

Supporting information

Realizing High Performance Bifunctional Energy Storage Device and Electrocatalytic Water Splitting Catalysts through Regulate Interface engineering of $\text{ZnCo}_2\text{O}_4@\text{Co}_3\text{O}_4$ nanosheets

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1. Experiments

The nickel foam as a current collector was sonicated cleaned in 0.1 M HCl emulsion and then washed with deionized water (DI water) and absolute ethanol to remove excess material. Finally, the nickel foam was heated at 60°C.

2.1 Fabrication of $ZnCo_2O_4$ nanowire arrays electrode

Zinc cobalt oxide ($ZnCo_2O_4$) material was hydrothermally grown on Ni foam. 0.87309 g $Co(NO_3)_2 \cdot 6H_2O$, 0.446235 g $Zn(NO_3)_2 \cdot 6H_2O$, 0.0926 g NH_4F , and 0.3003 g urea were liquefied in 60 mL DI water. A piece of pre-treated Ni foam was put into the above solution. The hydrothermal reaction was conducted at 120°C for 7 h. After the reaction was over, the sample was washed and dried at 60°C. Finally, $ZnCo_2O_4$ could be obtained by calcining in air at 350°C for 2 h.

2.2 Fabrication process of hierarchical $ZnCo_2O_4@Co_3O_4$ composite

Similar to the above experimental procedure, 0.1 mol/l $Co(NO_3)_2 \cdot 6H_2O$ solutions was used as electrolyte. $ZnCo_2O_4$ sample grown on Ni foam is utilized to the working electrode. The Ag/AgCl utilized as reference electrode, Pt foil as counter electrode. The electrodeposition was carried out at -1.0 V vs. RHE for 10 min. Finally, the sample was washed and dried at 60°C. Finally, $ZnCo_2O_4@Co_3O_4$ could be obtained by calcining in air at 350°C for 2 h.

2.3 Characteristic measurements

The phase structure of as-obtained samples (XRD) was studied by X-ray diffraction with Cu $K\alpha$ with a diffraction angle 2θ from 10 to 80°. The composition

and valence of chemical elements was examined by X-ray photoelectron spectroscopy on the sample surface (XPS, ESCALAB250). Scanning electron microscope (SEM, Zeiss-Sigma 500) and transmission electron microscope (TEM, JEM2100F) were used to investigate the morphologies and structures of the materials.

2.4 Electrocatalytic Characterization

The electrocatalytic tests of the samples contains CV, LSV and i-t, which were conducted in 1 M KOH electrolyte (pH = 13.7) under a three-electrode setup. In electrocatalysis experiments, the as-prepared products were used as the working electrode (0.5 cm × 0.5 cm) and Hg/HgO as reference electrode. To perform HER reaction, a graphite rod was employed as counter electrode. For OER reaction, a Pt plate was the counter electrode. All potentials were converted into RHE potentials through the Nernst equation:

$$E(\text{RHE}) = E(\text{Hg/HgO}) + 0.059 pH + 0.098 \quad (4)$$

where $E(\text{RHE})$ is the reversible hydrogen electrode potential, $E(\text{Hg/HgO})$ is the Hg/HgO electrode potential, and pH is the acid-base value of the electrolyte.

2.5 DFT calculations

Density Functional Theory (DFT) calculations were carried out using the Vienna Ab Initio Simulation Package (VASP). The exchange-functional is treated using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional. The cut-off energy of the plane-wave basis is set at 450 eV for optimize calculations of atoms and cell optimization. The vacuum spacing in a direction perpendicular to the plane of the catalyst is at least 20 Å. The Brillouin zone

integration is performed using $2 \times 2 \times 1$ Monkhorst-Pack k-point sampling for surface. The self-consistent calculations apply a convergence energy threshold of 10^{-5} eV. The equilibrium lattice constants are optimized with maximum stress on each atom within 0.02 eV/Å.

TOF values of the three electrocatalysts are depicted in Fig. S1. It can be found that $\text{ZnCo}_2\text{O}_4@\text{Co}_3\text{O}_4$ sample shows the values of 0.0012 s^{-1} (OER) and 0.001 s^{-1} (HER), which is much larger than ZnCo_2O_4 samples and Co_3O_4 products, confirming the superior electrocatalytic activity of $\text{ZnCo}_2\text{O}_4@\text{Co}_3\text{O}_4$ catalysts.

