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Sea Coral-like NiCo$_2$O$_4$@$(\text{Ni}, \text{Co})$OOH Heterojunctions for Enhancing Overall Water-Splitting

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It is highly challenging to develop efficient and low-cost catalysts to meet stringent requirements on high current density for industrial water electrolysis application. We developed sea coral-like NiCo$_2$O$_4$@$(\text{Ni}, \text{Co})$OOH heterojunctions, synthesized based on an epitaxial in-grown method using poly(ethylene glycol) (PEG) as a template, and explored its as efficient electrocatalyst for water-splitting. A two-electrode based alkaline electrolyzer was fabricated using NiCo$_2$O$_4$@$(\text{Ni}, \text{Co})$OOH, which achieved a current density value of 100 mA·cm$^{-2}$ with a low potential of 1.83 V and high current density reached 600 mA·cm$^{-2}$ at potential of 2.1 V along with a strong stability. These are superior to most reported data for the electrocatalysts operated at high current densities. In-situ calculations based on density function theory reveal that the occurrence of water-splitting on the NiCo$_2$O$_4$@$(\text{Ni}, \text{Co})$OOH heterojunction surface. First-principles molecular dynamics simulation reveals that the stretching vibrations of metallic bonds of NiCo$_2$O$_4$@$(\text{Ni}, \text{Co})$OOH heterojunctions open the hydrogen bonds of water. Understanding the mechanism of water-splitting at the heterojunction from in-situ theoretical calculations is helpful to develop new generation industrial catalysts.

Introduction

Hydrogen as one of the best sustainable energy carriers has been regarded as one of the alternatives fuels to meet the future global energy demand, which are environmentally friendly and carbon free. However, it is highly challenging to develop efficient and low-cost catalysts to meet the stringent requirements on high current density (or high power density) for industrial water electrolysis applications. $^1$ There is a significant progress in the past a few years for developing low-cost catalysts from earth-abundant and non-noble-metal materials for hydrogen evolution reaction (HER) (e.g., boride, phosphides, chalcogenides, and titanate) $^{2-5}$ and for oxygen evolution reaction (OER) (e.g., nitrides, oxides, hydroxides, and oxyfluoride). $^6$-$^9$

Transition metal sulfides, selenides, nitrides, and phosphides have been applied as active HER catalysts. $^{10-13}$ Many reports also claimed that these materials are highly efficient OER catalysts and popularly regarded as ‘bifunctional catalysts’. However, it is well-known that metal sulfides are thermodynamically less stable than metal oxides under oxidizing potentials and metal nitrides and phosphides are less stable than sulfides and so forth. $^{14}$ In fact, these oxidation processes are happening everyday in natural environments and are responsible for the transformation and formation of many minerals and rocks. Therefore, metal sulfides, selenides, nitrides, and phosphides can be oxidized easily to their corresponding metal oxides/hydroxides, especially in aqueous and strongly oxidative environments as the OER.

NiCo$_2$O$_4$, one of the popular cobalt-based spinel oxides, has become an emerging electrode material attributed to its easy material availability, simplified preparation, low cost, and good corrosion stability in alkaline electrolytes. $^{15-18}$ However, due to the requirement on large uphill-conversion-energy for water-splitting, it is difficult to significantly increase its electrochemical activities. $^{19, 20}$ Previous reports confirmed hierarchical NiCo$_2$O$_4$ hollow structures that consist of 1D nanostructures for high performance overall water-splitting and considered that nanostructures promoted the release of evolved gas bubbles and exhibited maximum catalytic performance. $^{21}$ NiCo$_2$O$_4$ surface modification with other materials facilitated proton transfer and dissociation and was regarded as an effective way to enhance the activity on the catalysts. $^{22, 23}$ For example, Wang et al. reported a novel hollow core-shell Ni@NiCo$_2$O$_4$ to improve the electronic conductivity of NiCo$_2$O$_4$ owing to the hollow Ni directly attached to the conductive Ni foam. The hollow core-shell Ni@NiCo$_2$O$_4$ electrode showed excellent catalytic activity with a current density of 10 mA·cm$^{-2}$ at a bias of 1.58 V. $^{24}$ These are not enough to reveal the catalytic nature and helpful to

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develop stronger catalysts. In recent years, the good optical property of semiconductor heterojunction has received extensive attention for applications in photoelectrochemical water splitting and nanomaterials. 25, 26 It leads to much enhanced electrocatalytic performance to develop heterojunction electrode materials, where the two structurally matching nanophases are synergized by an epitaxial in-grown interface. 27 Therefore, integrating the advantages of the HER and OER electrocatalysts to construct novel heterostructures, which possess binding affinities to both hydrogen and oxygen-containing intermediates, is extremely beneficial for enhancing the overall photoelectrochemical water-splitting activity. For example, Yang et al. proposed to form a hydrogen bonds O-H-O ads (O and O_ad denoted the surface oxygen atom of transition metal oxides and the oxygen atom of the adsorbed hydroxyl group or water molecule without bonded to transition metals, respectively) on a reconstructed nanocrystal surface to facilitate proton transfer and dissociation, leading to an enhanced water-splitting activity. 28 Previous reports have identified heterojunctions can reduce the energy barrier of water-splitting and optimize the intermediates adsorption/desorption from ex-situ theoretical calculations. 29, 30 However, understanding water-splitting on the heterojunction surfaces from in-situ theoretical calculations are pivotal for enhancing overall water-splitting, because of their outstanding chemisorptions of H2O and intermediates.

