

**Fe doping and interface engineering-induced dual electronic regulation of
CoSe₂/Co₉S₈ nanorod arrays for enhanced electrochemical oxygen evolution**

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Experimental section

Materials and reagents

The carbon cloth was purchased from Shanghai Hesen Electric. Co., Ltd. in China. Cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), urea, ammonium fluoride (NH_4F), sublimed S powder and Se powder were acquired from Aladdin Industrial Corporation. Commercial RuO_2 was purchased from Johnson Matthey Corporation. All the reagents were of analytical reagent grade and used without further purification.

Preparation of Fe-CoCH@CC nanorods array precursor

Prior to the synthesis, the carbon cloth (CC) was pre-treated in acetone, deionized (DI) water, and anhydrous ethanol by ultrasonication successively for 10 min. In a typical synthetic process, a piece of cleaned CC ($2 \times 4 \text{ cm}^2$) was immersed into 30 mL of mixed solution that contains 0.4 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 1.2 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 5 mmol of urea and 2.5 of mmol ammonium fluoride (NH_4F). Then, the mixture was transferred into a 50 ml Teflon-lined autoclave and heated at $120 \text{ }^\circ\text{C}$ for 6 h. After cooling to room temperature naturally, the obtained product was washed with deionized water and ethanol several times.

Preparation of Fe-(CoSe₂/Co₉S₈)@CC nanorods array

For the synthesis of Fe-(CoSe₂/Co₉S₈)@CC, a piece of the obtained Fe-CoCH@CC sample, 60 mg of Se powder and 20 mg of sublimed S powder were placed at the downstream, midstream and upstream of a porcelain boat, respectively, which was heated to $350 \text{ }^\circ\text{C}$ with a ramp rate of $2 \text{ }^\circ\text{C min}^{-1}$ for 2 hours under H_2/Ar ($V_{\text{H}_2}:V_{\text{Ar}} = 5:95$) atmosphere. For comparison, CoSe₂/Co₉S₈@CC was fabricated under the identical synthetic procedure apart from using CoCH@CC as reaction precursor. In addition, Fe-CoSe₂@CC and Fe-Co₉S₈@CC were also prepared under the identical

synthetic procedure except for the absence of S powder and Se powder, respectively.

Physicochemical characterizations

The morphology of products was evaluated by transmission electron microscopy (TEM, JEOL JEM-2100F, 200 kV) and scanning electron microscopy (SEM, Hitachi S-4800). X-ray diffraction (XRD) patterns on a Model D/max-rC X-ray diffractometer with a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$) was employed to analyze the crystallinity of the samples. The surface chemistry state of samples was examined by X-ray photoelectron spectroscopy (XPS) using a Thermo VG Scientific ESCALAB 250 spectrometer with an Al K α radiator. The vacancies were studied by the electron spin resonance (ESR) test using an ECS 106 ESR spectrometer (Bruker, Rheinstetten, Germany) with an X-band resonator (ER 4103TM).

Electrochemical measurements

All electrochemical tests were performed on a CHI 760E electrochemical workstation in 1.0 M KOH solution using a standard three-electrode system, in which the harvested self-supported electrode was directly served as working electrode, and a graphite rod and a saturated calomel reference electrode (SCE) were used as counter electrode and reference electrode, respectively. Linear sweep voltammetry (LSV) was carried out with a scan rate of 5 mV s^{-1} . The electrochemical double-layer capacitance (C_{dl}) using cyclic voltammetry (CV) method within a non-Faradaic potential range (1.1-1.2 V) at different scan rates ($2\text{-}10 \text{ mV s}^{-1}$). In this work, all potentials were calibrated to reversible hydrogen electrode (RHE).

