Electronic Supplementary Material (ESI) for Nanoscale.

High-Index Faceted Binary-Metal Selenide Nanosheet Arrays as Efficient 3D Electrode for Alkaline Hydrogen Evolution

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Experimental Section

Synthesis of NiFe-LDH/EG

In a typical experiment, EG was firstly prepared by electrochemical anodization of graphite foil at 10 V for 30 s with a Pt counter electrode in 0.1 M $(NH_4)_2SO_4$ electrolyte.[1] Next, as-prepared EG foil was placed into a homogeneous solution of $Fe(NO_3)_3 \bullet 9H_2O$ (0.033 g), $Ni(NO_3)_2 \bullet 6H_2O$ (0.093 g), trisodium citrate (0.01 g), urea (0.043 g), and H_2O (20 mL). The autoclave was then sealed and heated at 150 °C for 48 h to allow the growth of NiFe-LDH nanosheets on EG foil. The loading amount of NiFe-LDH/EG on graphite foil was ~3.3 mg cm^{-2}.

Synthesis of FeNiSe-NS/EG

2.0 g of Se powder and the obtained NiFe-LDH/EG were put at two separate positions in a porcelain boat with Se powder at the upstream side of the furnace. Then, the samples were annealed at 400 °C for 2 h with a heating rate of 5 °C min^{-1} under Ar atmosphere. The loading amount of FeNiSe-NS/EG on graphite foil was ~2.4 mg cm^{-2}.

Synthesis of Ni_3Se_2/EG

The Ni_3Se_2/EG with loading amount of ~2.0 mg cm^{-2} was synthesized by the same procedure without $Fe(NO_3)_3 \bullet 9H_2O$ precursor.

Synthesis of Fe-Se/EG

The Fe-Se/EG with loading amount of ~2.2 mg cm^{-2} was synthesized by the same procedure without $Ni(NO_3)_2 \bullet 6H_2O$ precursor.

Characterization

Field emission scanning electron microscope (FESEM) and energy dispersive spectra (EDX) measurements were collected on a Carl Zeiss NVision 40 instrument. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on JEOL JEM-2001F and Carl Zeiss Libra 120 apparatus. Atomic force microscopy (AFM) image was carried out on a NT-MDT 70 Moscow instrument. X-ray di□raction (XRD) measurements were carried out using a Bruker D8 Advance powder diffractometer. X-ray photoelectron spectroscopy (XPS) measurements were performed using an AXIS Ultra DLD system (Kratos). Fourier

transform infrared spectroscopy (FTIR) was recorded on a BRUKER TENSOR II spectrometer. Raman spectra were recorded on an NTEGRA Spectra system (NT-MDT). Iron quantitative analysis was carried using a Perkin Elmer Optima 7000DV ICP-OES. The BET surface area was determined by a Quadrasorb Adsorption Instrument with nitrogen adsorption at 77 K. Water contact angle analysis was performed on a "DSA-10" Kruss contact angle goniometer.

Electrochemical measurements

The HER catalytic measurements were conducted on CHI 760E electrochemistry workstation in a conventional three electrode cell in 1.0 M KOH electrolyte. An Ag/AgCl electrode was used as the reference electrode, a graphite rod was used as the counter electrode, and as-prepared electrode was used as the working electrode, respectively. Polarization curves were recorded at a scan rate of 1 mV s^{-1}. The electrochemical stability of electrode was conducted by chronoamperometric measurements at -0.3 V. EIS measurements were carried out from 100 K to 0.01 Hz with an amplitude of 10 mV AC. Commercial Pt/C catalyst was used as a reference sample under the same experimental conditions.

First-principles calculations

All first-principles-based calculations were conducted by applying the Cambridge Serial Total Energy Package (CASTEP) in Material Studio which performs the density functional theory (DFT) plane-wave pseudopotential method to carry out first principles quantum mechanics calculations. In the calculation, the generalized gradient approximation (GGA) within Perdew–Burke–Ernzerhof (PBE) form was used as the exchange–correlation function. The convergence tests of the total energy with respect to the k-points sampling and the energy-cutoff were carefully examined, using 3×3×1 Monkhorst-Pack k-points grid and a 700 eV energy-cutoff for plane-wave expansion. Valence states used were Fe-$3s^2 3p^6 3d^6 4s^2$, Ni-$3s^2 3p^6 3d^8 4s^2$, Se-$4s^2 4p^4$, P-$3s^2 3p^3$, O-$2s^2 2p^4$, and H-$1s^1$. In the super-cell configuration, a sufficiently large vacuum slab (about 15 Å) was maintained. The SCF tolerance was setup to 1e−6eV·$atom^{-1}$ for the geometrical optimization and phonon calculations.

