Coupling FeSe₂ with CoSe: an effective strategy to create stable and

efficient electrocatalyst for water oxidation

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Experimental section

Chemicals

Ni foam (NF) with a thickness of 1.6 mm and a pore density of 110 ppi was purchased from Changsha Keliyuan. Cobalt (II) chloride hexahydrate (CoCl₂· $6H_2O$), ferric (III) chloride hexahydrate (FeCl₃· $6H_2O$), Se powders, sodium borohydride (NaBH₄) were purchased from Alfa Aesar. Potassium hydroxide (KOH), hydrochloric acid (HCl), acetone and ethanol were all analytic grade (AR) and purchased from Sinopharm Chemical Reagent. All these chemical reagents were used as received without any further purification. Iridium oxide (IrO₂), ethanol (99.9%) and Nafion (5% in a mixture of lower aliphatic alcohols and water) were purchased from Alfa Aesar.

Synthesis of CoSe/FeSe₂ hybrids

In a typical procedure, Se powders (0.158 g, 2 mmol) were added into deionized water (30 mL) containing NaBH₄ (0.152 g). After ultrasonic dissolution for 10

minutes, a clear NaHSe solution was obtained. Then, 0.2 mmol $FeCl_3 \cdot 6H_2O$ and 0.6 mmol $CoCl_2 \cdot 6H_2O$ were added to the above solution with continuous stirring for 20 min. Thereafter, the resulting solution was transferred into a Teflon-lined stainless-steel autoclave, which was subsequently heated at 200 °C for 18 h. After cooling to room temperature, the black powders were collected and washed with distilled water and absolute ethanol for several times and dried at 60 °C.

Other Co_xFe_{1-x} -Se (x = 0.93, 0.85, 0.69, 0.51) catalysts were prepared using the similar method except that the feeding ratio of metal precursors was varied and the total amount of metal precursors (Co + Fe) was kept constant at 0.8 mmol. Specifically, the feeding ratio of Co/Fe was 11:1 for $Co_{0.93}Fe_{0.07}$ -Se, 5:1 for $Co_{0.85}Fe_{0.15}$ -Se, 2:1 for $Co_{0.69}Fe_{0.31}$ -Se and 1:1 for $Co_{0.51}Fe_{0.49}$ -Se. The final ratio of metals in Co_xFe_{1-x} -Se was determined by the average results of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis, which were similar with the feeding ratio. The preparing process of CoSe and FeSe₂ was the same as that of Co_xFe_{1-x} -Se in the absence of FeCl₃ or CoCl₂.

Material Characterization

Powder X-ray diffraction (XRD) patterns of all the samples were obtained by a Rigaku D/M ax-2400 at a scanning rate of 10° min⁻¹ over a 2θ range of 20-80°. Transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) characterization were performed on a TecnaiTM G2 F30 transmission electron microscope equipped with an EDX detector at an acceleration voltage of 200 kV. X-ray photoelectron spectroscope (XPS) data were collected through a VGESCALAB

MKII X-ray photo-electron spectrometer with a Mg-K α excitation source (1253.6 eV). The molar ratio of Co/Fe in CoSe/FeSe₂ composites was measured by the PQ 9000 inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Electrode preparation and electrochemical measurements

All electrochemical measurements were conducted using a computer-controlled Autolab PGSTAT302N under room temperature. Platinum plate and Hg/HgO electrode were used as counter and reference electrodes, respectively. Typically, the initial 4.0 mg catalysts and 30 μ L Nafion solution (5 wt%) were dispersed into 1 mL water-ethanol solution with volume ratio of 1:1 by sonicating for at least 0.5 h to form a homogeneous ink. Then, dropwise, the above dispersion was loaded onto the surface of NF (1 × 1 cm²). Finally, the electrode was dried for 10 h under ambient condition. After weighing and calculating by differential method, the final loading mass of the catalysts was 2.9 mg. For comparison, the electrocatalytic activity of benchmark IrO₂ was also investigated under the same condition.

Linear sweep voltammetry (LSV) was carried out at a scan rate of 5 mV s⁻¹ in 1.0 M KOH. All the polarization curves have been iR-corrected. Unless otherwise stated, the potentials reported in our work were converted to the reversible hydrogen electrode (RHE), where in 1 M KOH, E(RHE) = E(Hg/HgO) + 0.924 V. The overpotential (η) of OER at 10 mA cm⁻² was calculated according to the equation: η_{10} = E (vs. RHE) - 1.23, considering O₂/H₂O equilibrium at 1.23 V. The Tafel slope was obtained according to the Tafel equation. Electrochemical impedance spectra (EIS) were collected over a frequency range of 100 kHz to 10 mHz at a direct-current bias potential of 1.51 V at room temperature. The electrochemical active surface areas were estimated from the double-layer charging curves using cyclic voltammograms (CVs) at different scan rates of 100-200 mV s⁻¹ in a non-Faradaic region (0.924-0.974 V vs. RHE). The stability was tested by means of chronopotentiometry (CP) measurement under a constant current density of 10 mA cm⁻² and chronoamperometry (CA) measurement at a constant potential of 1.51 V. The durability test was performed by cycling the electrode potential (1.20-1.60 vs. RHE) at 200 mV s⁻¹ for 1000 cycles.

