# Supporting Information

Strong hydrophilicity  $NiS_2/Fe_7S_8$  heterojunctions encapsulated in N-doped carbon nanotubes for enhanced oxygen evolution reaction

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# **<u>1. Electrochemical Experiments</u>**

### 1. Experimental methods

(1) Preparation of N-CNTs@Ni<sub>x</sub>Fe<sub>v</sub>

4 g melamine, 0.05 g glucose and nickel nitrate: iron nitrate in different molar ratios (3:1, 2:1, 1:1, 1:2, 1:3) were mixed and grinded evenly. The mixture was transferred to a clean and dry ceramic boat and heated to 800 °C in the middle of the tubular furnace for 2 h. Ar was used as protective gas (heating rate was 2 °C min<sup>-1</sup>).

#### (2) Preparation of N-CNTs@NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub>

The precursor N-CNTs@Ni<sub>3</sub>Fe and excessive thiourea were placed in different clean and dry ceramic boats, and placed in two connected tubular furnaces. The ceramic boat with excessive thiourea was placed in the upstream position of tubular furnace 1 as a gas preparation chamber, the ceramic boat with N-CNTs@Ni<sub>3</sub>Fe was placed in the downstream position of the tubular furnace 2 as a reaction chamber. The tubular furnace 1 was heated to 200 °C for 3 h, while Furnace 2 is heated to 500 °C for 3 h, and Ar is used as protective gas (heating rate is 1 °C min<sup>-1</sup>).

#### (3) Preparation of N-CNTs@NiSe<sub>2</sub>/Fe<sub>3</sub>Se<sub>4</sub>

The precursor N-CNTs@Ni<sub>3</sub>Fe and the same mass Se powder were mixed and ground evenly, and then transferred to a clean and dry ceramic boat, the boat placed in the middle of tubular furnace heated to 500 °C for 3 h, Ar was used as protective gas (heating rate was 1 °C min<sup>-1</sup>).

#### 2. Material characterizations

The morphologies of N-CNTs@Ni<sub>x</sub>Fe<sub>y</sub>, N-CNTs@NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub>, N-CNTs@NiSe<sub>2</sub>/Fe<sub>3</sub>Se<sub>4</sub> and the lattice structural information of N-CNTs@NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub> were observed by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The phase composition of samples was detected by X-ray diffraction (XRD) with Cu K $\alpha$  radiation ( $\lambda$ = 1.5418 Å). The detail

chemical composition was characterized by X-ray photoelectron spectroscopy (XPS). Nitrogen adsorption-desorption isotherm was recorded at 77 K, the specific surface area of samples was detected by Brunauer-Emmett-Teller (BET) model. The structural information of CNTs was measured by Laser-Raman spectrometer (532 nm laser excitation). The static contact angles were measured using a contact angle goniometer (SDC200, Shengding, China).

#### **3. Working electrode preparation.**

All of the electrochemical measurements were performed under the identical conditions with the same catalyst mass loading. First, 4.3 mg the as-prepared catalyst was ultrasonically dispersed in 1500 uL mixture of DI water, ethanol and Nafion solution (5.0 wt%). Then, 15 uL of the catalyst dispersion (2.87 mg mL<sup>-1</sup>) was transferred onto the glassy carbon rotating disk electrode (RDE, 0.196 cm<sup>2</sup>) and dried overnight in vacuum drying oven at room temperature. The mass loading of catalyst was 0.22 mg cm<sup>-2</sup>. The resulting electrode served as working electrode.

## 4. Electrochemical performance testing.

(1) The electrochemical properties of catalysts were investigated by the **Par/PARSTAT MC equipped with RDE.** A carbon rod served as counter electrode, saturated calomel electrode (SCE) acted as reference electrode. All the potentials were referred to reversible hydrogen electrode (RHE), where  $E_{\text{RHE}} = E_{\text{SCE}} + 0.244 \text{ V} + 0.0591 \times \text{pH}$  (pH = 14).

(2) OER performance test. The OER polarization curve was measured by linear sweep voltammetry with a scanning rate of 5 mV s<sup>-1</sup>.

