

Electronic Supplementary Information

Nickel Chalcogenides as Selective Ethanol Oxidation Electro-catalysts and Their Structure Performance Relationships

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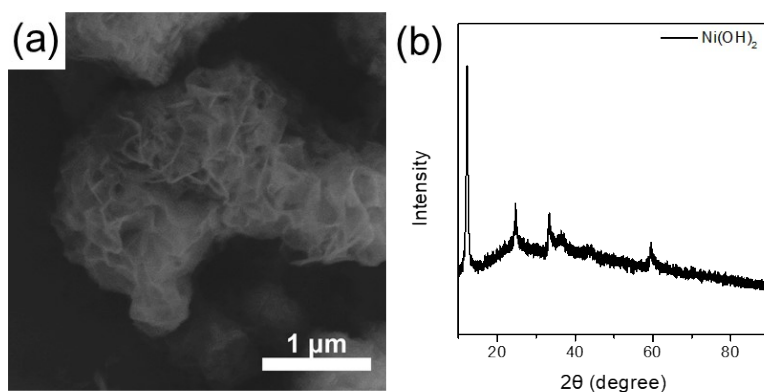
Experimental section

Chemicals

Ethanol (99.9%, Aladdin), potassium hydroxide (KOH, 99.999%, Aladdin), nickel (II) sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 98%, Macklin), sodium hydroxide (NaOH, 99.999%, Aladdin), hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 98%, Aladdin), ethylenediaminetetraacetic acid (EDTA, 95%, Macklin), selenium (99%, Aladdin), sulfur (99%, Aladdin), sodium selenite ($\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$, 99%, Sigma) were used as received without further purification.

Synthesis of $\text{Ni}(\text{OH})_2$ precursor

The synthetic procedure was carried out follow the literature¹. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (1.05 g) and urea (6 g) were dissolved in deionized water (150 mL). The solution was heated at 100°C with magnetic stirring for 6 hours in a flask. Subsequently, it was collected by centrifugation and rinsed for several times. Finally, the product was obtained by freeze-drying. The characterization results of the $\text{Ni}(\text{OH})_2$ precursor was shown below: (a) SEM image and (b) XRD pattern.



Synthesis of NiO

The NiO microspheres were synthesized by heating the $\text{Ni}(\text{OH})_2$ precursor to 250°C at a rate of 5°C min^{-1} in air. And the reaction time was set 2 h.

Synthesis of NiS and NiSe_2

To prepare the NiSe_2 microspheres, 50 mg of $\text{Ni}(\text{OH})_2$ and 200 mg of selenium powder were first placed in a ceramic boat. The ceramic boat was then transferred to a tubular furnace, and heated to 350°C at a rate of 3°C min^{-1} in a nitrogen atmosphere and kept at this temperature for 2 h.

The NiS microspheres were synthesized through similar procedure replacing selenium with sulfur.

Synthesis of NiSe and Ni₃Se₂

The synthesis of NiSe and Ni₃Se₂ microspheres were carried out follow the literature². For NiSe microsphere, NiSO₄·6H₂O (0.263 g) was placed in a Teflon lined autoclave with a capacity of 50 mL and dissolved in deionized water (30 mL). EDTA (1.0 g) and NaOH (1.0 g) were then added with magnetic stirring. Then Na₂SeO₃·5H₂O (0.519 g) was added. Finally, hydrazine hydrate (10 mL) was added to the mixture to form a transparent solution. The autoclave was sealed and heated to 180°C for 5 h, and then the autoclave was cooled naturally to room temperature. The products were filtered and collected, washed with deionized water and anhydrous ethanol, and dried at 60°C.

Ni₃Se₂ was prepared by similar procedure, except changing the amounts of NiSO₄·6H₂O and Na₂SeO₃·5H₂O to 0.789 g and 0.173 g, respectively. And the reaction time was 7 h.