In this paper, we designed and fabricated sea coral-like NiCo2O4@Ni, CoOOH heterojunctions for water-splitting. The approach includes formation of the precursors by integrating PEG into sea coral-like NiCo2-PEG intermediate compounds (from Ni/Co-based nitrate with the mole ratio of Ni to Co being 1/2) and conversion of NiCo2O4@Ni, CoOOH heterojunctions using epitaxial in-grown method. The NiCo2O4@Ni, CoOOH heterojunctions exhibited high catalytic activity and excellent durability, achieving a current density of 10 mA cm−2 at a low overpotential of 120 mV for HER and 220 mV for OER, respectively. A NiCo2O4@Ni, CoOOH|NiCo2O4@Ni, CoOOH two-electrode alkaline electrolyzer achieved a current density of 100 mA cm−2 at a low cell bias of 1.83 V. First-principles molecular dynamics simulation reveals that the stretching vibrations of metallic bonds of the NiCo2O4@Ni, CoOOH heterojunctions open the hydrogen bonds of water.

**Experimental Section**

**Preparation and characterization**

Morphology, chemical compositions, and electrochemical characterization of all samples presented in the supporting information.

**Computational Detail**

Density function theory (DFT) calculation was performed using a plane-wave pseudopotential function, aided by the Accelrys Materials Studio (Accelrys Inc.) graphical front end interface. The exchange correlation functional was applied using a generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerh (PBE) functional. 31 The geometries of all the systems were optimized, in which a conjugated gradient technique was used in a direct minimization of the Kohn-Sham energy functional, and pseudopotentials were employed to represent the core electrons. Plane-wave functions were used as basis sets. 32

**Initial adsorption structures**

As shown in Figure 1a, the XRD patterns of crystalline NiCo2O4@Ni, CoOOH showed that the peaks of (311) and (001) were the main strong peaks of NiCo2O4 and (Ni, Co)OOH, respectively. According to the XRD result and previous finding, 33 NiCo2O4(311), (Ni, Co)OOH(001) and NiCo2O4@Ni, CoOOH heterojunction (a layer (Ni, Co)OOH(001) coated onto NiCo2O4(311)) were selected for geometrical optimization. The energy cutoff was 489.8 eV and k-point mesh of 2 x 2 x 1 was used for the geometrical optimization calculations. To simulate a realistic surface catalysis reaction, our calculations were at 100% high coverage regimes on the surface with 1/4 of a monolayer of intermediates (H2, H+, H2O*, HO*, O*, HO2*, and O2) and 3/4 of a monolayer of water.

The coverage regime was described in previous literature. 34 The intermediates of H2O*, H+, H2O*, HO*, O*, HO2*, and O2* were put on the top of NiCo2O4@Ni, CoOOH surface. The initial distances between intermediates and the corresponding active sites were set as 1.0 Å. The adsorption energy was defined as $E_{\text{ads}} = E_{\text{total}} - E_{\text{surf}} - 3 	imes E_{\text{H2O}} - E_{\text{surf}}$, where $E_{\text{total}}$ and $E_{\text{surf}}$ are the total energies of the surface with and without adsorbates (including three water and one intermediate), respectively, $E_{\text{H2O}}$ is the energy of water, and $E_{\text{surf}}$ is the energy of intermediates (H2, H*, H2O*, HO*, O*, HO2*, O2*, and O2).

**First-principles molecular dynamics (FPMD) simulations**

The optimized H2O/NiCo2O4@Ni, CoOOH interface model was adopted for the FPMD simulations, in which the bottom layer atoms were fixed and other atoms and water molecules were allowed to relax. The energy cutoff was 489.8 eV and a k-point mesh of 2 x 2 x 1 was used for the FPMD calculations. The FPMD calculations were run for 200 steps to reach equilibrium in the NVE using eXtended-Lagrangian (XL-BOMD) molecular dynamics at a temperature of 273 K with a time step of 1 fs for motion equation integration. 35, 36

**Results and Discussion**

Scheme 1 illustrates the synthesis approach and microstructure of NiCo2O4@Ni, CoOOH heterojunction. The chemical reaction mechanisms for NiCo2O4@Ni, CoOOH heterojunction can be summarized Reaction 1-7. To simplify the reaction equations, the PEG400 molecule, HO(CH2)nO-H (n = 8-9), is written as ROH and the anion, HO(CH2)nO−, as written RO−.

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\begin{align*}
\text{Ni}^{2+} + 2\text{ROH} & \leftrightarrow \text{Ni(RO)}_2^+ + 2H^+ \\
\text{Co}^{3+} + 3\text{ROH} & \leftrightarrow \text{Co(RO)}_3^+ + 3H^+ \\
\text{Ni(RO)}_2^+ + 3\text{Co(RO)}_3^+ + 8\text{H}_2\text{O} & \rightarrow (\text{Ni,2Co(OH)})_8 + 8\text{ROH} \\
8(\text{Ni,2Co(OH)})_8 & \rightarrow 4\text{NiO} + 4\text{Co}_2\text{O}_3 + 4\text{Ni,CoOOH} + 30\text{H}_2\text{O} + 5\text{SO}_2 \\
\text{NiO} + \text{Co}_2\text{O}_3 & \rightarrow \text{NiCo}_2\text{O}_4 \\
\text{NiCo}_2\text{O}_4 + (\text{Ni,Co})\text{OOH} & \rightarrow \text{NiCo}_2\text{O}_4@\text{(Ni,Co)}\text{OOH} 
\end{align*}
\]

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The complexation reaction of PEG400 and Ni$^{2+}$ (or Co$^{3+}$) has been proposed by Faidi et al (Reactions 1 and 2). The NiCo$_2$-PEG intermediate compounds combine with H$_2$O thus forming the (Ni, 2Co)(OH)$_2$, which generate NiO, Co$_2$O$_3$, and (Ni, Co)OOH during the following pyrolysis process (Reactions 3 to 4). NiCo$_2$O$_4$ is produced by reaction between NiO and Co$_2$O$_3$ (Reaction 5). The NiCo$_2$O$_4$(Ni, Co)OOH heterojunction is formed with an epitaxial the (Ni, Co)OOH growth on NiCo$_2$O$_4$ (Reaction 6). Finally, the PEG is pyrolysed into CO$_2$ and H$_2$O (Reaction 7).