(3) The electrochemical active surface area (ECSA) test. The ECSA of samples were measured by cyclic voltammetry (CV) measurements, which were conducted by sweeping the potential across the non-Faradaic region with different scan rates from 10 mV s<sup>-1</sup> to 50 mV s<sup>-1</sup>. The potential range was typically a 0.10 V window centred at open-circuit potential (OCP) of the system to test electrochemical double-layer capacitor ( $C_{dl}$ ) and point fitting was carried out.

(4) Electrochemical impedance spectroscopy (EIS) test. EIS of samples was carried out by AC impedance method in the frequency range of 0.01 Hz to 100 KHz at OCP.

(5) Catalyst stability test. The stability of catalyst was tested at 1.56 V for 24 h by chronoamperometry.

(6) Faradic efficiency test of OER. To investigate the Faradic efficiency of samples for OER, rotating ring disk electrode (RRDE) were measured on a Par/PARSTAT MC device with a Pt ring electrode. The  $I_{\text{disk}}$  was keep at 10 mA cm<sup>-2</sup> current density for oxidizing H<sub>2</sub>O to generate O<sub>2</sub>, and the  $E_{\text{ring}}$  was 0 V for 100 s and sudden to -0.6 V for 300 s to reduce the formed O<sub>2</sub> from disk in N<sub>2</sub>-saturated 1.0 M KOH solution. The collection efficiency of RRDE was determined to be 0.32 under 1600 rpm. The Faradic efficiency is calculated by:

Faradic efficiency =  $(I_{\text{ring}} / 0.32) / I_{\text{disk}} \times 100\%$ 

# **2. Supplementary Figures**



**Fig. S1.** SEM images of (a, b) N-CNTs@NiFe<sub>3</sub>, (c, d) N-CNTs@NiFe<sub>2</sub>, (e, f) N-CNTs@NiFe, (g, h) N-CNTs@Ni<sub>2</sub>Fe, (i, j) N-CNTs@NiFe<sub>3</sub>.

By adjusting the proportion of Ni: Fe, N-CNTs with different morphologies were grown by autocatalysis, and the alloy particles with different proportions were coated. SEM images showed that when the content of Fe was 3 times then Ni, CNTs were basically agglomerated without obvious tubular shape, when the content of Ni increased gradually, CNTs grow well and have uniform size for 100 nm in diameter.



**Fig. S2.** The XRD patterns of N-CNTs@NiFe<sub>3</sub>, N-CNTs@NiFe<sub>2</sub>, N-CNTs@NiFe, N-CNTs@Ni<sub>2</sub>Fe, N-CNTs@NiFe<sub>3</sub>.

Combining XRD spectra, it can be seen that the self-catalyzed CNTs correspond to JCPDS#41-1487 of C. When Ni: Fe = 1:3, the Fe<sub>3</sub>C crystalline phase corresponds to JCPDS#35-0772 was formed, which is also the main reason for the incomplete formation of carbon pipes leading to agglomeration.

When the content of Ni increases gradually, the ratio of Ni: Fe = 1: 2, Ni: Fe = 1: 1, and Ni: Fe = 2: 1, respectively, besides the formation of NiFe alloy (JCPDS#47-1417), the peak of elemental Ni corresponding to JCPDS#04-0850 is independent, when the content of Ni increases to Ni: Fe = 3: 1, Ni<sub>3</sub>Fe alloy (JCPDS#38-0419) is completely formed, and it confirms that the positive role of Ni in catalyzing the growth of CNTs.



**Fig. S3** LSV curves of OER for N-CNTs@NiFe<sub>3</sub>, N-CNTs@NiFe<sub>2</sub>, N-CNTs@NiFe, N-CNTs@Ni<sub>2</sub>Fe, N-CNTs@Ni<sub>3</sub>Fe.