Loading catalyst on carbon supports

5 mg of high surface area carbon (Vulcan XC-72, Carbot Co.) was dispersed in a mixture of 5 mL of ethanol and 5 mL of water. Then the as-prepared Ni-based catalyst were added dropwise to the dispersion. The mixture was magnetically stirred for 10 h, and the carbon-supported catalysts were collected by filtration. The catalyst content was measured by ICP-OES using a Thermo-Fisher ICAP 6300 Radial instrument.

Physical Characterization

The XRD patterns were obtained on a Rigaku D/Max 2500 VB2+/PC X-ray powder diffractometer equipped with Cu K α radiation ($\lambda = 0.154$ nm) operating at 40 kV and 40 mA. All of the diffraction data were collected at a scanning rate of 10° min⁻¹. The TEM images were conducted by a HITACHI HT7700 transmission electron microscope. The XPS spectra were recorded on a Thermo Fisher ESCALAB 250Xi XPS system with a monochromatic Al K α X-ray source. The binding energies derived from XPS measurements were calibrated to the C 1s at 284.8 eV.

Electrochemical Measurements

The electrochemical measurements were operated in a three-electrode system controlled by a potentiostat (CHI 760E). A graphite electrode and a saturated calomel electrode were used as the counter and reference electrode, respectively. The electrolytes for the ethanol oxidation reaction were Ar-saturated 1 M ethanol and 1 M KOH. The OER polarization curves were obtain in O₂-saturated 1 M KOH electrolyte. The catalysts were drop-casting on a glassy carbon electrode and used as the working electrode. The catalyst ink was prepared by dispersing 2 mg of catalyst in the mixed

solution of isopropanol (750 μL), water (240 μL), and Nafion solution (20 μL , Alfa Aesar, 5 wt%). 6 μL of the ink was dropped onto a glassy carbon electrode (5 mm in diameter, PINE instruments). The Ni loadings were controlled as 0.0122 mg cm^{-2} . The polarization curves were iR uncorrected.

The turnover frequency (TOF) was calculated by the following equation:

$$\text{TOF}=(j/4F)/N \quad (\text{eq. 1})$$

where the j is the current density, the F is faraday's constant, and the N is the mole number of active sites. The number of active sites was electrochemically estimated by integrating the Ni redox peak in the CV curves with the approximation that one electron transfers at one electrochemically active Ni site.

