Electronic Supplementary Information

One-pot synthesis of iron-nickel-selenide nanorods for efficient and durable electrochemical oxygen evolution

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Experimental details:

Material Synthesis

Ferrous nitrate, sodium tetrahydroborate and selenium were all of analytical grade (AR) and were used without any additional purification. Iridium dioxide (IrO_2) was purchased from Sigma-Aldrich. Nickel foam was purchased from Changsha Keliyuan. Ethanol (99.9%) and Nafion (5% in a mixture of lower aliphatic alcohols and water) were purchased from Alfa Aesar.

The Ni foam (3cm×3cm) was cleaned with acetone, ethanol, and deionized water, respectively. Se powder (0.059 g) was added into deionized water (1.5 mL) containing $NaBH_4$ (0.065 g). After ultrasonic dissolving for 5 minutes, a clear NaHSe solution was obtained. Then, 100 μL 1 M $Fe(NO_3)_3$ solution was dispersed into 30 ml of ethanol, followed by the addition of the freshly prepared NaHSe solution under N_2 flow. Thereafter, the mixture was transferred into a Teflon-lined stainless steel autoclave contained the cleaned Ni foam, which was subsequently heated at 180 ºC for 25 h. After the autoclave was cooled down to room temperature, the Fe-Ni-Se/NF sample was taken out from the autoclave and washed with copious amount of deionized water. And then the Fe-Ni-Se/NF sample was dried under vacuum at 60 ^oC for overnight.

In comparison, 50 μL 1 M $Fe(NO_3)_3$ and 150 μL 1 M $Fe(NO_3)_3$ solution were used to prepare the catalysts with different amount of Fe. Ni-Se/NF sample was prepared by the same synthetic method without adding ferrous nitrate aqueous solution. NiSe/NF sample was also prepared using 0.08 g of Se powder under the identical conditions.

The mass of Fe-Ni-Se catalyst on NF was calculated as follows. The weight increment (x mg) of NF can be directly weighted after the growth of Fe-Ni-Se. A stoichiometric formula of Fe-Ni-Se is $Fe_{0.035}Ni_{1.13}Se$ by ICP-MS results. Fe-Ni-Se loading =x mg × ($M_{Fe+Ni+Se}/M_{Fe+Se}$)= x mg × ((0.035×56)+(1.13×59)+79)/((0.035×56)+79))=1.82x mg. For Fe-Ni-Se/NF electrode, the loading mass is about 3.0 mg cm^{-2}. For Ni-Se/NF electrode, the loading mass is about 3.8 mg cm^{-2}.

Material Characterization

The crystal structure of the prepared samples were characterized by powder X-ray diffraction (XRD, Rigaku D/max 2400 X-ray generator, Cu Kα radiation, λ = 1.5406 Å) at a scanning rate of 6^{o} min^{-1} from 10 to 80^{o}. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 microscopy (operating voltage, 7 kV). Transmission electron microscope (TEM) and high resolution TEM (HRTEM) charaterizations were carried out on Philips Tecnai F20 operated at 200 kV. X-ray photoelectron spectroscopy (XPS) data were collected on a PHI-5702 instrument. The stoichiometric ratio of Fe/Ni/Se in Fe-Ni-Se nanorod was conducted on the inductively coupled plasma-mass spectrometry (ICP-MS). In this measurement, the Fe-Ni-Se/NF sample was first treated by sonication in ethanol. The solution was centrifuged and vacuum-dried. And then the Fe-Ni-Se powder sample was obtained.