By investigating the water oxidation properties of N-doped CNTs encapsulated precursors with different Ni:Fe ratios, it was found that the performance of catalysts increased gradually with the increasing of Ni content, but under higher voltage, too much oxygen was produced and the Ni<sub>x</sub>Fe<sub>y</sub>-O bond interaction was stronger, which made it difficult to dissociate and desorption quickly. And O attachment on the surface of the catalyst affected its electrical conductivity, resulting in jitter of the test curve and a decline in performance. This indicated that although N-CNTs@Ni<sub>x</sub>Fe<sub>y</sub> has good catalytic performance, it does not play a good role in the product desorption.



**Fig. S4.** (a, b) SEM and (c) XRD pattern of N-CNTs@NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub>; (d, e) SEM and (f) XRD pattern of N-CNTs@NiSe<sub>2</sub>/Fe<sub>3</sub>Se<sub>4</sub>.

The morphologies and crystal surface information of N-CNTs@NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub> and N-CNTs@NiSe<sub>2</sub>/Fe<sub>3</sub>Se<sub>4</sub> were observed by FE-SEM and XRD. It can be seen that the carbon nanotubes retained the tubular morphology with a diameter of about 80 nm after sulfurization, and the nanoparticles encapsulated in tube were obviously seen (Fig. S4a and b). XRD results (Fig. S4c) showed that NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub> heterojunction was formed by Ni<sub>3</sub>Fe alloy after sulfurization reaction, NiS<sub>2</sub> corresponds to (200), (210), (211), (220), (311), (023), (321) lattice planes respectively, and Fe<sub>7</sub>S<sub>8</sub> showing a prominent lattice plane for (206). The surface of CNTs after selenization becomes rough, and obvious metal particles are wrapped (Fig. S4d, e). XRD characterization (Fig. S4f) shows that NiSe<sub>2</sub>/Fe<sub>3</sub>Se<sub>4</sub> heterojunctions were formed by selenization reaction, NiSe<sub>2</sub> corresponds to (200), (210), (211), (311), (023), (321) lattice planes respectively, and Fe<sub>3</sub>Se<sub>4</sub> shows three obvious crystal planes for (-114), (114), (222), which prove that N-CNTs@NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub> and N-CNTs@NiSe<sub>2</sub>/Fe<sub>3</sub>Se<sub>4</sub> have been successfully synthesized.



Fig. S5. The EDS spectra of N-CNTs@NiS<sub>2</sub>/ Fe<sub>7</sub>S<sub>8</sub>.



Fig. S6. The ball-and-stick model of (a)  $NiS_2$  and (b)  $Fe_7S_8$ .



Fig. S7. The ball-and-stick model of (a)  $NiSe_2$  and (b)  $Fe_3Se_4$ .



**Fig. S8.** Raman spectra a) and N<sub>2</sub> adsorption and desorption curve (the inset shows the pore size distribution diagram) b) of N-CNTs@Ni<sub>3</sub>Fe, N-CNTs@NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub> and N-CNTs@NiSe<sub>2</sub>/Fe<sub>3</sub>Se<sub>4</sub>. In inset Fig. S8b, the pore size distribution shows that the samples have mesoporous structure, which provides a large space for the stable catalysis of active sites.



Fig. S9. XPS survey spectrum of N-CNTs@Ni\_3Fe, N-CNTs@NiS\_2/Fe\_7S\_8 and N-CNTs@NiSe\_2/Fe\_3Se\_4.



**Fig. S10.** The XPS high-resolution spectra of a) N 1s and b) C 1s in N-CNTs@Ni<sub>3</sub>Fe, N-CNTs@NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub> and N-CNTs@NiSe<sub>2</sub>/Fe<sub>3</sub>Se<sub>4</sub>, respectively.