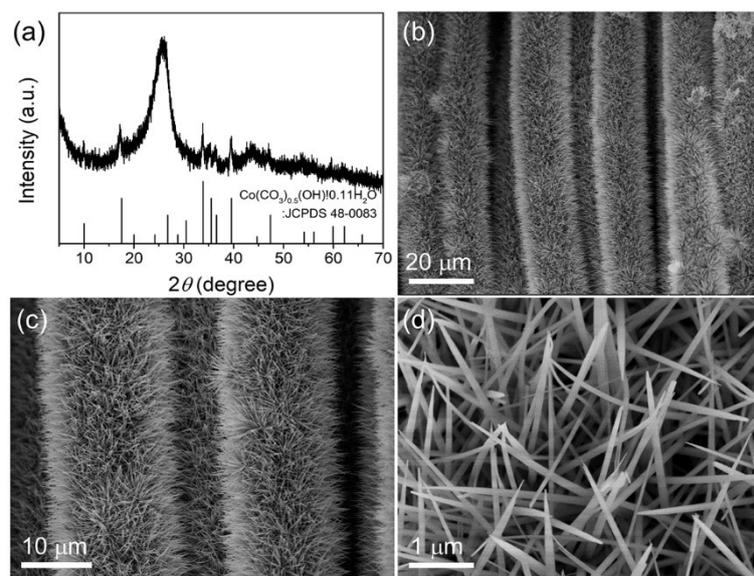


Fig. S1 (a) XRD pattern and (b)-(d) SEM images of the Fe-CoCH@CC precursors.

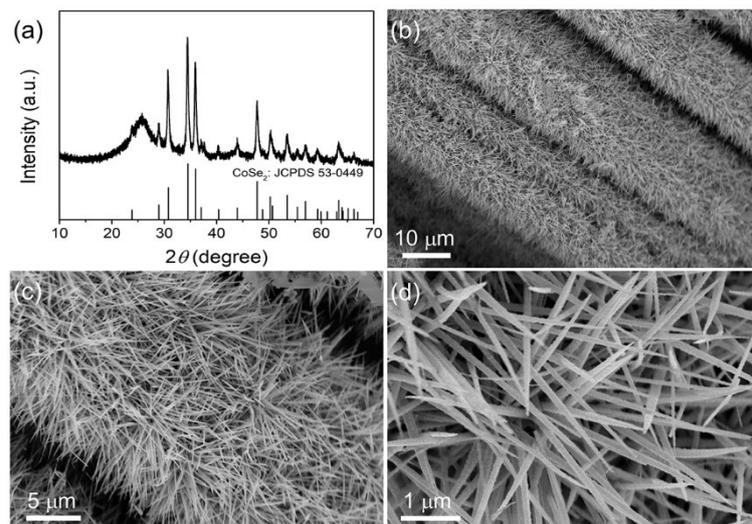


Fig. S2 (a) XRD pattern and (b)-(d) SEM images of the Fe-CoSe₂@CC precursors.

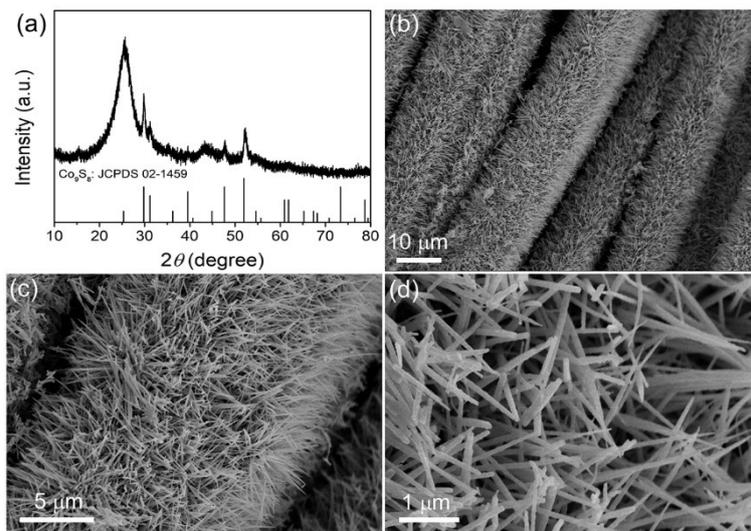


Fig. S3 (a) XRD pattern and (b)-(d) SEM images of the Fe- Co_9S_8 @CC precursors.