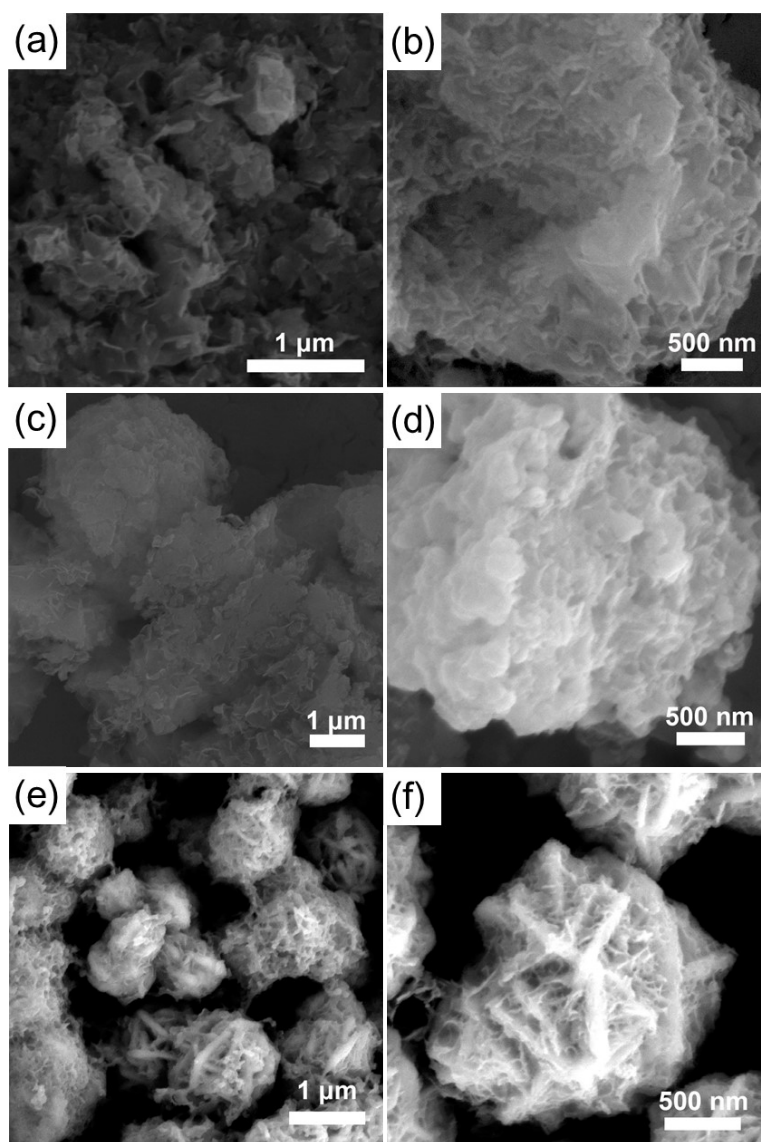


Figure S1. SEM images of the obtained NiX microspheres. (a,b) NiO. (c,d) NiS. (e,f) NiSe.

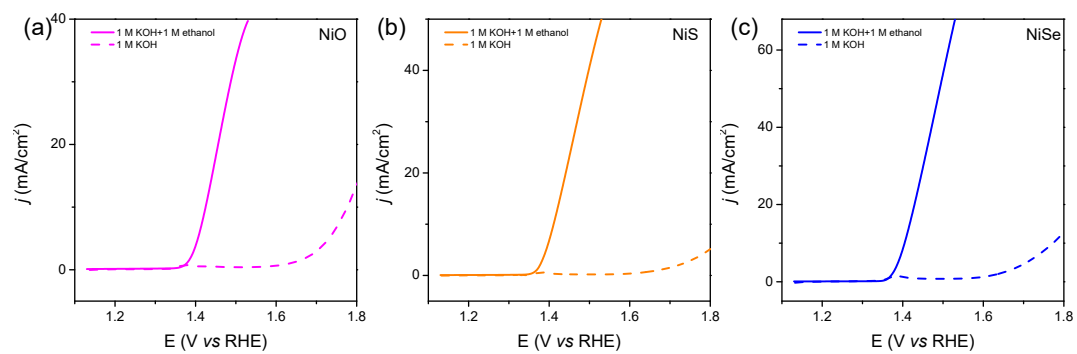


Figure S2. Polarization curves of the catalysts obtained in 1.0 M KOH with and without 1.0 M ethanol at a scan rate of 50 mV s⁻¹. (a) NiO. (b) NiS. (c) NiSe.

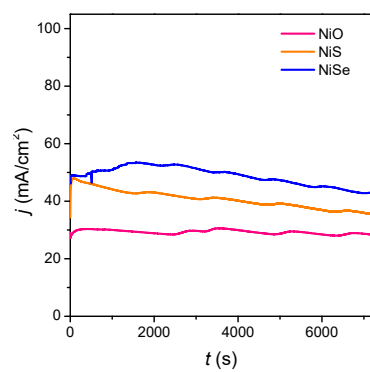


Figure S3. Chronoamperometry curves of NiO, NiS and NiSe in 1.0 M KOH with 1.0 M ethanol at 1.5 V.