Electrochemical Tests

Electrochemical measurements were carried out with a computer-controlled CHI 760E electrochemistry workstation under room temperature. A three-electrode system consisting of a working electrode (the catalyst on Ni foam), a saturated calomel electrode (SCE), and a graphite rod counter electrode was used. For comparison, electrocatalytic performance of the benchmark IrO_2 electrode (loaded on nickel foam) and Ni foam were also investigated under the same condition. Voltammetry studies were performed in 1.0 M aqueous KOH electrolyte. Linear sweep voltammetry was recorded at a scan rate of 5 mV s^{-1}. All the polarization curves of oxygen evolution reaction were iR-corrected. Unless otherwise stated, all potentials were converted to the reversible hydrogen electrode (RHE) potential in all measurements. In 1.0 M KOH solution, the potential of SCE was calibrated as +1.067 V with respect to RHE.

Electrochemical impedance spectra were obtained over a frequency range of 100 kHz to 10 mHz at a direct-current bias potential of 1.52 V at room temperature. Chronoamperogram was measured to evaluate the catalyst durablility at 1.49 V in 1.0 M KOH solution.

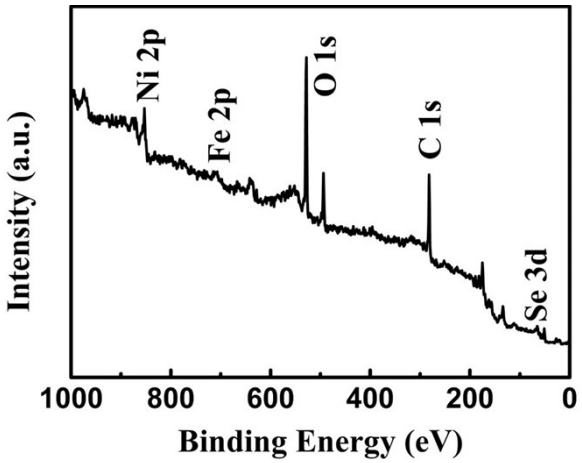

Fig. S1 XPS survey spectrum of the prepared Fe-Ni-Se/NF.

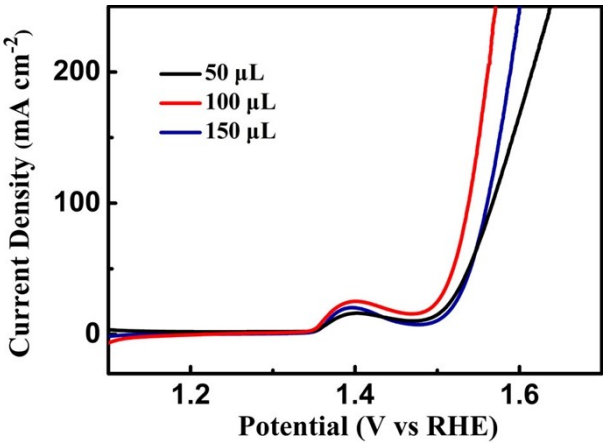

Fig. S2 The polarization curves of the catalysts with different amount of Fe.

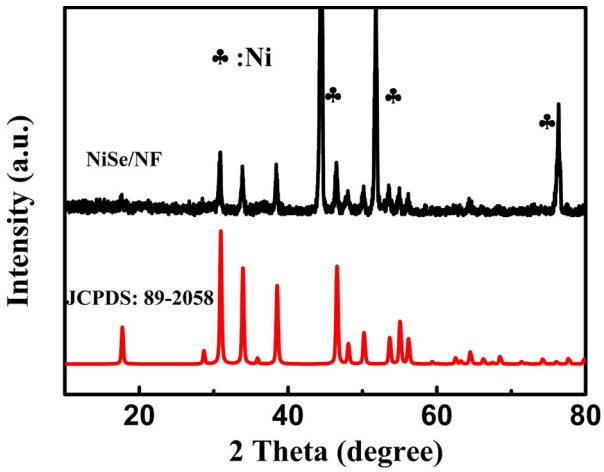

Fig. S3 XRD pattern of NiSe/NF and the standard powder diffraction pattern of NiSe.