The turnover frequency (TOF) value is calculated according to the following equation:

 $TOF = (J \times A) / (4 \times F \times n)$

where J is the current density at a given overpotential, A is the geometric area of the electrode (1 cm²), 4 represents 4 electrons/mol of O₂, F is the Faraday constant (96485.3 C mol⁻¹), and n is the mole number of metal ions in the as-prepared samples. In this work, all metal ions in Co_xFe_{1-x} -Se were assumed to be catalytically active no matter whether they are accessible to the electrolyte or not. Therefore, the calculated TOF value represents the lowest limit (*J. Am. Chem. Soc.*, 2014, **136**, 15670-15675). For example, at $\eta = 300$ mV, the $Co_{0.75}Fe_{0.25}$ -Se electrode generates a current density of 141.4 mA cm⁻². The TOF of $Co_{0.75}Fe_{0.25}$ -Se electrodes at $\eta = 300$ mV can be calculated as follows:

TOF = $(0.1414A \text{ cm}^{-2} \times 1 \text{ cm}^{-2})/(4 \times 96485.3 \text{ C mol}^{-1} \times 2.9 \times 10^{-3} \text{ g} \div 137.89 \text{ g mol}^{-1})$ = $1.7 \times 10^{-2} \text{ s}^{-1}$ For the rotating ring-disk electrode (RRDE) measurements, the as-synthesized $Co_{0.75}Fe_{0.25}$ -Se hybrids were coated onto RRDE with Nafion as the binder, which consists of a glassy carbon disk electrode and a Pt ring electrode. A scan rate of 5 mV s⁻¹ and a rotation rate of 1500 rmp were applied for RRDE test. Firstly, in order to determine electron transfer number (N) for OER by detecting the HO₂⁻ formation, the ring potential was constantly held at 1.50 V versus RHE in O₂-saturated 1 M KOH solution. On the other hand, the Faradaic efficiency (FE) was determined by collecting the ring current when fixing the disk current at 100 µA and ring potential at 0.4 V versus RHE in N₂-saturated 1 M KOH solution. The FE was calculated as follows:

$$FE = I_{ring} / (C_e \times I_{disk})$$

Where I_d is the disk current, I_r is the ring current, and C_e is the current collection efficiency (0.21 in this study), which was determined using the same configuration with an IrO₂ thin-film electrode. The electron transfer number (N) can be calculated from the disk current (I_d) and ring current (I_r) of RRDE.

$$N = 4 \times I_d / (I_d + I_r / C_e)$$

The OER mechanism under alkaline conditions (Chem. Soc. Rev., 2017, 46, 337-365)

$$M + OH^{-} \rightarrow M-OH + e^{-}(1)$$

$$M-OH + OH^{-} \rightarrow M-O + H_2O_{(l)} + e^{-}(2)$$

$$M-O+OH^{-} \rightarrow M-OOH + e^{-}$$
 (3)

 $\textbf{M-OOH} + \textbf{OH}^{\scriptscriptstyle -} \rightarrow \textbf{M} + \textbf{O}_{2(g)} + \textbf{H}_2\textbf{O}_{(l)} + \textbf{e}^{\scriptscriptstyle -} (4)$

M is the catalytic active site. Under alkaline conditions, OER starts with the adsorption and discharge of OH⁻ anion on the surface of catalysts to form adsorbed OH species, followed by the reaction of OH⁻ with the adsorbed OH species to produce H₂O and adsorbed atomic O. The next step involves the reaction of OH⁻ with the adsorbed atomic O to form adsorbed OOH species, which then react with additional OH⁻ to form adsorbed O₂ and H₂O. At last, the adsorbed O₂ desorbs from the catalyst surface (eqn (1)-(4)). Generally, the forming reaction of adsorbed OOH species is identified as the rate-limiting step in OER (*J. Am. Chem. Soc.*, 2011, 133, 5587). The OER activities of transition metal-based materials can be enhanced by modulating their electronic structure due to the significant effect of the interaction of adsorbed OOH species and 3d orbital of transition metal. (*J. Am. Chem. Soc.*, 2017, 139, 8320. *Nat. Commun.*, 2013, 4, 2439.)



Fig. S1 Schematic illustration of CoSe/FeSe₂ hybrids for preparation (a) and its application

in OER (b).



Fig. S2 (a) TEM images of CoSe. (b) HRTEM image of CoSe.



Fig. S3 (a) TEM image of FeSe₂. (b) HRTEM image of FeSe₂.



Fig. S4 EDX spectrum of $Co_{0.75}Fe_{0.25}$ -Se hybrid.