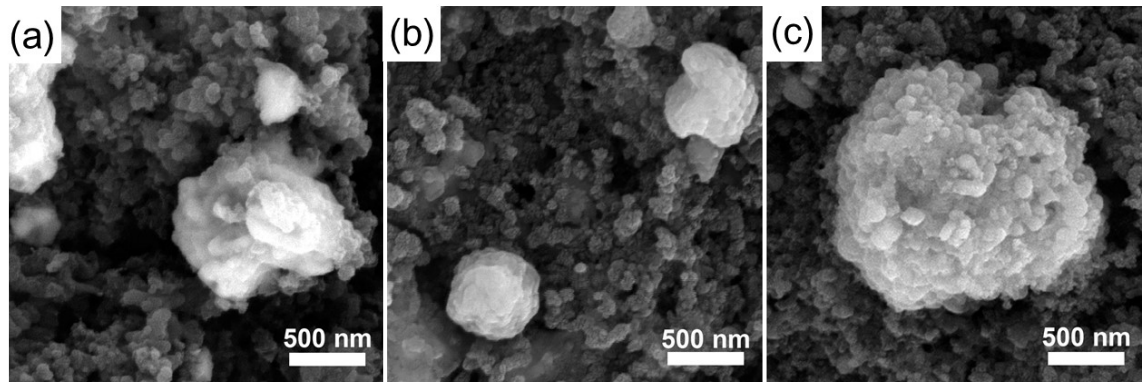


Figure S4. SEM image after stability test of (a) NiO, (b) NiS and (c) NiSe.

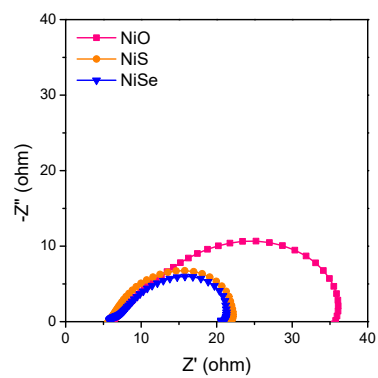


Figure S5. Nyquist plots of the NiX catalysts obtained at 1.40 V in 1 M KOH with 1 M ethanol.

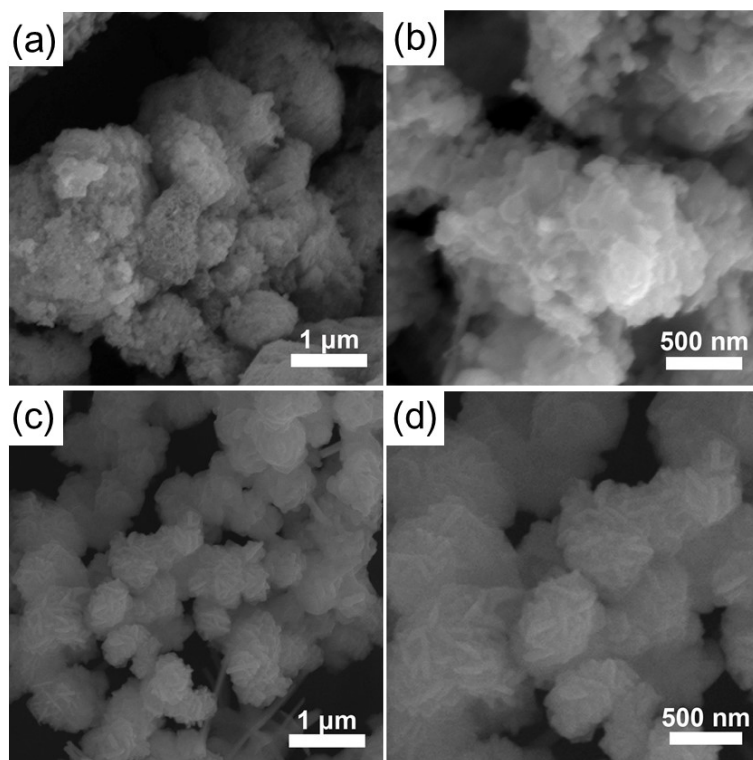


Figure S6. SEM images of the nickel selenide microspheres with different phases. (a, b) NiSe_2 . (c, d) Ni_3Se_2 .

