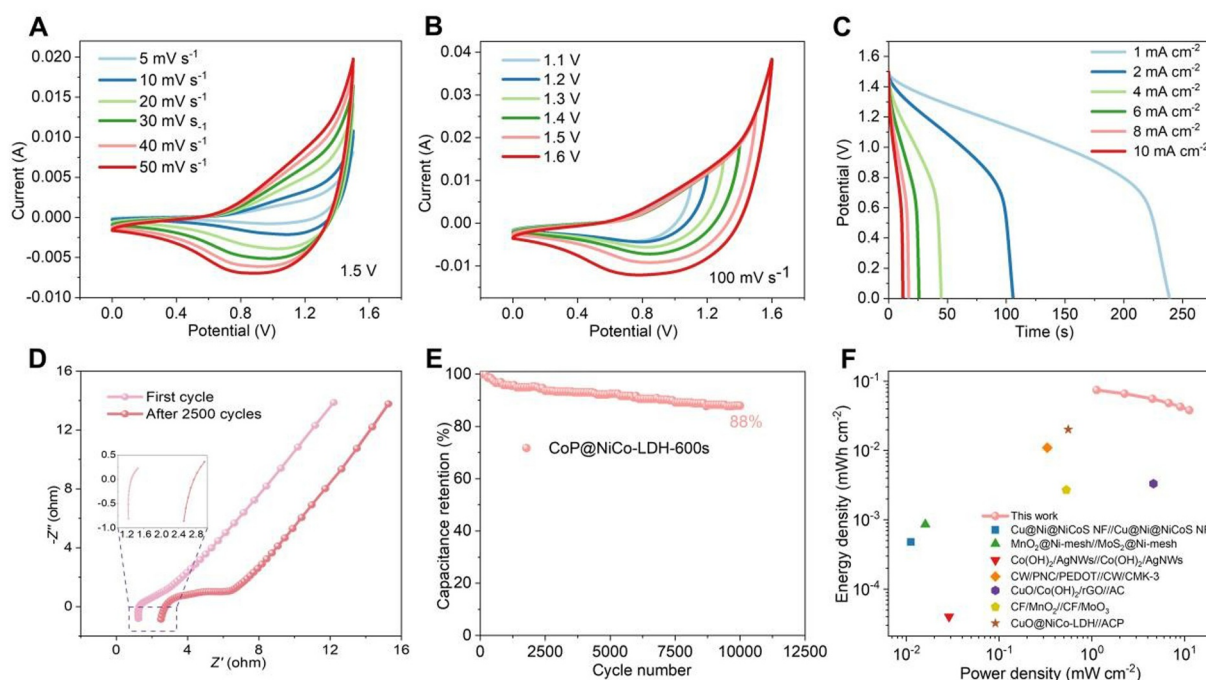


FIGURE 6 | Electrochemical performance of ASC device. (A) CV curves at different scanning rates. (B) CV curves at different voltage windows. (C) GCD curves. (D) Electrochemical impedance plots (inset shows the high frequency region). (E) Cycle stability test. (F) Ragone plot.