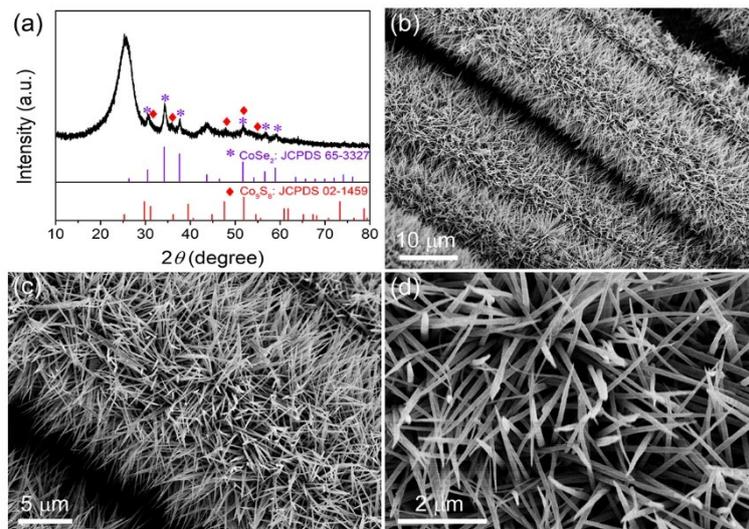


Fig. S4 (a) XRD pattern and (b)-(d) SEM images of the CoSe₂/Co₉S₈@CC precursors.

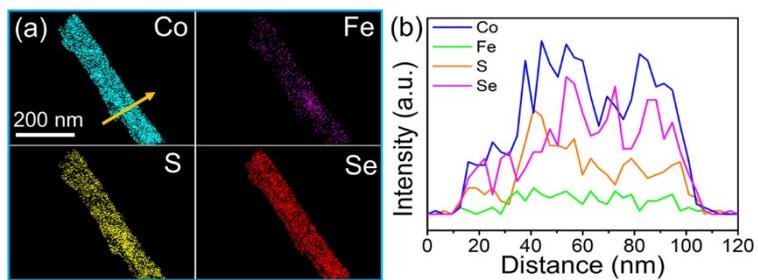


Fig. S5 (a) Elemental mapping images and (b) EDX line-scan profiles of the harvested Fe-(CoSe₂/Co₉S₈)@CC.

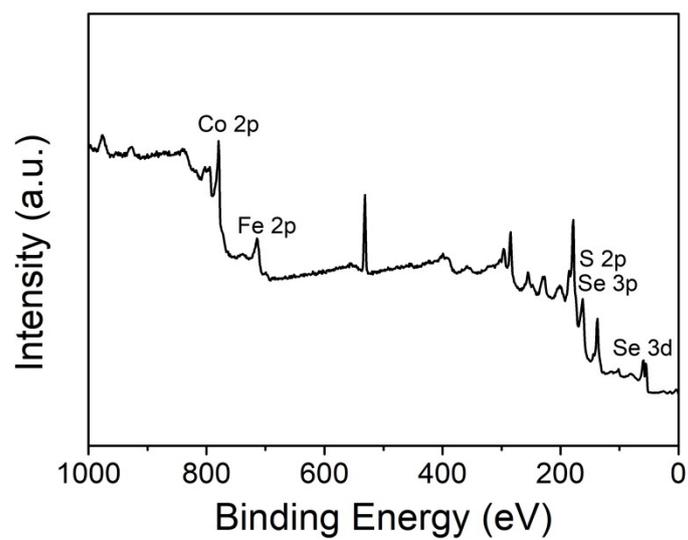


Fig. S6 XPS survey spectrum of the harvested Fe-(CoSe₂/Co₉S₈)@CC.