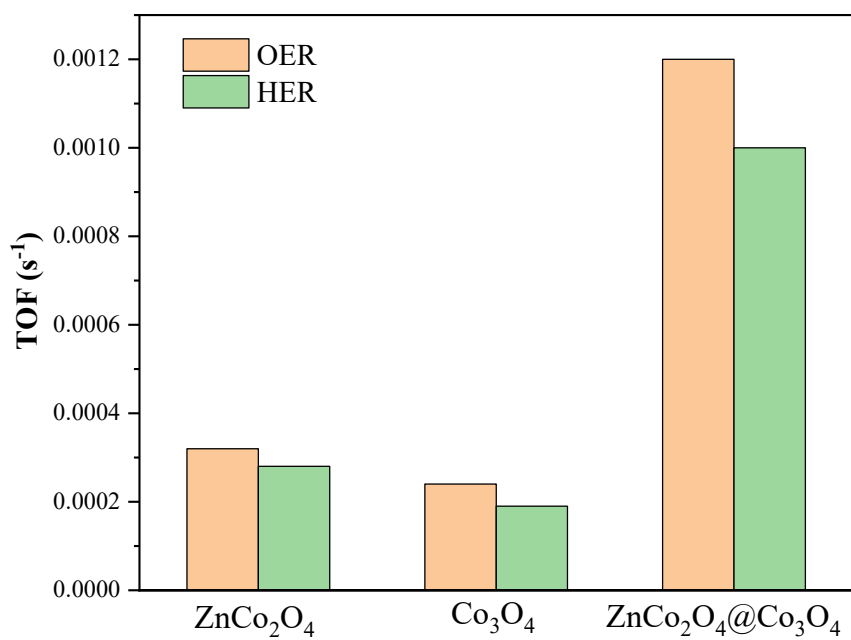


Fig. S1 TOF values of the three electrocatalysts

Fig. S2(a, b) show the SEM images of the prepared sample after cycling. It can be found that the as-prepared sample is composed of the large number of nanosheets. Compared with the samples before the cycle, it was found that the morphology of the samples did not change, which confirmed that the prepared samples possess an excellent structural stability.

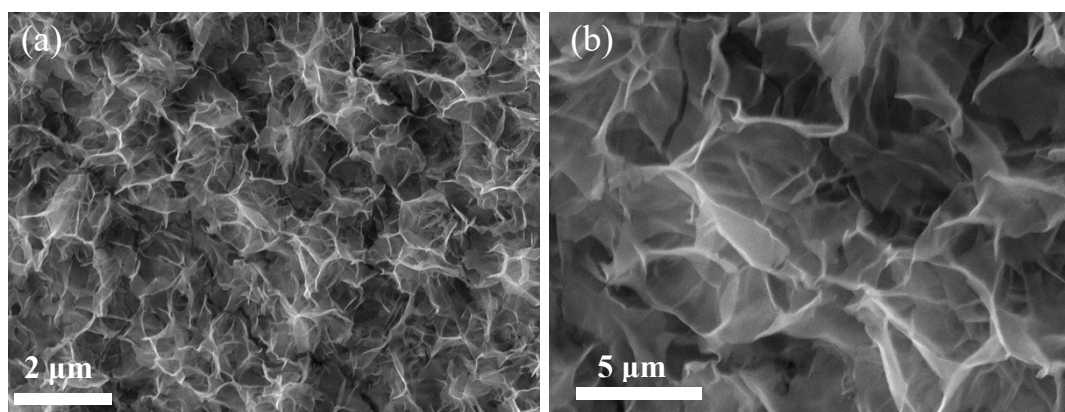


Fig. S2 (a, b) SEM images of the as-prepared $\text{ZnCo}_2\text{O}_4@\text{Co}_3\text{O}_4$ samples after cycle