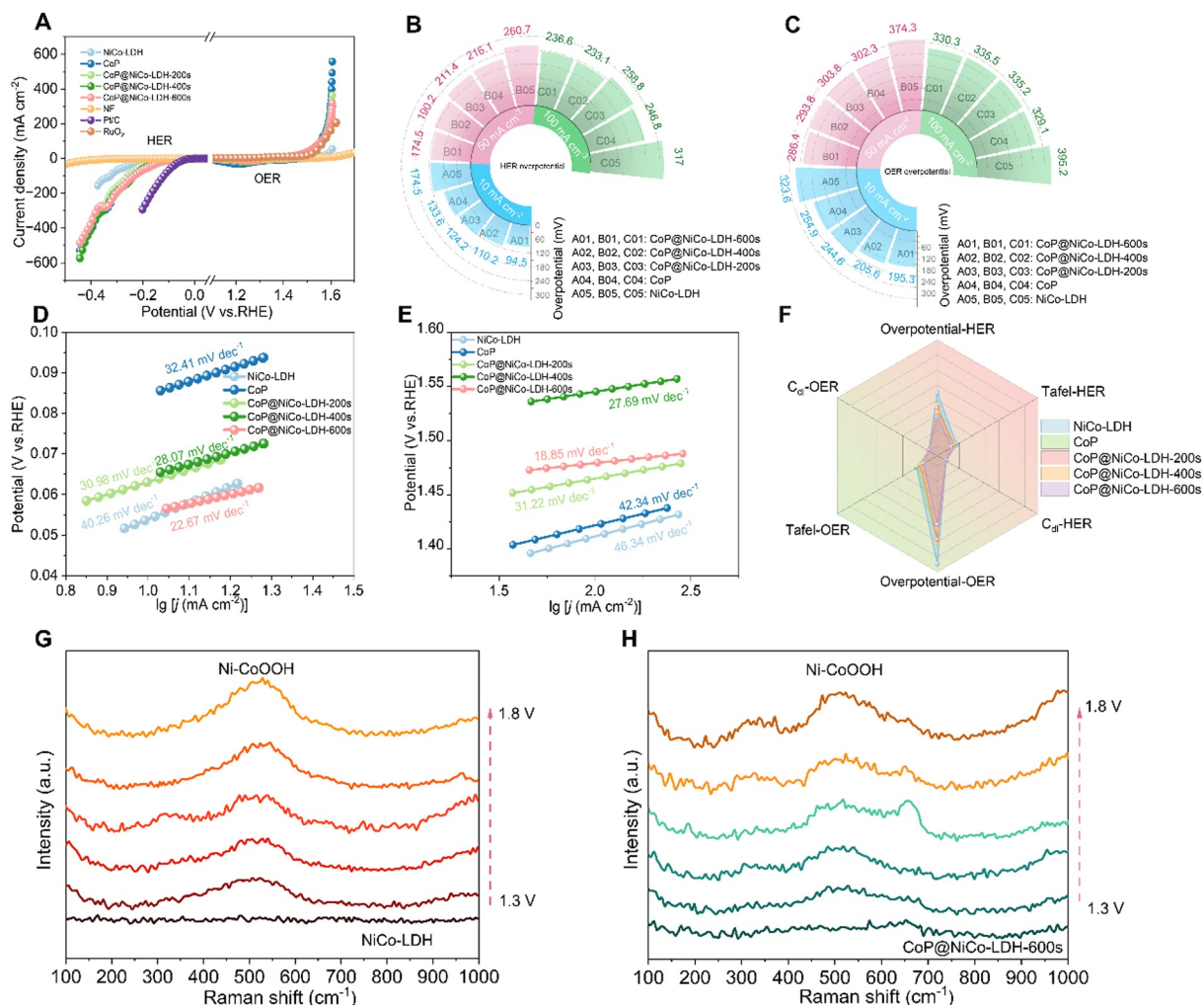


FIGURE 7 | Electrochemical performance. (A) LSV curves for HER and OER. (B) Overpotential sector diagram of HER. (C) Overpotential sector diagram of OER. (D) Tafel curves of HER. (E) Tafel curves of OER. (F) Comprehensive comparisons. In situ Raman spectra of (G) NiCo-LDH and (H) CoP@NiCo-LDH.

formation of Ni/Co oxyhydroxide-related species during anodic polarization. Notably, compared with pristine NiCo-LDH, CoP@NiCo-LDH-600s is a more pronounced spectral evolution and stronger oxyhydroxide-related Raman response under the same conditions, suggesting that the introduction of CoP facilitates the surface reconstruction process and promotes the generation of catalytically active Ni/Co oxyhydroxide during OER. These operando results further support that the superior OER activity of CoP@NiCo-LDH-600s originates not only from the favorable initial heterointerfacial electronic coupling but also from its more efficient active-phase evolution under working conditions.