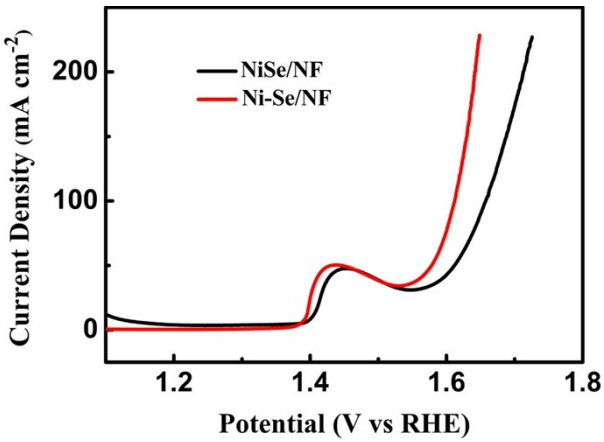

Fig. S4 Polarization curves of Ni-Se/NF and NiSe/NF in 1.0 M KOH at a potential sweep rate of 5 mV/s.

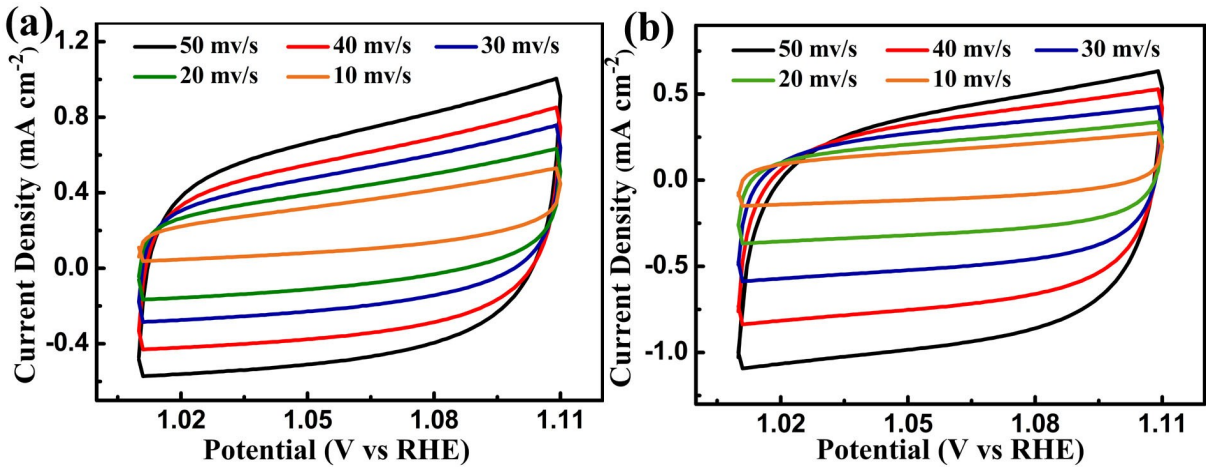

Fig. S5 Electrochemical double-layer capacitance measurements. The cyclic voltammograms (CVs) measurements with various scan rates for (a) Fe-Ni-Se/NF and (b) Ni-Se/NF in 1.0 M KOH.

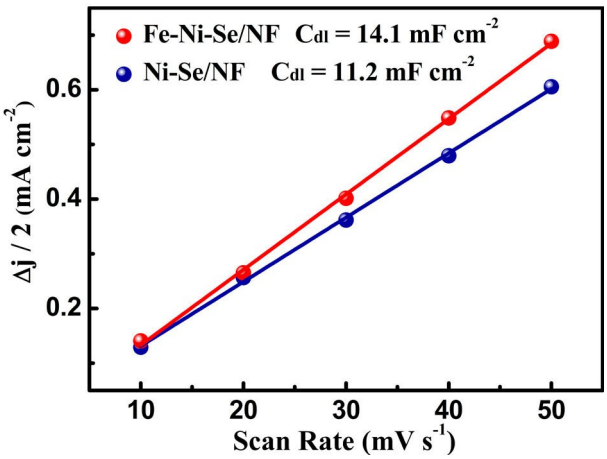

Fig. S6 Electrochemical double-layer capacitance measurements. Linear fitting of the capacitive currents of the catalysts against the scan rate to fit a linear regression.