XPS was then employed to further investigate the structural characteristics. The survey spectra in Fig. S3a confirms that the Zn, Co, O and C four elements can be found on the whole of samples. Fig. S3b shows the Co 2p spectrum. the peaks located at 789.6 and 804.6 eV belong to the related of Co^+ species. The binding energies of 781.3 and 785.4 eV can be indexed to the Co^{3+} .^{1,2} Two satellites reveal the co-existence of the $\text{Co}^{3+}/\text{Co}^{2+}$ peaks. The binding energies of 1021.5 and 1044.2 eV can be ascribed to the $\text{Zn}2p_{3/2}$ and $\text{Zn}2p_{1/2}$ (Fig. S3c).^{3,4} The O 1s spectra (Fig. S3d) exhibit three distinct peaks, labeled as O1, O2, and O3. The O1 peak at 531.1 eV corresponds to metal-oxygen bonds, while the peaks at 533.2 eV and 534.5 eV

correspond to surface species and water molecules, respectively.^{5,6}

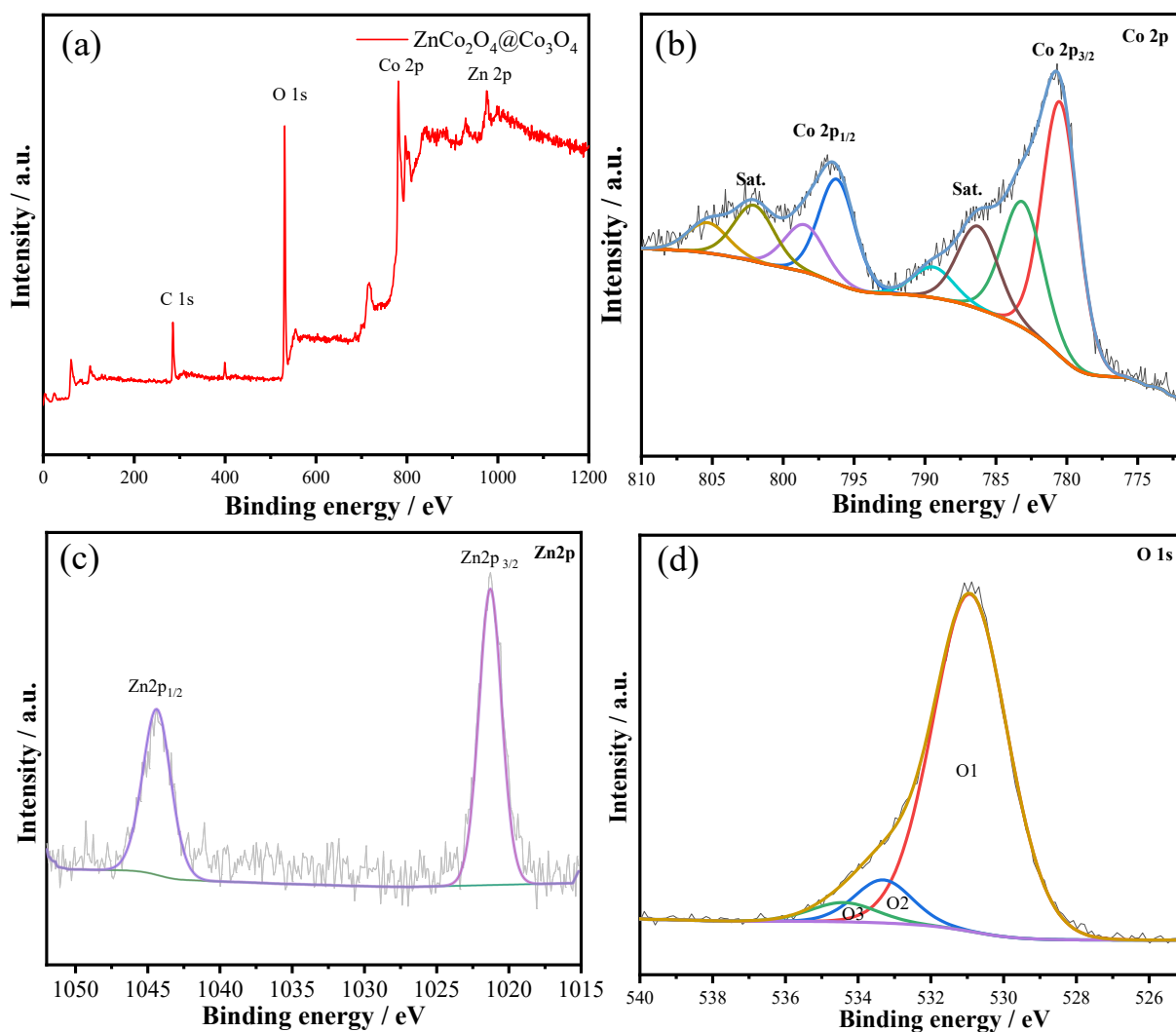


Fig. S3 XPS of the as-prepared samples after cycle, (a) full spectrum (b) Co 2p (c) Zn 2p (d) O1s