Figure 1a shows the XRD patterns of crystalline NiCo$_2$O$_4$(Ni, Co)OOH heterojunction. The XRD peaks at 31.1°, 36.7°, 44.6°,and 59.1° correspond to (220), (311), (400), and (511) of NiCo$_2$O$_4$ (JCPDF # 20-0781) and at 19.1°, 38.7°, and 65° correspond to (001), (101), and (440) of (Ni, Co)OOH (JCPDF # 29-0491) components. The peaks of (311) and (001) is the main strong peaks of NiCo$_2$O$_4$ and (Ni, Co)OOH, respectively. According to the XRD result, NiCo$_2$O$_4$(311), (Ni, Co)OOH(001) and NiCo$_2$O$_4$(Ni, Co)OOH heterojunction (a layer (Ni, Co)OOH(001) coated onto NiCo$_2$O$_4$(311)) were selected for computational geometrical optimisation.

Figure 1a shows the XRD patterns of crystalline NiCo$_2$O$_4$(Ni, Co)OOH heterojunction. The absorption peaks at 1000-1000 cm$^{-1}$ (blue) and 1350-1450 cm$^{-1}$ are assigned to the bending and stretching vibration modes of oxygen-hydrogen groups for chemisorbed/physisorbed water molecules onto the NiCo$_2$O$_4$(Ni, Co)OOH surface. The peak located from 400 to 900 cm$^{-1}$ is assigned to the NiO and Co$_2$O$_3$ stretching vibration modes (blue). The absorption peaks at 1550 to 1600 cm$^{-1}$ and 1350 to 1450 cm$^{-1}$ are assigned to the H$_2$O bending vibration mode and OOH stretching vibration mode, respectively (green).

The XPS analysis results further prove the ingredients of NiCo$_2$O$_4$(Ni, Co)OOH heterojunction with the same information of those from the XRD (Figure 1a) and FT-IR analysis (Figure 1b). Figure 1c shows the high-resolution XPS spectrum of O1s, which can be deconvoluted into three peaks. The first peak at 529.39 eV is assigned to the metal oxides, which are related to NiO and Co$_2$O$_3$. The peak at 531.5 eV can be assigned to the oxygen in the hydroxide group (OH$^-$), which are linked with surface phases of y-NiOOH and y-CoOOH. The peaks at 533.5 can be assigned to the surface adsorption of H$_2$O. The XPS spectrum of Co in the NiCo$_2$O$_4$(Ni, Co)OOH can be deconvoluted into four peaks (Figure 1d). The characteristic peaks Co$^{3+}$ at 795.6 eV, which is ascribed to CoOOH. The peaks of 854.4 and 872.1 eV are attributed to NiO (Figure 1e). Whereas the peaks at 856.0 and 873.6 eV are corresponding to NiOOH (Figure 1e).
CoOOH (Figure 2f). The lattice parameter at the black arrowhead was measured to be 0.24 nm, corresponding to the (311) crystal plane of NiCo$_2$O$_4$ (Figure 2f). The HRTEM results are in good agreements with the XRD analysis (Figure 1a) and SAED pattern (Figure 2d inset). In brief, SEM and (HR)TEM analysis show that the hierarchical structures of the NiCo$_2$O$_4$@Ni, CoOOH heterojunction are consisted of capillary (mesoporous, with width of 5 nm) channels, petals with medium pore diameter (macroporous, with width of 100 nm) channels, and the stamen with large (microns) channels. These results can well-explain the BET measurement results of a wide pore size distribution and large surface areas (Figure S2).

Figure 2. Results of NiCo$_2$O$_4$@Ni, CoOOH heterojunction for a) the field emission scanning electron microscopy (FE-SEM) b) a photograph of sea coral, c) the corresponding EDX mapping images of C, O, Co and Ni elements, d) the transmission electron microscopy (TEM) with SAED pattern (inset), e) and f) the high resolution transmission electron microscopy (HR-TEM).

The activities of nanostructured catalysts could be partially enhanced due to their increased electrochemical surface areas (see Supporting Information for details of the electrochemical surface area (ECSA)). 44 We have corrected the electrochemical measurements by removing the contribution of ECSA. Figures 3a and 3b present the HER and OER polarization curves for the NiCo$_2$O$_4$@Ni, CoOOH heterojunction in 1.0 M KOH solution at a scan rate of 5 mV s$^{-1}$. The NiCo$_2$O$_4$@Ni, CoOOH heterojunction has an potential of ~120 mV at a current density of 10 mA cm$^{-2}$ (Figure 3a), which is lower than that of the Pt/C (~60 mV), but is higher than that of NiCo$_2$O$_4$ (~180 mV). Figure 3b presents the OER polarization curves with a current density of 10 mA cm$^{-2}$, and the overpotential values follows the order from low to high with a sequence of: RuO$_2$ (200 mV) <NiCo$_2$O$_4$@Ni, CoOOH(220 mV) <NiCo$_2$O$_4$(240 mV), whereas the previously reported NiCo$_2$O$_4$@NiO@Ni with a larger OER overpotential (280 mV). 45 The NiCo$_2$O$_4$@Ni, CoOOH heterojunction exhibits a better electrocatalytic activity than the data of the NiCo$_2$O$_4$. Table S1 shows the comparison of HER and OER activity for NiCo$_2$O$_4$@Ni, CoOOH heterojunction with other recently published highly active electrocatalysts in alkaline electrolyte (1 M KOH). Clearly, NiCo$_2$O$_4$@Ni, CoOOH heterojunction exhibits excellent property of HER and OER in alkaline electrolyte.