The electrochemically active surface area (ECSA) is a crucial factor for evaluating the number of active sites in electrocatalysts and is determined using LSV. In Figure 8A,B, the double-layer capacitance (C_{dl}) values were measured. The C_{dl} values of the composite material in the HER and OER processes reach 0.03498 and 0.11195 mF cm⁻², respectively, indicating that it possesses more active sites and higher surface reactivity in both processes. EIS results in Figure 8C,D further confirm the

superior electrochemical performance of CoP@NiCo-LDH-600s, as evidenced by the smallest intercept on the real axis and the steepest slope in the low-frequency region. These features indicate reduced internal resistance and faster ion-transport kinetics. The Bode plot in Figure 8E illustrates the variation of phase angle with frequency for the CoP@NiCo-LDH-600s composite at different potentials, revealing its dynamic behavior during electrochemical reactions. The phase angle is relatively small, indicating strong ionic conductivity and a rapid charge transfer process. In the mid-frequency region, the phase angle gradually increases and forms a peak, reflecting the dominance of inner-layer electron transfer processes, which correspond to the charge conduction behavior within the material. As the potential increases (from 1.374 to 1.578 V), the phase angle becomes larger, and the peak frequency shifts slightly toward the lower frequency, suggesting that the interfacial charge transfer becomes more significant at higher potentials, accompanied by enhanced charge storage behavior. In the low-frequency region, the phase angle decreases more rapidly at higher potentials, indicating that high potentials facilitate the acceleration of the OER, resulting in higher electrochemical