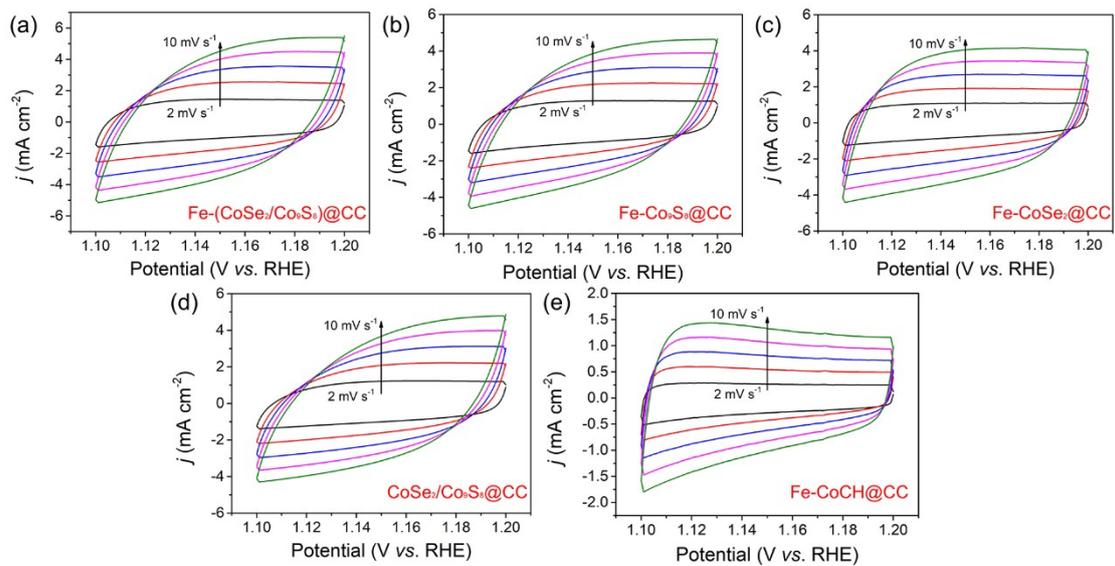


Fig. S7 CV curves of (a) Fe-(CoSe₂/Co₉S₈)@CC, (b) Fe-Co₉S₈@CC, (c) Fe-CoSe₂@CC, (d) CoSe₂/Co₉S₈@CC and (e) Fe-CoCH@CC.