Fig. S5 (a) Overpotentials required at $J = 10 \text{ mA cm}^{-2}$. (b) TOFs calculated from the currents at η

= 300 mV. (c) Mass activities at η = 300 mV. (d) The double layer capacity $C_{dl}.$



Fig. S6 Nyquist plots.



Fig. S7 CV curves of CoSe (a), Co_{0.93}Fe_{0.07}-Se (b), Co_{0.85}Fe_{0.15}-Se (c), Co_{0.75}Fe_{0.25}-Se (d),

Co_{0.69}Fe_{0.31}-Se (e), Co_{0.51}Fe_{0.49}-Se (f), FeSe₂ (g) with different scan rates from 100 mV s⁻¹ to 200

mV s⁻¹ in 1 M KOH.



Fig. S8 (a) Ring current of Co_{0.75}Fe_{0.25}-Se hybrids on a RRDE (1500 rpm) in O₂-saturated 1.0 M

KOH with the ring potential of 1.50 V. (b) Ring current of $Co_{0.75}Fe_{0.25}$ -Se hybrids on a RRDE

(1500 rpm) in N₂-saturated 1.0 M KOH solution with the ring potential of 0.40 V. The inset presents the FE testing mechanism of the RRDE, the black columns on the sides are Pt ring electrodes. The Pt ring electrode and glassy-carbon electrode are separated by a non-conductive PTFE barrier (white columns).



Fig. S9 XPS spectra of Co 2p (a), Fe 2p (b), Se 3d (c) and O 1s (d) for Co_{0.75}Fe_{0.25}-Se catalysts

after OER stability test.

Catalysts	1	2	3	4	5
Precursor ratio	11:1	5:1	3:1	2:1	1:1
ICP result	0.93:0.07	0.85:0.15	0.75:0.25	0.69:0.31	0.51:0.49

Table S1 The molar ratio of Co/Fe in different catalysts

Table S2 Comparison of OER catalytic performance with the reported metal selenides

Catalyst	Electroly te	Substrate	Overpotential at 10 mA cm ⁻² (mV)	Tafel slope (mV/dec)	Reference
Co _{0.75} Fe _{0.25} -Se	1 M	NF	246	41.4	This

nanocomposite	KOH				work
Ultrathin CoSe ₂	0.1 M	CC	220	4.4	1
nanosheet	КОН	GC	320	44	1
Mn ₃ O ₄ /CoSe ₂	0.1 M	GC	450	49	2
	КОН				
(Ni, Co) _{0.85} Se	1 M	carbon fabric	255	79	3
nanotube	КОН	collector			
a-CoSe	1 M	Ti	292	69	4
	КОН				
FeSe ₂	1 KOH	NF	245	-	5
FeSe ₂	1 M	Ni piece	330	48.1	6
nanoplatelet	КОН	i i piece	220		0
CeO2/CoSe2	0.1 M	GC	288	44	7
	КОН	30	200		
NiCo ₂ Se ₄ holey	1 M	GC	300	53	8
nanosheet	КОН	66	500		0
NiSe-Ni _{0.85} Se	1 M	carbon naner	300	98	9
hybrid	КОН	euroon puper	aper 500	20	-
Coral-like CoSe	1 M	GC	295	40	10
	КОН	00	2)5	40	10
NiSe nanowire	1 M	NE	~320	54	11
	КОН	111	~320	54	11
NiSe/NiO _x	1 M	NE	2/3	128.8	12
	KOH	181	243	120.0	12
CoSe ₂	1 M	CC	330	70	12
microsphere	KOH	UC		19	15
Au-CoSe ₂	0.1 M	CC	303	42	14
nanobelt	КОН	UC			14
Co _{0.85} Se@NC	1 M	GC	260	75	15
	КОН				15

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Catalyst	Electrolyte	Current Density (mA/cm ²)	Overpotential (mV)	Reference
Co _{0.75} Fe _{0.25} -Se nanohybrids	1 M KOH	10	246	This work
NiFe oxide	1 M NaOH	0.5	280	1
Ni _{0.69} Fe _{0.31} O _x /C	1 M KOH	10	280	2
Fe-Ni-O _x NPs	1 M KOH	10	286	3
Ni-Fe oxide film	0.1 M KOH	2	329	4
Fe ₆ Ni ₁₀ O _x	1 M KOH	10	286	5
$Ni_{0.9}Fe_{0.1}O_x$	1 M KOH	10	336	6
Fe ₄₀ Ni ₆₀ O _x film	0.1 M KOH	1	250 ± 30	7
Ni _{1-x} Fe _x O _y nanorods	1 M KOH	10	302	8
Fe _{11%} -NiO/NF	1 M KOH	10	206	9
Ni-Fe-O composite	1 M KOH	10	244	10

Table S3 Comparison of OER catalytic performance with the reported Ni-Fe oxides.

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