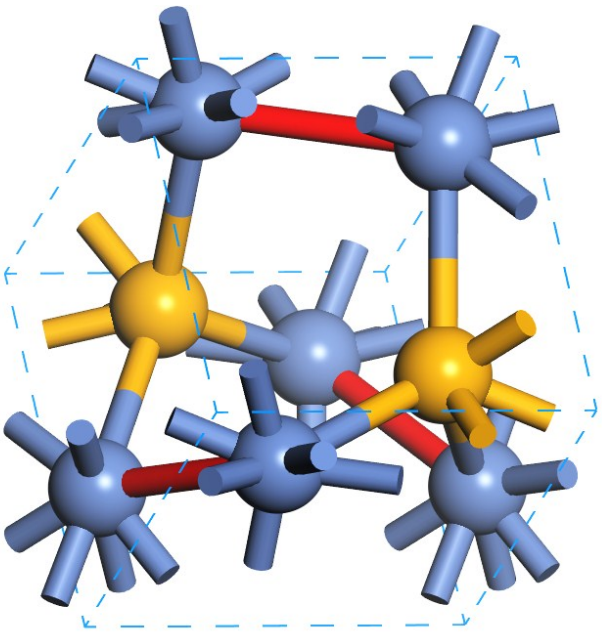

Figure S1. The schematic diagram of the unit cell of Ni_3Se_2. The Ni-Ni bonds are colored red.

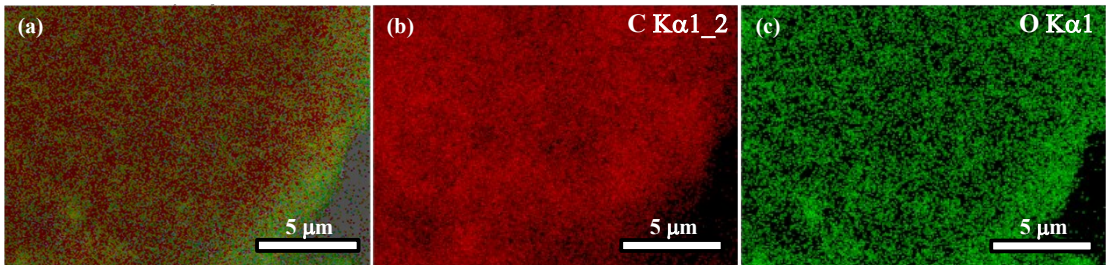

Figure S2. (a-c) FESEM image and corresponding elemental mappings of FeNiSe-NS/EG.

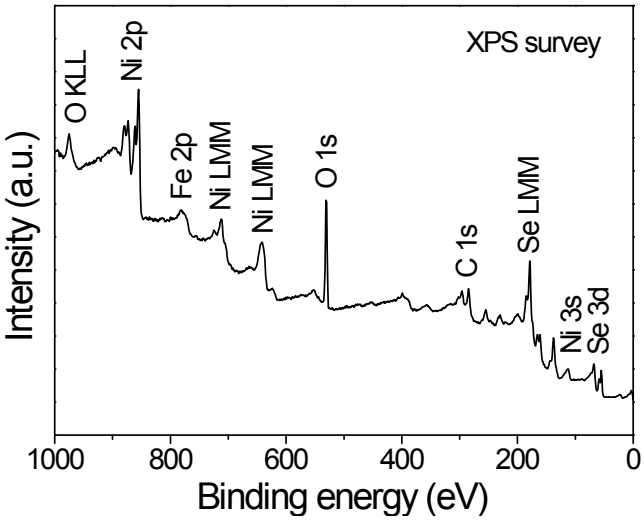

Figure S3. The XPS survey spectrum of FeNiSe-NS/EG.

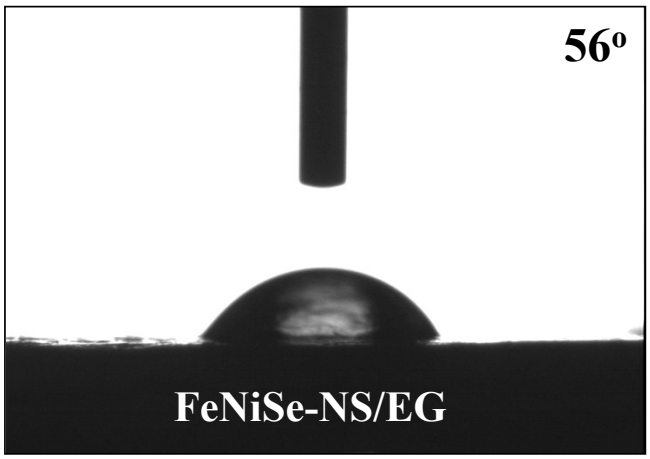

Figure S4. Contact wetting angel of FeNiSe-NS/EG.