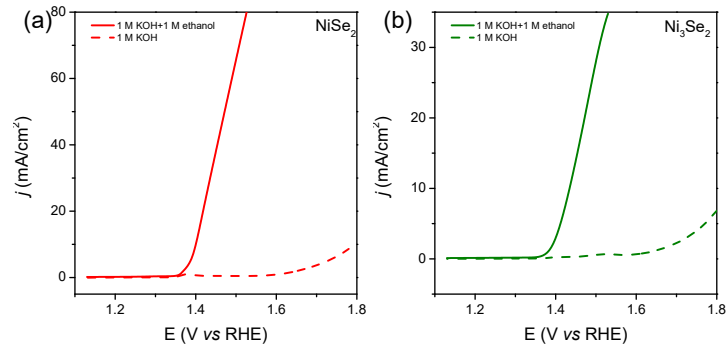


Figure S7. Polarization curves of the (a) NiSe₂ and (b) Ni₃Se₂ obtained in 1.0 M KOH with and without 1.0 M ethanol at a scan rate of 50 mV s⁻¹.

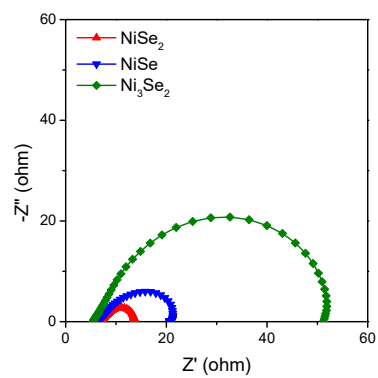


Figure S8. Nyquist plots of the Ni selenides catalyst obtained at 1.40 V in 1 M KOH with 1 M ethanol.

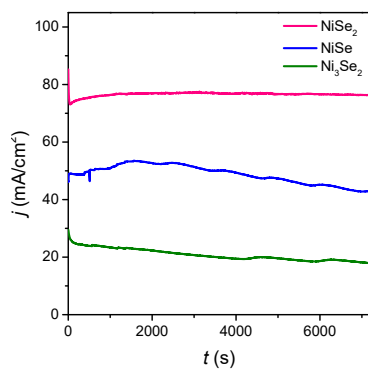


Figure S9. Chronoamperometry curves of Ni-selenide with different phases in 1.0 M KOH with 1.0 M ethanol at 1.5 V.

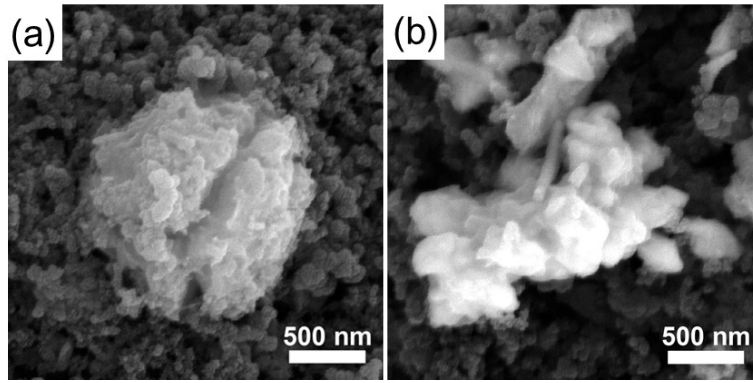


Figure S10. SEM image after stability test of (a) NiSe_2 and (b) Ni_3Se_2 .