The catalytic kinetics of NiCo$_2$O$_4$@Ni, CoOOH heterojunction assessed by the Tafel plots are shown in Figures 3c and 3d, which were derived from the Koutecky-Levich plots (Figure S3). The Tafel slopes provide the detailed information of reaction mechanism and catalytic activity. A smaller Tafel slope indicates that the overpotential of the catalytic reaction is lower at the same dynamic current density or apparent current density. 46 As shown in Figure 3c, the obtained Tafel slope of the NiCo$_2$O$_4$@Ni, CoOOH (60 mV·dec$^{-1}$) is lower than that of NiCo$_2$O$_4$ (63 mV·dec$^{-1}$). The results show that the NiCo$_2$O$_4$@Ni, CoOOH heterojunction has a superior HER reaction kinetics (Figure 3c). The result of Tafel plot for OER reaction kinetics shows that the NiCo$_2$O$_4$@Ni, CoOOH (48 mV·dec$^{-1}$) has a slope value which is lower than that of NiCo$_2$O$_4$ (53 mV·dec$^{-1}$), indicating that the NiCo$_2$O$_4$@Ni, CoOOH has a faster OER reaction kinetics than NiCo$_2$O$_4$. We further analysed the catalytic dynamics in terms of turn-over frequency (TOF) of NiCo$_2$O$_4$@Ni, CoOOH and NiCo$_2$O$_4$ towards the HER and OER. The TOF (0.22 s$^{-1}$) of the NiCo$_2$O$_4$@Ni, CoOOH heterojunction is higher than that of NiCo$_2$O$_4$ (0.15 s$^{-1}$) which were obtained at an overpotential of 0.20 V for HER (Figure 3c inset). TOF (0.2 s$^{-1}$) of the NiCo$_2$O$_4$@Ni, CoOOH heterojunction is also higher than that of NiCo$_2$O$_4$ (0.12 s$^{-1}$) for OER under an overpotential of 0.20 V (Figure 3d inset). Here, we further studied the Faradic efficiency of the OER for various electrodes using the RRDE technique. When a constant current (300 µA) was applied to the disk electrode for O$_2$ generation, a ring current of about 59.7 µA and 58 µA could be detected on the ring electrodes with NiCo$_2$O$_4$@Ni, CoOOH and NiCo$_2$O$_4$ catalysts (Figure S4a and S4b). Therefore, the Faradic efficiency of NiCo$_2$O$_4$@Ni, CoOOH and NiCo$_2$O$_4$ was determined to be 99.5% and ~96.7%, suggesting that the former has higher catalytic activity towards OER.

Figure 3. Electrochemical measurements: linear sweep polarization curves (LSV) of NiCo$_2$O$_4$@Ni, CoOOH (curve 1), NiCo$_2$O$_4$ (curve 2), Pt/C (curve 3), RuO$_2$ (curve 4) for a) HER and b) OER; the corresponding Tafel slopes of NiCo$_2$O$_4$@Ni, CoOOH (black) and NiCo$_2$O$_4$ (red) for c) HER and d) OER; The turnover frequency (TOF) of specific activity and mass activity at overpotential of 200 mV for in 1 M KOH (inset).

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We then further demonstrated high-performance two-electrode water electrolysis cells (NiCo₂O₄@(Ni, Co)OOH || NiCoO₂@Ni, Co)OOH) for overall water splitting. The NiCo₂O₄@(Ni, Co)OOH heterojunction merely required bias voltages of 1.61, 1.66, and 1.83 V to reach current densities of 10, 20, and 100 mA·cm⁻² (Figure 4a). This is superior to previously reported electrocatalysts (Table S2), for examples, NiCo₂O₄ hollow microcuboids (1.74 V at 20 mA·cm⁻²) 21, NiFe/NiCo₂O₄/NF (1.67 V at 20 mA·cm⁻²) 47, and NiCo₂O₄ nanosheet array (1.74 V at 20 mA·cm⁻²) 48. Our fabricated NiCo₂O₄@(Ni, Co)OOH exhibited an excellent stability for 28 hours of water electrolysis without obvious degradation during a test at a constant potential of 1.83 V (Figure 4a inset). Furthermore, The NiCo₂O₄@(Ni, Co)OOH || NiCo₂O₄@(Ni, Co)OOH exhibited the stability for 30 h with the current density increased from 0.1 to 0.6 A·cm⁻² in the two-electrode device (Figure 4b) and the XRD and HRTEM of NiCo₂O₄@(Ni, Co)OOH heterojunction was shown after 30 h water-splitting in Figure S5. The results showed that high current density approached 0.6 A·cm⁻² (6,000 A·m⁻²) at potential of 2.1 V with a good stability for 10 hours. The photograph of water electrolysis in the inset in Figure 4b exhibited gas evolution on both electrodes at a current density of 100 mA·cm⁻². It was shown in the supporting information Movie S1. The gas chromatography survey clearly confirms that the produced bubbles are H₂ and O₂ (Figure S6a). The Faradaic efficiency (FE) of experimental H₂ (black square) and O₂ (red sphere) production were versus the theoretic 98% efficiencies (solid line) for overall water splitting of NiCo₂O₄@(Ni, Co)OOH in 1 M KOH at 100 mA·cm⁻² (Figure S6b). The concentrations of Co and Ni were detected by inductively coupled plasma mass spectrometry (ICP-MS). The levels of Co and Ni in the solution after durability test were 0.5 and 0.3 μg·L⁻¹, respectively. The level is lower than 50 μg·L⁻¹ of the environmental protection standard (Discharge Standard of Water Pollutants for Industry (GB8978-1996)). It is important to confirm the environmental safety of the process. Our newly designed catalyst can satisfy the stringent requirements of high current density in the industrial water electrolysis applications.

**Figure 4.** a) Electrolyzer properties of NiCo₂O₄@(Ni, Co)OOH || NiCo₂O₄@Ni (Co)OOH (the dot horizontal line is a guide to show a current density of 10, 20, and 100 mA·cm⁻²) and the chronoamperometric curves for long-term water electrolysis at a static potential of 1.83V (inset). b) Multi-current steps of NiCo₂O₄@Ni, Co)OOH || NiCo₂O₄@Ni, Co)OOH for long-term with the current density increased from 0.1 to 0.6 A·cm⁻² in the two-electrode device. The inset is an optical photograph of NiCo₂O₄@Ni, Co)OOH || NiCo₂O₄@Ni, Co)OOH for the generation of H₂ and O₂ at a current density of 100 mA·cm⁻².