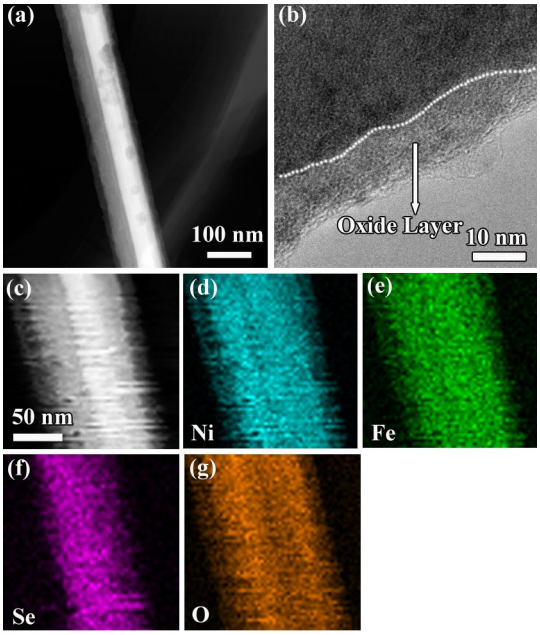

Fig. S7 (a,b) TEM image and (c-g) EDX maps of Fe-Ni-Se nanorods after OER measurements.

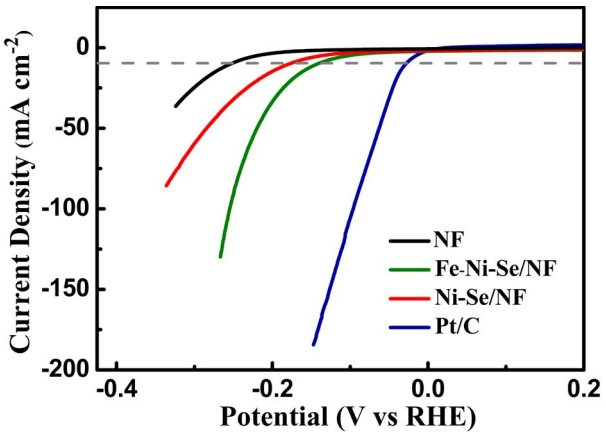

Fig. S8 Polarization curves of NF, Ni-Se/NF, Fe-Ni-Se/NF and Pt/C in 1.0 M KOH at a potential sweep rate of 5 mV/s.

Table S1. Comparison of the OER activity of the Fe-Ni-Se/NF to that of nickel-based catalysts grown on Ni foam reported in the literature.

Catalysts	Electrolyte	J_{geo} (current density in mA cm^{-2} @ overpotential in mV)	Tafel slope (mV dec^{-1})	Substrate	Reference
Co-Ni-Se/C	1 M KOH	50@η=300	63	Ni foam	13
Ni_3Se_2	1 M KOH	100@η=315	40.2	Ni foam	21
NiSe nanowires	1 M KOH	20@η=270	64	Ni foam	27
$Ni_{0.76}Fe_{0.24}Se$	1 M KOH	10@η=197	56	Ni foam	28
$MoO_x/Ni_3S_2/NF$	1 M KOH	100@η=310	50	Ni foam	29
$Mo_{(1-x)}W_xS_2$ /Ni_3S_2	1 M KOH	10@η=285	83	Ni foam	30
NiS/Ni foam	1 M KOH	50@η=335	89	Ni foam	31
$FeNi_3N/NF$	1 M KOH	10@η=202	40	Ni foam	32
Ni_3Se_2–Ni foam	1 M KOH	10@η=270	142	Ni foam	33
Fe–NiSe/NF	1 M KOH	10@η=233	48	Ni foam	34
Fe-Ni-Se/NF	1 M KOH	60@η=290	61	Ni foam	This work