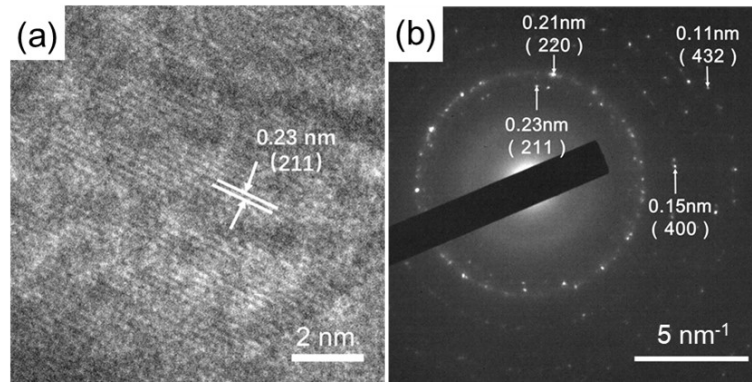


Figure S11. (a) HRTEM image of NiSe₂ after stability test. (b) the corresponding SAED pattern.

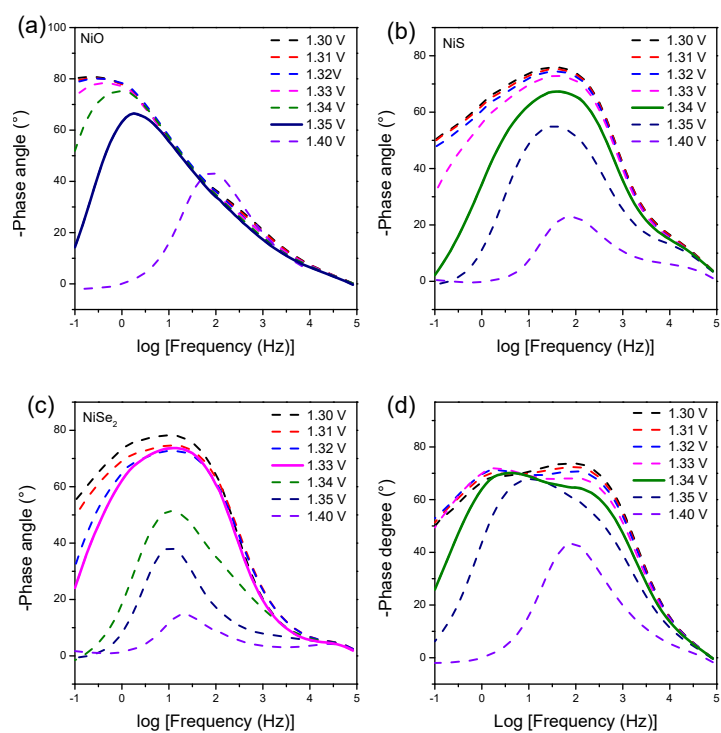


Figure S12. Bode plots of the different Ni-based catalyst.