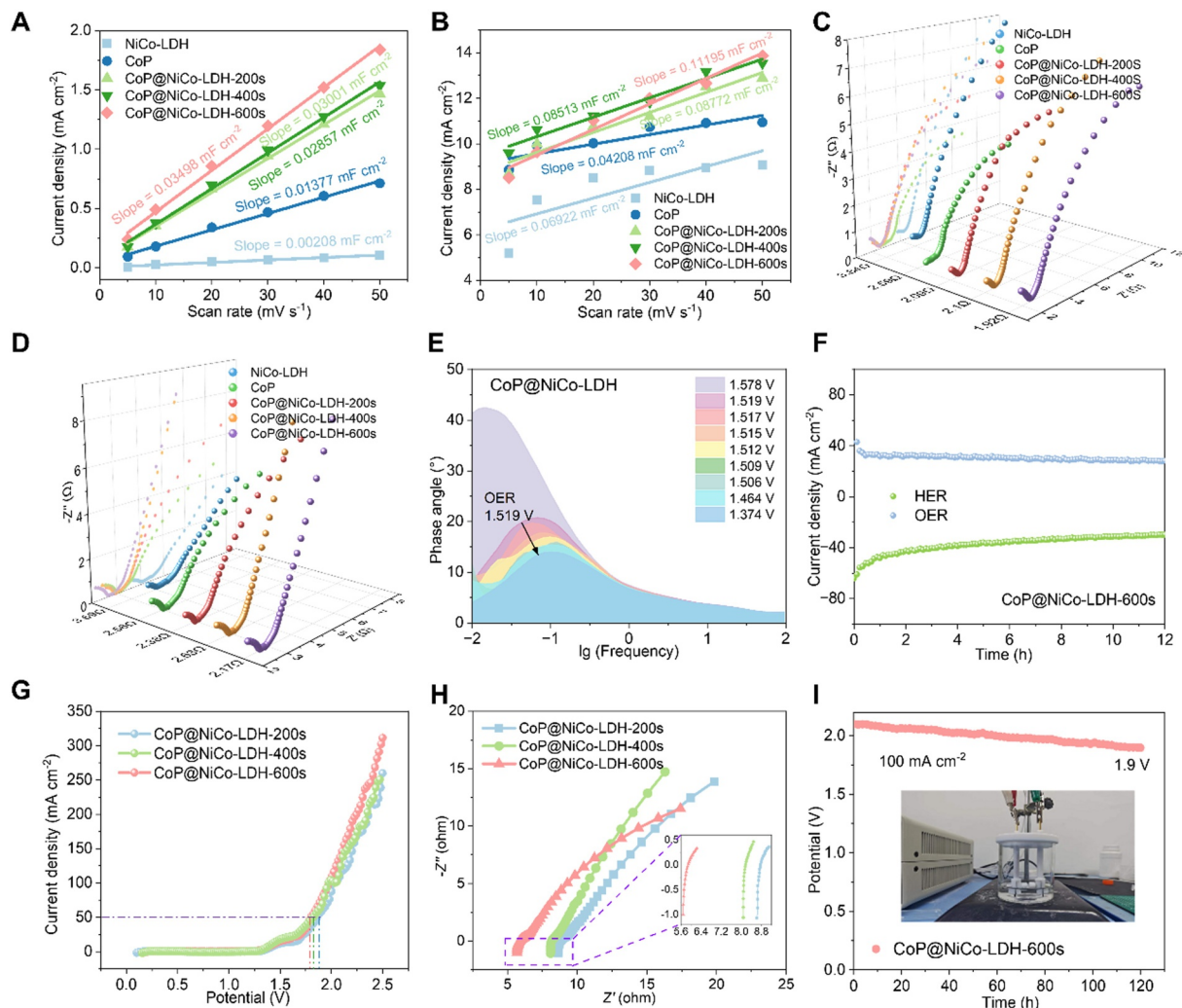


FIGURE 8 | Electrochemical performance. (A) Double-layer capacitance for HER. (B) Double-layer capacitance for OER. (C) 3D Nyquist plots for HER. (D) 3D Nyquist plots for OER. (E) Bode-phase plots of CoP@NiCo-LDH under different operating potentials. (F) Stability tests of HER and OER. (G) LSV curves at 5 mV s⁻¹. (H) Nyquist plots for water splitting. (I) Time-potential curve of water electrolysis at 100 mA cm⁻².

activity. These results indicate that CoP@NiCo-LDH-600s exhibits efficient charge-transfer characteristics and favorable OER kinetics at elevated potentials.

The long-term stability of CoP@NiCo-LDH-600s during HER and OER was further evaluated by time-dependent tests under fixed applied potentials. In Figure 8F, the catalyst maintains a cathodic current density of approximately 30–60 mA cm⁻² for HER and an anodic current density of approximately 28–40 mA cm⁻² for OER over 12 h, with only slight fluctuation. Importantly, in both cases, the operating current density remains well above 10 mA cm⁻² throughout the test period, indicating good operational durability of CoP@NiCo-LDH-600s under sustained electrolysis conditions. These results further support its promising stability for practical electrocatalytic water-splitting applications. The CoP@NiCo-LDH-600s catalyst was further used to construct a two-electrode electrolyzer. Using 1 M KOH as electrolyte, CoP@NiCo-LDH-600s-based electrolyzer requires only 1.8 V to achieve 50 mA cm⁻² (Figure 8G), which is lower than the other composite catalysts. Additionally, Figure 8H compares the EIS of the three composite materials. The inset is an enlarged view of the high-frequency region

marked by the purple dashed line in Figure 8H, showing that the 600s composite has the lowest R_s . Figure 8I presents the stability test results for prolonged water electrolysis. The results show that the current remains stable during prolonged electrolysis, indicating excellent long-term stability. These test results not only validate the potential application of the CoP@NiCo-LDH-600s catalyst in water electrolysis but also highlight its high efficiency and reliability. To further evaluate the structural stability of the catalyst after prolonged electrochemical operation, post-test XRD and SEM characterizations were carried out. The XRD patterns (Supporting Information S1: Figure S5) before and after the stability test remain nearly unchanged, without obvious peak shift or new-phase formation, indicating that the bulk crystalline framework of the catalyst is largely preserved during the electrochemical process. Meanwhile, the post-test SEM image (Supporting Information S1: Figure S6) shows that the hierarchical nanostructure is still maintained without obvious collapse or severe aggregation. These results indicate that although surface electronic redistribution may occur during electrocatalysis, the overall crystalline framework and morphology of CoP@NiCo-LDH-600s remain stable.

DFT calculations were performed to gain insight into the electronic-structure modulation and corresponding free-energy changes induced by the formation of the CoP@NiCo-LDH heterostructure. In Figure 9A–C, atomic models of CoP, NiCo-LDH, and CoP@NiCo-LDH illustrate a well-defined hetero-interface between the CoP phase and the NiCo-LDH layers. To further elucidate the electron redistribution at the heterojunction, Bader charge analysis was conducted on the Co and Ni sites, which are potential catalytic centers. The Bader charge effectively characterizes electron gain or loss at specific atomic sites. The results reveal that both Co and Ni atoms in CoP@NiCo-LDH exhibit reduced Bader charges compared to their counterparts in the pristine phases, indicating a lower extent of electron depletion. This local electron enrichment generally corresponds to a reduced oxidation state, which can enhance the ability of metal centers to modulate reaction intermediates during HER and OER.