The lower overpotential and Tafel slope of NiCo₂O₄@(Ni, Co)OOH than that of NiCo₂O₄ suggest that the NiCo₂O₄@(Ni, Co)OOH heterojunction can lower down the activation energy of water-splitting and also enhance the activity of the catalysis processes. In order to understand this effect on the enhanced overall water-splitting performance of NiCo₂O₄@(Ni, Co)OOH heterojunction, we performed density function theory (DFT) calculations to investigate the binding energies of the intermediates (H₂O⁴⁺, HO⁴⁺, O²⁻, OO²⁻, OO²⁻, O²⁺, H²⁺, and O²⁺ species) and product (O₂ and H₂) on the NiCo₂O₄ and the NiCo₂O₄@(Ni, Co)OOH surfaces, respective.

Figure 5a shows the models for NiCo₂O₄and NiCo₂O₄@(Ni, Co)OOH heterojunction surface and water-splitting reaction on NiCo₂O₄@(Ni, Co)OOH heterojunction surfaces in an alkaline electrolyte. The four electron reaction paths (Figure 5a) (1-4) are shown:

1. Cathode: 2H₂O + 2e⁻ → 2OH⁻ + H₂ (8)
2. Anode: 4OH⁻ → HO²⁻ + 3OH⁻ + e⁻
   - → O²⁻ + H₂O + OH⁻ + 2e⁻ (9)
   - → HOO⁻ + H₂O + OH⁻ + 3e⁻ (10)
   - → O²⁻ + 2H₂O + 4e⁻ (11)

We calculated the energy for Reactions 8-12 and its change (ΔE). The catalytic performance can be estimated by the magnitude of potential, which determines the rate-limiting step toward the HER and OER, i.e., ΔE₇₁₀. The ΔE₇₁₀ is Max [ΔE₁, ΔE₂, ΔE₃, ΔE₄] (Figure 5a). Figure Sb shows the corresponding binding energies of H₂, H₂O, H⁺, H₂O⁻, O²⁻, HOO⁻, O²⁻, and O₂ on the NiCo₂O₄@Ni, Co)OOH heterojunction surface (black histogram) and NiCo₂O₄ surface (red histogram), and their difference (greenbox). These are two normal distribution for red histogram and black histogram, where the distribution ranges from ΔE₇₁₀ to ΔE₇₁₀, and ΔE₇₁₀, to ΔE₇₁₀, respectively. While, the trend of their binding energies difference (green box) is two sanddle-shaped distribution from ΔE₇₁₀ to ΔE₇₁₀. The detials are summarized in Table 1. For the cathodic reaction (i.e., the HER), the binding energy values of the H⁺ (ΔE₇₁₀) on NiCo₂O₄@Ni, Co)OOH heterojunction and NiCo₂O₄ surface are 1.08 and 2.74 eV, and the binding energy difference is −1.68 eV. The value of ΔE₇₁₀ on the two catalysts is the maximum among those of ΔE₇₁₀, ΔE₇₁₀, and ΔE₇₁₀, (Table 1). Accordingly, we conclude the adsorption of H⁺ is the potential-determining step during the HER process. For the cahrondic reaction, the ΔE₇₁₀ is the maximum among those of ΔE₇₁₀, ΔE₇₁₀, ΔE₇₁₀, ΔE₇₁₀, and ΔE₇₁₀, on the NiCo₂O₄@Ni (Co)OOH heterojunction and NiCo₂O₄ surface, respectively. The ΔE₇₁₀ on the NiCo₂O₄@Ni, Co)OOH heterojunction and NiCo₂O₄ surface are 1.74 and 4.42 eV, and their binding energy difference is −3.48 eV. Therefore, the O²⁻...
adsorption is the potential-determining step for the OER. The $\Delta E_{\text{O}}$ is bigger than $\Delta E_{\text{H}}$, indicating electron reaction path 3 is the slowest step (Figure 5a). The calculation results clearly show that the NiCo$_2$O$_4$@Ni, Co)OOH heterojunction surface has lower binding energy for the HER and OER if compared with the NiCo$_2$O$_4$ surface (Figure 5b). A low binding energy facilitates the dissociation of H$_2$O molecules and eventually release of H$_2$ and O$_2$. For example, the difference in binding energy of H$_2$ on the NiCo$_2$O$_4$@Ni, Co)OOH heterojunction surface and NiCo$_2$O$_4$ surface is 1.14 eV, meaning the NiCo$_2$O$_4$@Ni, Co)OOH heterojunction can facilitate the release of H$_2$ compared with NiCo$_2$O$_4$. The difference in binding energy of H* is $\sim$1.68 eV, meaning the NiCo$_2$O$_4$@Ni, Co)OOH heterojunction needs a less energy compared with NiCo$_2$O$_4$. Our DFT calculations demonstrate that the activation energy of water-splitting can be lowered by NiCo$_2$O$_4$@Ni, Co)OOH heterojunction than that of NiCo$_2$O$_4$.

![Figure 5](image-url)

**Figure 5.** a) Water splitting reactions on the NiCo$_2$O$_4$@Ni, Co)OOH heterojunction surface in an alkaline electrolyte. b) The energy-difference (green) of the corresponding binding energies of H$_2^*$, H*, H$_2$O*, HO*, O*, HOO* and O$_2^*$ dissociation on NiCo$_2$O$_4$@NiCoO$_3$ surface (red) and NiCo$_2$O$_4$@Ni, Co)OOH surface (black).