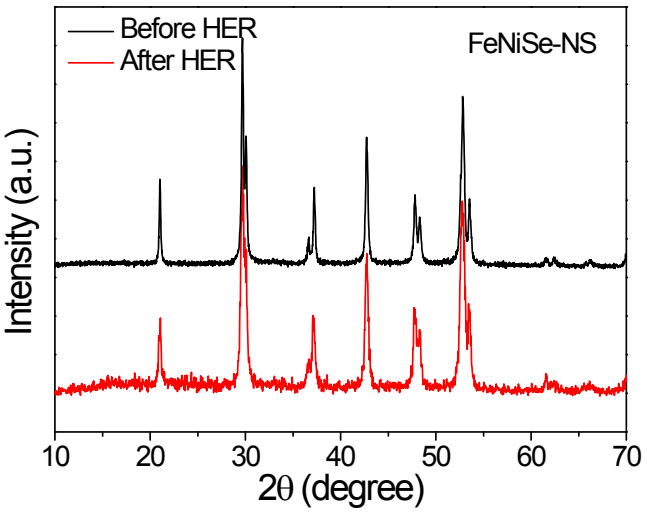

Figure S5. XRD patterns of FeNiSe-NS/EG before and after the HER.

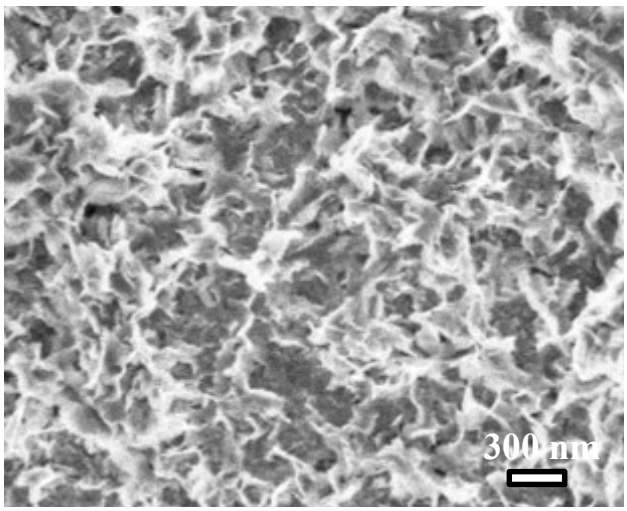

Figure S6. FESEM image of FeNiSe-NS/EG after 10 h HER electrolysis.

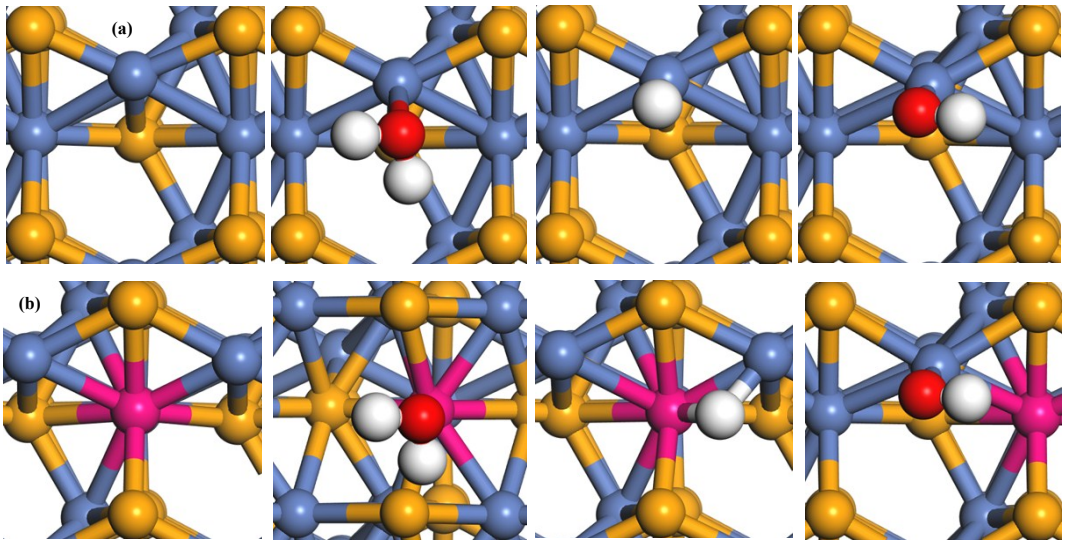

Figure S7. The DFT calculated models (Volmer-Tafel-Heyrovsky mechanism) for (003) facets of (a) Ni_3Se_2 and (b) Ni_3Se_2|Fe without and with groups adsorbed.