To further investigate the electronic structural evolution upon heterojunction formation, the projected density of states (PDOS) of the materials was computed (Figure 9D–F). In pristine CoP, the states near the Fermi level are predominantly derived from Co 3d and P 3p orbitals, with the spin-up and spin-down Co 3d band centers located at -3.51 and -1.72 eV, respectively. Upon

formation of CoP@NiCo-LDH, the PDOS becomes more complex. Notably, the Co 3d band centers shift closer to the Fermi level (-0.53 and -0.72 eV), and the Ni 3d band centers rise from -2.73 – -1.62 eV in NiCo-LDH to -0.61 – -0.83 eV in the heterostructure. This shift indicates more moderate adsorption strengths for catalytic intermediates, which are favorable for enhanced activity.

The free energy changes associated with OER were also evaluated for Co and Ni sites in CoP, NiCo-LDH, and CoP@NiCo-LDH (Figure 9G). The OER follows a stepwise pathway: $* \rightarrow *OH \rightarrow *O \rightarrow *OOH \rightarrow *$. The incorporation of bimetallic centers plays a critical role in reducing the energy barriers of these intermediate steps. Notably, the rate-determining step on CoP@NiCo-LDH requires only 0.55 eV, significantly lower than those of pristine CoP (2.78 eV) and NiCo-LDH (0.61 eV), underscoring the enhanced catalytic efficiency of the heterostructure. For the HER, the key step involves the adsorption/desorption of hydrogen intermediates (H^*) on the catalyst surface. Structural models of H^* adsorption were constructed to simulate this process at the atomic scale. In Figure 9H, the energy of hydrogen adsorption was calculated. Pristine CoP shows a hydrogen adsorption free energy of 0.54 eV, indicating suboptimal H^* adsorption and therefore sluggish HER kinetics.