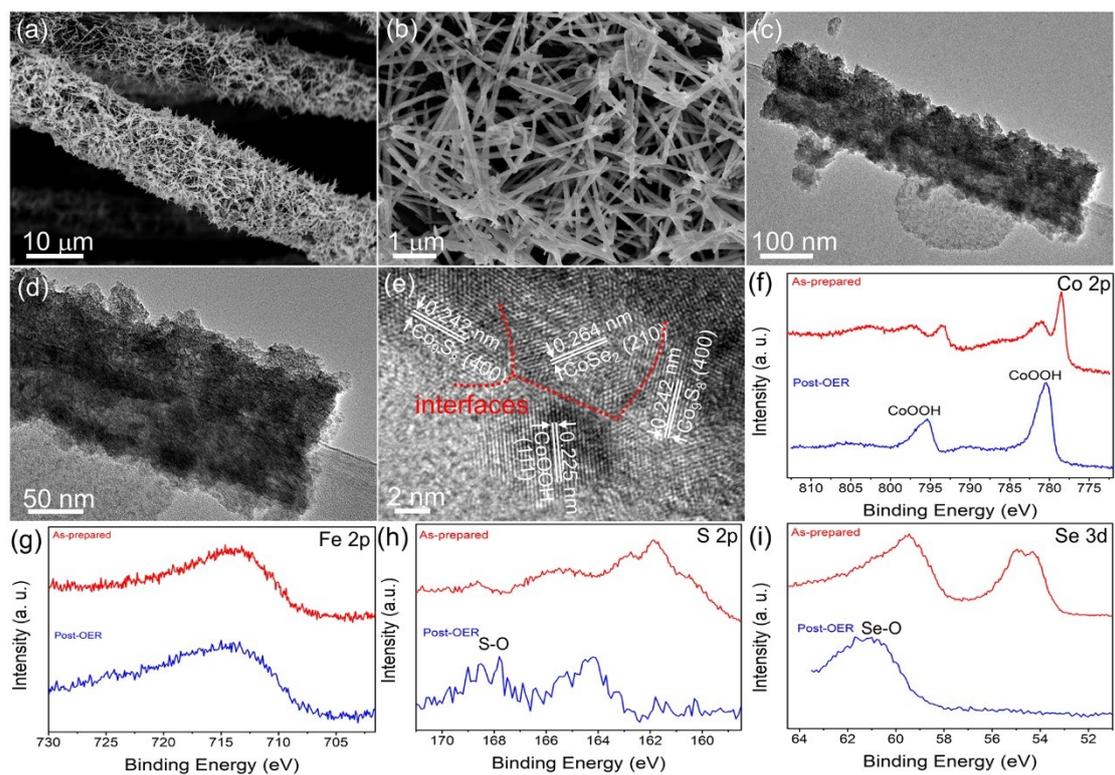


Fig. S8 Morphological and surface chemistry state of the Fe-(CoSe₂/Co₉S₈)@CC electrode after OER stability test. (a)-(b) SEM images, (c)-(d) TEM images, (e) HRTEM image, (f) Co 2p XPS spectra, (g) Fe 2p XPS spectra, (h) S 2p XPS spectra and (i) Se 3d XPS spectra.

Table S1 Comparison the OER performance of Fe-(CoSe₂/Co₉S₈)@CC electrode with those recently reported transition metal chalcogenide-based electrocatalysts in 1.0 M KOH solution.

Catalysts	$\eta_{j = 10 \text{ mA cm}^{-2}}$ /mV	Tafel slope /mV dec ⁻¹	References
Fe-(CoSe₂/Co₉S₈)@CC	243	44.5	This work
Co ₄ S ₃ /Mo ₂ C-NSC	268	61.2	<i>Appl. Catal. B.</i> , 2020, 260, 118197.
Co/CoS/Fe-HSNC-700	250	62.6	<i>Chem. Eng. J.</i> , 2021, 403, 126385.
H-Fe-CoMoS	282	58	<i>Nano Energy</i> , 2020, 75, 104913.
CoO-CoSe ₂ @N-CNTs/rGO	250	68	<i>Chem. Eng. J.</i> , 2021, 422, 129982.
CoFe-based zemannite-type selenite	274	45.6	<i>Chem. Eng. J.</i> , 2020, 399, 125799.
V-NiS/NiS ₂	220	72	<i>Adv. Energy Mater.</i> , 2023, 13, 2300978.
P-CoNi ₂ S ₄	288	40	<i>Angew. Chem. Int. Ed.</i> , 2021, 60, 22885.
NF-C/CoS/NiOOH	296	52.90	<i>Nanomicro Lett.</i> , 2020, 12, 162.
CoS/Co/MoC-N,S-PCNFs-20	289	124.5	<i>Chin Chem Lett.</i> , 2021, 32, 2243.
NiFe LDH/NiS	230	110.7	<i>Adv. Energy Mater.</i> , 2021, 11, 2102353.
Ni(CN) ₂ /NiSe ₂	270	68	<i>Adv. Mater.</i> , 2022, 34, 2104405.
Cu-NiS ₂	232	46	<i>Small</i> , 2020, 16, 1905885.
Am-Mo-NiS _{0.5} Se _{0.5}	238	48	<i>Angew. Chem. Int. Ed.</i> , 2023, 62, e202215256.
Co _{1-x} S/Co(OH)F/CC	269	71	<i>ACS Nano</i> , 2022, 16, 15460.