First-principles molecular dynamics (FPMD) simulations provides a dynamic model to monitor the water-splitting on the surfaces of NiCo$_2$O$_4$ (Ni, Co)OOH, and NiCo$_2$O$_4$@Ni, Co)OOH heterojunction, respectively. Figures 6a-6c and 6d-6f show the initial and final structures of water on the surfaces of NiCo$_2$O$_4$@Ni, Co)OOH heterojunction before and after the molecular dynamics simulations (the detailed simulation animations of movies are shown in Movie S2). From the analysis results of NiCo$_2$O$_4$@Ni, Co)OOH heterojunction, the stretch vibrations of the metallic bond (one metal atom is bonded to another secondary metal atom) open the hydrogen bond of the water (Movie S2). For the NiCo$_2$O$_4$, the simulation results show a similar decomposition mechanism of water as that of the NiCo$_2$O$_4$@Ni, Co)OOH heterojunction. Whereas for the (Ni, Co)OOH, there needs a hydrogen bond stretches of O$_2^*$−H−O$_{ad}$ in order to break the bonds of water. 28 There are weak vibrations of the atoms from the second layer and below for the NiCo$_2$O$_4$ (Movie S2), if compared with that of the (Ni, Co)OOH). Compared to the NiCo$_2$O$_4$, a monolayer of (Ni, Co)OOH on the NiCo$_2$O$_4$ surface can enhance the activity based on above results of the binding energy. The FPMD results show the water-splitting mechanisms for different materials. For the NiCo$_2$O$_4$@Ni, Co)OOH heterojunction and NiCo$_2$O$_4$, it is the stretching vibrations of the metallic bonds to open the hydrogen bonding of water; whereas for the (Ni, Co)OOH, it is the stretching vibrations of short hydrogen bonds of O$_2^*$−H−O$_{ad}$ to open the hydrogen bonding of water.

![Figure 6](image-url)

**Figure 6.** The Initial structures of a)-c) and final structures of d)-f) taken from the first principle molecular dynamics (FPMD) simulations of water on NiCo$_2$O$_4$, (Ni, Co)OOH, and NiCo$_2$O$_4$@Ni, Co)OOH heterojunction at 273K, respectively.

The DFT calculation shown above already demonstrated that adsorption energy of the NiCo$_2$O$_4$@Ni, Co)OOH heterojunction with the corresponding intermediates is much lower than that of the NiCo$_2$O$_4$ surface, thus facilitating the dissociation of the H$_2$O molecule and the release of H$_2$ and O$_2$. In-situ calculations based on density function theory reveal that the occurrence of water-splitting on the NiCo$_2$O$_4$@Ni, Co)OOH heterojunction surface. First-principles molecular dynamics simulation reveals that the stretching vibrations of the metallic bonds in the NiCo$_2$O$_4$@Ni, Co)OOH heterojunction have opened the hydrogen bonding of water. Hence, we believe that the coral-like NiCo$_2$O$_4$@Ni, Co)OOH heterojunction is promising for the industrial applications in future.

**Table 1.** Binding energies of H$_2$, H−H*, H*, H$_2$O*, HO*, O*, HOO*, O−O*, and O$_2$ (\(\Delta E\) in eV) on the NiCo$_2$O$_4$@Ni, Co)OOH heterojunction surfaces, and their energy-differences.
Conclusion

In summary, the sea coral-like NiCoO$_2$@(Ni, Co)OOH heterojunction exhibited high catalytic activity and excellent durability, achieving a current density of 10 mA cm$^{-2}$ at a low overpotential of 120 mV for HER and 220 mV for OER, respectively. A NiCoO$_2$@(Ni, Co)OOH || NiCoO$_2$@(Ni, Co)OOH two-electrode alkaline electrolyzer achieved a value of 100 mA cm$^{-2}$ at a low cell bias of 1.83 V. Furthermore, the high current density approached 0.6 A cm$^{-2}$ at 2.1 V along with 10 h stability. DFT calculations demonstrate that the activation energy of water-splitting can be lowered by forming the NiCoO$_2$@(Ni, Co)OOH heterojunctions than that of NiCoO$_2$. The FPMD results revealed the different water-splitting mechanisms: e.g., for NiCoO$_2$@(Ni, Co)OOH heterojunction and NiCoO$_2$, it was the stretching vibrations of the metallic bonds to open the hydrogen bonding of water; whereas for the (Ni, Co)OOH, it was the stretching vibrations of shorter hydrogen bonds of O$_{\ldots}$H-O$_{\text{ad}}$ to open the hydrogen bonding of water. We believe that NiCoO$_2$@(Ni, Co)OOH heterojunctions meet the stringent requirements of high current density from industrial water electrolysis applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

ARTICLE

The efficient and low-cost sea coral-like NiCo$_2$O$_4$@/(Ni, Co)OOH heterojunctions catalysts meet the high current density for industrial water electrolysis applications.
Supporting Information

Sea Coral-like NiCo$_2$O$_4$@Ni, CoOOH Heterojunctions for Enhancing Overall Water-Splitting

Leiming Tao$^1$, Man Li$^1$, Shaohang Wu$^1$, Qinglong Wang$^1$, Xin Xiao$^1$, Qingwei Li$^1$, Mingkui Wang$^1$, YongQing Fu$^2$, *, and Yan Shen$^1$, *
**Supplementary Experimental Section**

**Characterization Measurements**

Morphology, chemical compositions, and crystalline structures of all the samples were characterized using various methods. X-ray diffraction (XRD) measurements were performed using an X-pert PRO diffractometer (PANalytical B.V.) with a Cu Ka X-ray source, operated at 40 kV and 40 mA. Surface and internal microstructures were investigated using a field emission scanning electron microscope (FE-SEM, Nova NanoSEM 450) and a high resolution transmission electron microscope (HRTEM, 300 kV Titan Probe corrected TEM, Titan G2 60-300). Surface chemical states of the samples were analyzed using an X-ray photoelectron spectroscopy (XPS, Thermofisher-ESCALab 250). Brunauer-Emmett-Teller (BET) surface areas ($S_{BET}$) and pore size distributions of samples were determined using a Micromeritics ASAP 2000 Nitrogen Adsorption apparatus. All the samples were degassed at 180 °C prior to the BET measurements. The determination of Co and Ni was carried out on an ELAN DRC-e ICP-MS (PerkinElmer Instruments Co. Ltd., USA)