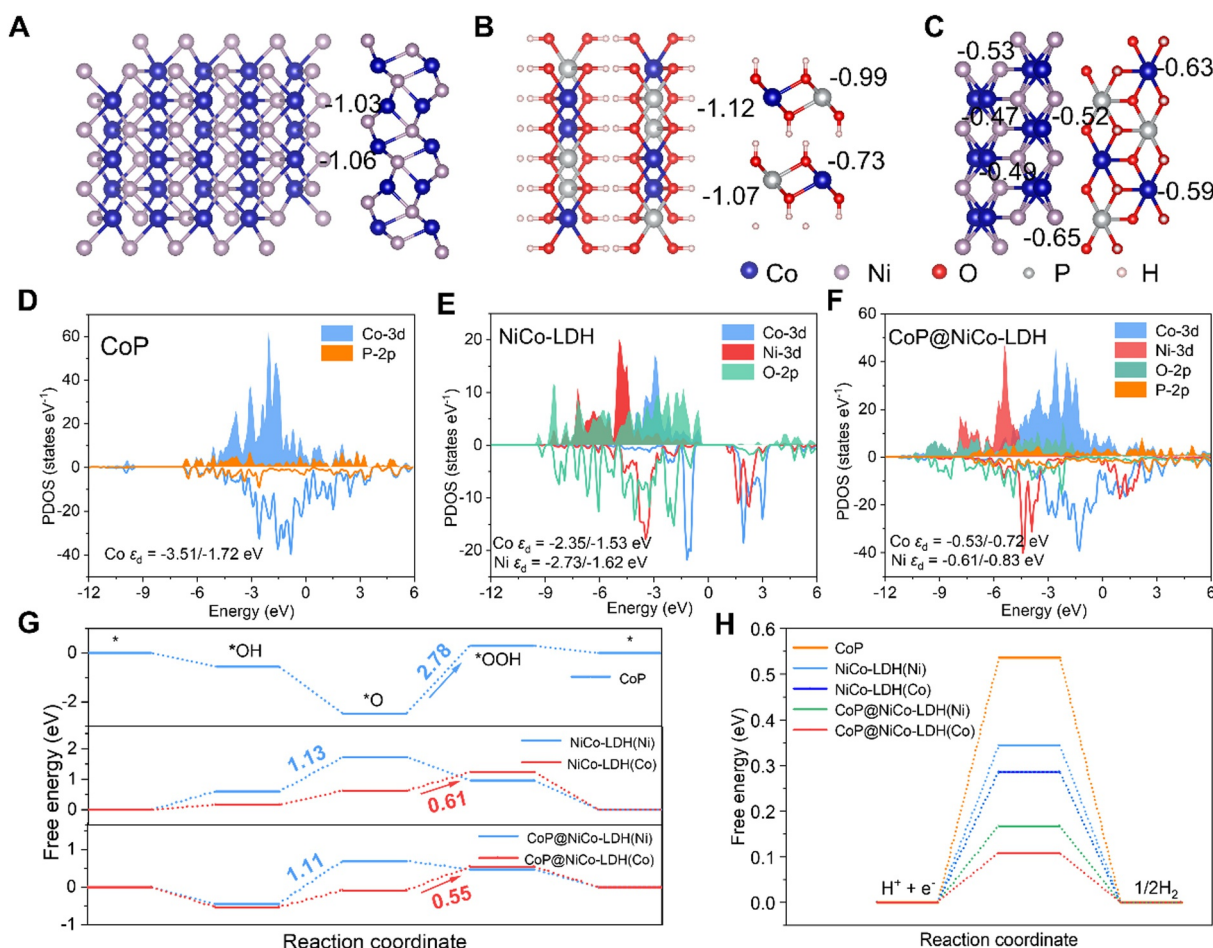


FIGURE 9 | Density functional theory calculations. Bader charge and the models of (A) CoP, (B) NiCo-LDH, and (C) CoP@NiCo-LDH. Projected density of states of (D) CoP, (E) NiCo-LDH, and (F) CoP@NiCo-LDH. (G) Calculated free energy diagrams of OER on CoP, NiCo-LDH (Ni and Co sites), and CoP@NiCo-LDH (Ni and Co sites). (H) Calculated free energy diagrams of HER on CoP, NiCo-LDH (Ni and Co sites), and CoP@NiCo-LDH (Ni and Co sites).

In contrast, CoP@NiCo-LDH shows an optimized free energy of -0.09 eV, which is close to the value of 0 eV. This near-thermoneutral adsorption facilitates both H^* formation and H_2 evolution, thereby lowering the kinetic barrier for HER. In summary, the construction of the CoP@NiCo-LDH hetero-interface not only modulates the material's electronic structure but also, through synergistic effects, significantly optimizes the adsorption free energy of key intermediates. This leads to markedly improved catalytic performance in both OER and HER processes.

4 | Conclusions

This study successfully fabricated a CoP@NiCo-LDH nanowire array with Ni-O, Ni-O-M, and Co-P units and systematically explored its potential applications in supercapacitors and electrocatalytic water splitting. Experimental results indicated that the material exhibited excellent electrochemical performance in supercapacitors, achieving a specific capacity of 892 C g^{-1} at 1 A g^{-1} , with 88% capacitance retention after 10,000 cycles. Furthermore, the assembled supercapacitor achieved an energy density of $74.6\text{ }\mu\text{Wh cm}^{-2}$ and a power density of 1.125 mW cm^{-2} , showcasing the material's potential for high-efficiency energy storage devices. In electrocatalytic tests, CoP@NiCo-LDH demonstrated remarkable long-term stability for water electrolysis, requiring overpotentials of only 195.3 mV for OER and 94.5 mV for HER at 10 mA cm^{-2} . The formation of the heterostructure effectively modulates the electronic structure and optimizes the adsorption energies of key reaction intermediates, thereby enhancing the catalytic activity. The integration of innovative hydrothermal and electrochemical deposition techniques in this study provides a robust foundation for the development of novel high-efficiency energy conversion materials.

Author Contributions

Ruiyu Li: data curation, writing – original draft. **Meizhen Dai:** investigation, methodology, writing – original draft. **Huaiya Zhou:** formal analysis. **Tiantian Wang:** software, validation. **Depeng Zhao:** funding acquisition, supervision. **Hengqi Liu:** resources, software. **Hongru Hao:** software. **Rongda Zhao:** formal analysis, writing – review and editing. **Fufa Wu:** funding acquisition, supervision. **Lihua Miao:** data curation, software.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

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