N 1s orbitals can be divided into three peaks, showing that N is doped into CNTs by three kinds for pyridinic-N (398.68 eV), pyrrolic-N (400.94 eV) and graphitic-N (405.74 eV). As can be seen from Fig. S10a, the contents of pyridinic-N and pyrrolic-N remained basically unchanged, while graphitic-N in N-CNTs@NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub> decreased significantly, which also proves that the treatment of H<sub>2</sub>S opens part of the N-C bonds and forms irregular carbon, which is very helpful to the conductivity and catalytic performance of catalyst. The orbitals of C 1s (Fig. S10b) can be divided into three peaks, an distinct peak at 284.61 eV corresponds to C-C bond, and a peak at 285.69 eV corresponds to the C-N bond, this proves that the N atom has been successfully doped into the C skeleton, a weak peak at 289.83 eV is the C=O bond, which is due to a small part of oxidation on the surface of CNTs when it was exposed to air.



Fig. S11. The contact angle of (a) N-CNTs@Ni<sub>3</sub>Fe, (b) N-CNTs@NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub> and (c) N-CNTs@NiSe<sub>2</sub>/Fe<sub>3</sub>Se<sub>4</sub>.



Fig. S12 CV curves and the electrical double-layer capacitor of (a-c) N-CNTs@Ni<sub>3</sub>Fe, (d-f) N-CNTs@NiS<sub>2</sub>/Fe<sub>7</sub>S<sub>8</sub> and (g-i) N-CNTs@NiSe<sub>2</sub>/Fe<sub>3</sub>Se<sub>4</sub> under different scanning rates.

Materials	Support	Electrolyte	Overpotential (mV)	Tafel slope (mV dec <sup>-1</sup> )	Reference
N-CNTs@NiS <sub>2</sub> /Fe <sub>7</sub> S <sub>8</sub>	GCE	1.0 M KOH	330 (50 mA cm <sup>-2</sup> )	51.49	This work
N-CNTs@NiSe <sub>2</sub> /Fe <sub>3</sub> Se <sub>4</sub>	GCE	1.0 M KOH	360 (50 mA cm <sup>-2</sup> )	72.32	This work
NiFe@C	NF	1.0 M KOH	274 (10 mA cm <sup>-2</sup> )	57	[3]
Au <sub>1</sub> –CoSe <sub>2</sub>	GCE	1.0 M KOH	303 (10 mA cm <sup>-2</sup> )	42	[5a]
Ni <sub>3</sub> Se <sub>2</sub>	GCE	0.1 M KOH	470 (1.32 mA cm <sup>-2</sup> )	46	[5b]
AI-CoP/CC	СС	1.0 M KOH	265 (10 mA cm <sup>-2</sup> )	67	[6]
$Fe_{0.09}Co_{0.13}$ -NiSe <sub>2</sub> CFC	CFC	1.0 M KOH	251 (10 mA cm <sup>-2</sup> )	63	[7a]
NiFeS	NF	0.1 M KOH	286 (10 mA cm <sup>-2</sup> )	56.3	[8]
NiS/NiS <sub>2</sub>	GCE	1.0 M KOH	416 (100 mA cm <sup>-2</sup> )	156.5	[12a]
NiS <sub>2</sub> /CoS <sub>2</sub> /C	GCE	1.0 M KOH	310 (20 mA cm <sup>-2</sup> )	78	[12b]
hcp-NiFe@NC	GCE	1.0 M KOH	226 (10 mA cm <sup>-2</sup> )	41	[14]
Ni <sub>3</sub> S <sub>4</sub> /N,P-HPC	GCE	0.1 M KOH	370 (10 mA cm <sup>-2</sup> )	96	[15]
Ni <sub>0.5</sub> Fe <sub>0.5</sub> Se <sub>2</sub>	GCE	1.0 M KOH	235 (10 mA cm <sup>-2</sup> )	34.7	[18]
CoOOH-RGO	GCE	1.0 M NaOH	248 (10 mA cm <sup>-2</sup> )	32	[19]
Fe <sub>7</sub> S <sub>8</sub> sheet	GCE	1.0 M KOH	270 (10 mA cm <sup>-2</sup> )	43	[20]
CoPS/Al <sub>2</sub> O <sub>3</sub> -3	GCE	1.0 M KOH	250 (10 mA cm <sup>-2</sup> )	68.4	[21]

Table S1. Comparison OER performance of N-CNTs@NiS $_2$ /Fe $_7$ S $_8$  with other electrocatalysts.