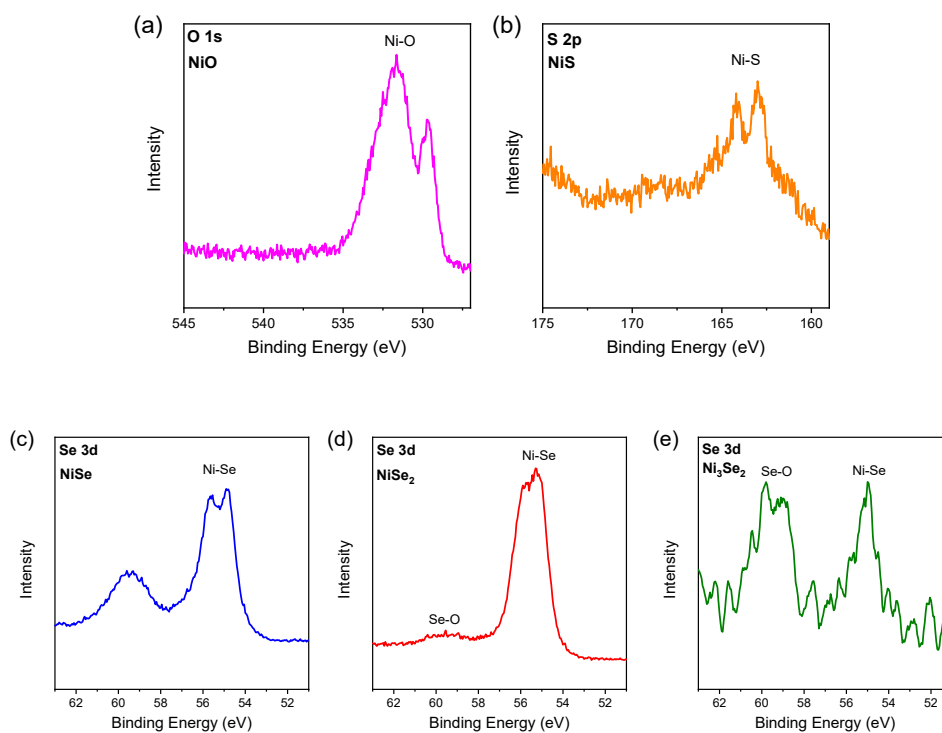


Figure S13. High resolution XPS spectra of (a) O 1s for NiO. (b) S 2p for NiS. (c) Se 3d for NiSe. (d) Se 3d for NiSe₂. (e) Se 3d for Ni₃Se₂.

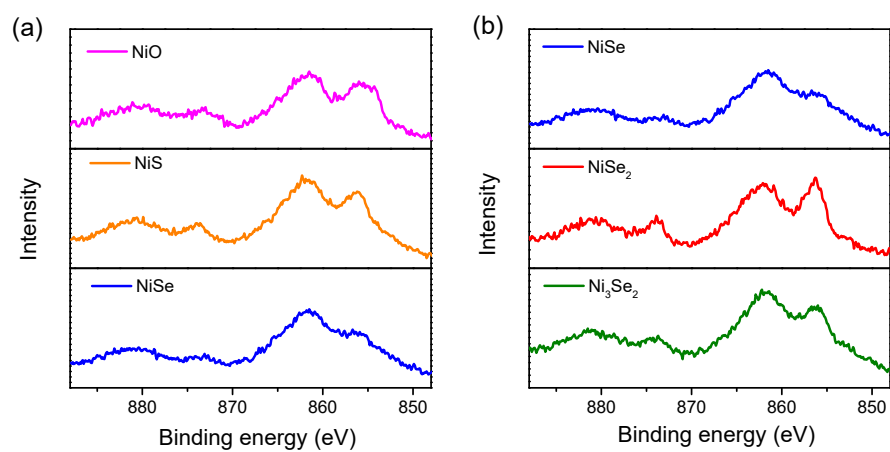


Figure S14. High-resolution Ni 2p XPS spectra of the catalyst after stability tests. (a) NiO, NiS and NiSe. (b) NiSe₂, NiSe and Ni₃Se₂.

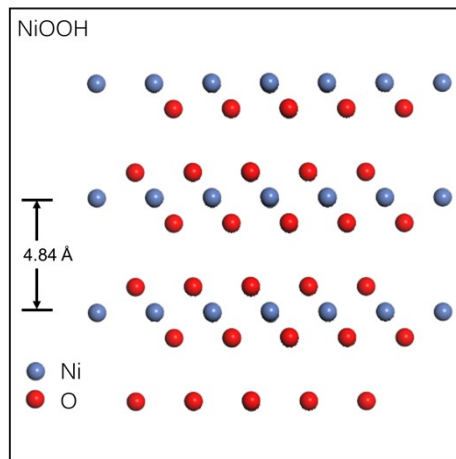


Figure S15. The scheme of the interlayer structure of β -NiOOH.

1. A. H. Shao, X.-X. Zhang, Q.-S. Zhang, X. Li, Y. Wu, Z. Zhang, J. Yu and Z.-Y. Yang, *ACS. Appl. Energ. Mater.*, 2021, **4**, 3431-3438.
2. Z. Zhuang, Q. Peng, J. Zhuang, X. Wang and Y. Li, *Chem. Eur. J.* , 2005, **12**, 211-217.