**Electrochemical Measurements**

The catalytic activity of the prepared NiCo$_2$O$_4$@Ni, Co)OOH loaded onto glassy carbon electrodes towards oxygen evolution and hydrogen evolution reactions was studied by voltammetry in a three-electrode electrochemical cell. For comparison purposes, the electrodes of Pt/C, RuO$_2$ and NiCo$_2$O$_4$ were also characterized. For the electrode preparation, NiCo$_2$O$_4$@Ni, Co)OOH sample of 2 mg was dispersed into a 1 mL mixture of water, ethanol and nafion (5 wt. % solution in a mixture of lower aliphatic alcohols and water, Aldrich) with a volume ratio of 1:3.85:0.15, under an ultra-sonication for 30 min. The final catalyst ink suspension has a concentration 2.0 mg·mL$^{-1}$, and its suspension of 19.8 µl was then transferred onto a polished glassy-carbon electrode of 5 mm in diameter, resulting in a mass loading of 0.2 mg·cm$^{-2}$.

Measurements of cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted using an electrochemical station (CHI 750D, CH Instruments). Glassy carbon (GC) electrode (5 mm in diameter, Pine Instruments) was used as the working electrode. A graphite electrode was used as the auxiliary electrode, and then Hg/HgO was used as the reference electrode. The electrochemical impedance spectroscopy was used (Autolab PGSTAT302N) with a frequency range from 1 mHz to 1 MHz with a potential amplitude of 10 mV. Unless stated otherwise, the tests were made without R compensation in 1.0 M KOH solution.

Measurements using rotating ring-disk electrodes (RRDEs) were conducted in 1 M KOH electrolyte at room temperature using a three-electrode system (Pine Instruments and WaveDriver Workstation). The potentials were measured using the reference data from the Hg/HgO, and a carbon electrode was used as the counter electrode. Several cyclic voltammetry cycles were taken from 0 to 0.8 V (vs Hg/HgO) to stabilize the HER and OER performance of the catalyst before the final polarization curves were recorded. This is because recently it was reported that the amount of Pt deposited onto the catalyst surface after multiple circular scanning improved the catalytic performance. A graphite electrode was used as the counter electrode in this study. All the potentials measured were calibrated with the reversible hydrogen electrode (RHE) using the following equation:

$$E_{RHE} = E_{H_2/O_2} + 0.098V + 0.059pH$$  \hspace{1cm} (S1)

For oxygen evolution reaction OER (or HER) tests, all the electrochemical electrodes were firstly optimized by performing a potential cycling between 1.1 and 1.6 V (or 0 and −0.3V for HER) at 50 mV·s$^{-1}$ in a solution of 1 M KOH until stable voltammogram curves were obtained. Polarization curves and Tafel plots were recorded at two different scan rates of 5 mV·s$^{-1}$ and 0.1 mV·s$^{-1}$, respectively. Impedance value (R) of the 1M KOH solution was measured to be 6.9 Ω at room temperature. Tafel plots of the samples were obtained according to those reported in the literature. RRDE measurement was conducted in a solution of N$_2$-saturated 1M KOH for seven times with various rotation speeds (i.e., 400, 620, 900, 1225, 1600, 2025, 2500 r.p.m., respectively).

**Electrochemical Surface Area (ECSA)**

The ECSA is the product of $R_fS$, in which $R_f$ stands for the roughness factors, which is obtained from the ratio of $C_{dl}$ of the test sample and the $C_s$ (= 60 μF·cm$^{-2}$) of a smooth surface, and $S$ stands for the real surface area of the smooth metal electrode, which generally equals to
the geometric area of the carbon electrode.\(^5\) The values of \(C_{dl}\) were obtained using cyclic voltammetry and the results are shown in Figures S3a and S3b. The total catalytic activity areas are varied, but in the order from high to low values as follows: \(\text{NiCo}_2\text{O}_4@(\text{Ni, Co})\text{OOH}(296) > \text{RuO}_2(91) > \text{Pt/C}(6)\).\(^6\) This suggests that the \(\text{NiCo}_2\text{O}_4@(\text{Ni, Co})\text{OOH}\) presents a high reaction activity on the same surface area.

Figures S3c and S3d show the results of the rotating ring-disk electrode (RRDE) for HER and OER without \(i_R\), which are calculated using the Koutecký-Levich equation:\(^7\)

\[
\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_L} = \frac{1}{i_K} + 1 \times \frac{1}{0.62nFAD^{2/3} \omega^{1/2} v^{-1/6} C_0^0} \quad (S2)
\]

in which \(i\) is the measured current, \(i_K\) and \(i_L\) are the kinetic- and diffusion-limiting currents, \(\omega\) is the angular velocity of the disk (\(\omega=2\pi N\), \(N\) is the linear rotation speed), \(n\) is the overall number of electrons transferred in oxygen reduction. \(F\) is the Faraday constant (\(F=96,485 \text{ C} \cdot \text{mol}^{-1}\)). \(A\) is activity area, \(C_0\) is the bulk concentration of \(\text{O}_2\), \(v\) is the kinematic viscosity of the electrolyte, and \(D_0\) is the diffusion rate constant. Koutecký-Levich plots were obtained in an \(\text{N}_2\)-saturated 1M KOH solution using the RRDE and results are shown in Figures S3e and S3f.\(^3\)

**The Faradaic efficiency (FE) was obtained according to the previous literature:**\(^8\)

\[
\text{FE} = \frac{I_{\text{ring}}}{C_e \times I_{\text{disk}}} \quad (9)
\]

Here, \(I_{\text{disk}}\) is the given current on the disk electrode. \(I_{\text{ring}}\) is the collection current on the Pt ring electrode at a constant potential of 0.4 V versus RHE. \(C_e\) is the oxygen collection coefficient (~0.2) for this type of electrode configuration.

Chronopotentiometry was applied with a given potential (1.53 and -0.3 V) to maintain constant \(\text{O}_2\) and \(\text{H}_2\) generation. \(\text{N}_2\) was constantly purged into the cathodic compartment at a flow rate of 5 cm\(^3\)·min\(^{-1}\) and the compartment were connected to the gas-sampling loop of a gas chromatograph (GC2020, Hubei Hengxinshiji Scientific Instrument Co.). A thermal conductivity detector (TCD) was used to detect and quantify the generated \(\text{O}_2\) and \(\text{H}_2\).

**Movie S1.** The water splitting process of electrolysis cells (\(\text{NiCo}_2\text{O}_4@(\text{Ni, Co})\text{OOH} || \text{NiCo}_2\text{O}_4@(\text{Ni, Co})\text{OOH}\)) recorded at the current density of 100 mA cm\(^{-2}\).

**Movie S2.** First-principles molecular dynamics (FPMD) simulations animations of movies provides a dynamic model to monitor the water-splitting on the surfaces of \(\text{NiCo}_2\text{O}_4\), (Ni, Co)OOH, and \(\text{NiCo}_2\text{O}_4@(\text{Ni, Co})\text{OOH}, \) respectively.
Supplementary Figures

**Figure S1.** FE-SEM images of coral-like NiCo$_2$-PEG precursor in (a) and (b) the corresponding higher magnifications.
Figure S2. N₂ absorption-desorption isotherm with the pore size distribution (inset).
Figure S3. Electrochemical capacitance measurements results; a) typical cyclic voltammograms; b) charging current density differences ($j$) vs scan rates curve ($v$) in the potential region 0 − 0.05 V in 1 M KOH at 25 °C; The rotating ring-disk electrode (RRDE) measurements c) HER and d) OER without $iR$ with rotation speeds of 400, 625, 900, 1225, 1600, 2025, 2500 r.p.m., respectively; Koutecky-Levich plots of electrocatalyzed e) HER and f) OER for NiCo$_2$O$_4$@(Ni, Co)OOH
Figure S4. Faraday efficiency of (a) NiCo$_2$O$_4$@Ni, CoOOH and (b) NiCo$_2$O$_4$ electrodes using the RRDE technique in N$_2$-saturated 1 M KOH solution. When a constant current (300 μA) was applied to the disk electrode O$_2$ generation, a ring current was detected immediately.
**Figure S5.** (a) the XRD of NiCo$_2$O$_4$@Ni, CoOOH heterojunction for fresh (curve 1) and 30h sample (curve 2) with the current density increased from 0.1 to 0.6 A·cm$^{-2}$ in the two-electrode device, (b) the HR-TEM after 30h with the current density increased from 0.1 to 0.6 A·cm$^{-2}$ in the two-electrode device
**Figure S6.** a) Gas chromatography curves of NiCo$_2$O$_4$@Ni, CoOOH after water splitting at the given overpotential of 0.2 V. The gas chromatography survey clearly confirms that the produced bubbles are H$_2$ and O$_2$. b) The Faradaic efficiency (FE) of experimental H$_2$ (red square) and O$_2$ (red sphere) production versus the theoretic 98% quantities (black solid) for overall water splitting of NiCo$_2$O$_4$@Ni, CoOOH in 1 M KOH at 100 mA·cm$^{-2}$. 
**Supplementary Tables**

**Table S1.** Comparison of HER and OER activity for NiCo$_2$O$_4$@(Ni, Co)OOH heterojunction with other recently published highly active electrocatalysts in alkaline electrolyte (1 M KOH). Unless stated otherwise, the tests were made in 1.0 M KOH solution.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>HER $\eta$ (mV)</th>
<th>Tafel $\text{mA cm}^{-2}$</th>
<th>OER $\eta$ (mV)</th>
<th>Tafel $\text{mA cm}^{-2}$</th>
<th>Reference</th>
</tr>
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<tr>
<td>NiCo$_2$O$_4$@(Ni, Co)OOH</td>
<td>120</td>
<td>60</td>
<td>220</td>
<td>48</td>
<td>This work</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$@NiO@Ni Core/Shell Nanocone Array</td>
<td>120</td>
<td>43</td>
<td>240</td>
<td>58</td>
<td><em>Adv. Func. Mater.</em>, 2016, 26, 3515.</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$ nanosheet array</td>
<td>105</td>
<td>62.1</td>
<td>270</td>
<td>51.9</td>
<td><em>J. Catal.</em>, 2018, 357, 238.</td>
</tr>
</tbody>
</table>
Table S2. Comparison of overall water-splitting performance for NiCo$_2$O$_4$@(Ni,Co)OOH heterojunction with the recently reported materials.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Overpotential (mV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 mA cm$^{-2}$</td>
<td>20 mA cm$^{-2}$</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$@(Ni,Co)OOH</td>
<td>380</td>
<td>430</td>
</tr>
<tr>
<td>Co1MnIC</td>
<td>450</td>
<td>472</td>
</tr>
<tr>
<td>VOOH</td>
<td>390</td>
<td>470</td>
</tr>
<tr>
<td>Co-doped NiO/NiFe$_2$O$_4$</td>
<td>353</td>
<td>450</td>
</tr>
<tr>
<td>FeCoNi-LTH/NiCo$_2$O$_4$/CC</td>
<td>310</td>
<td>400</td>
</tr>
<tr>
<td>FeCo-FeCoNi-CC</td>
<td>430</td>
<td>570</td>
</tr>
<tr>
<td>Ni$<em>2$Co$</em>{0.5}$Fe/NF</td>
<td>390</td>
<td>570</td>
</tr>
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<td>NiCo$_2$S$_2$-NF</td>
<td>400</td>
<td>590</td>
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<tr>
<td>Co$_3$O$_2$-MTA</td>
<td>400</td>
<td>470</td>
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Supplementary References