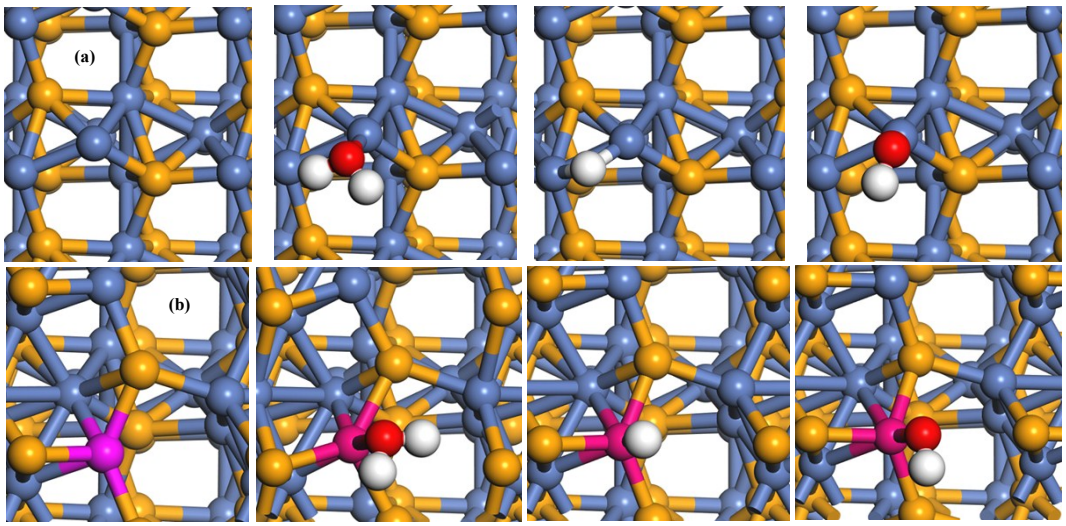

Figure S8. The DFT calculated models (Volmer-Tafel-Heyrovsky mechanism) for (101) facets of (a) Ni_3Se_2 and (b) Ni_3Se_2|Fe without and with groups adsorbed.

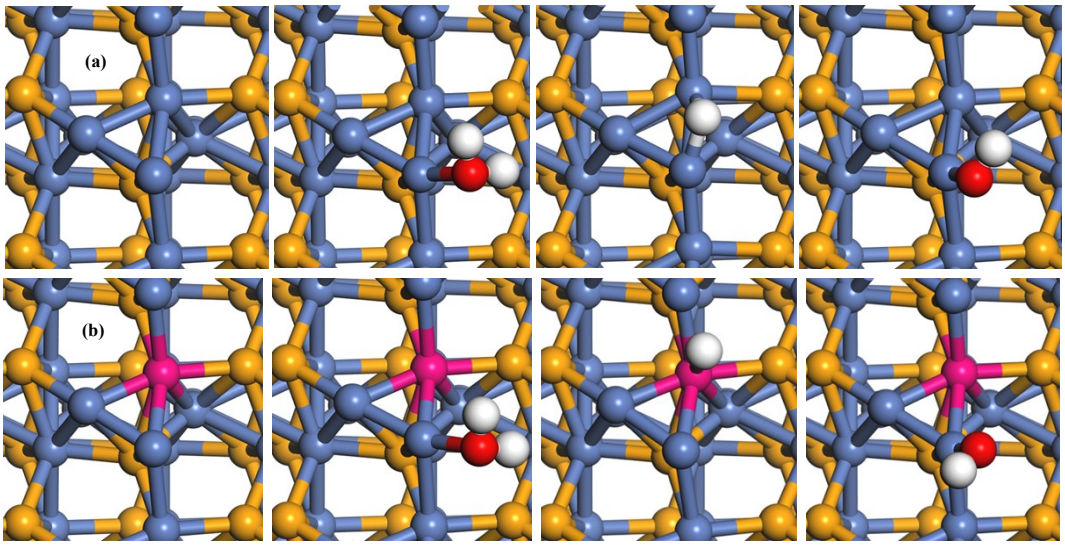

Figure S9. The DFT calculated models (Volmer-Tafel-Heyrovsky mechanism) for (202) facets of (a) Ni_3Se_2 and (b) Ni_3Se_2|Fe without and with groups adsorbed.

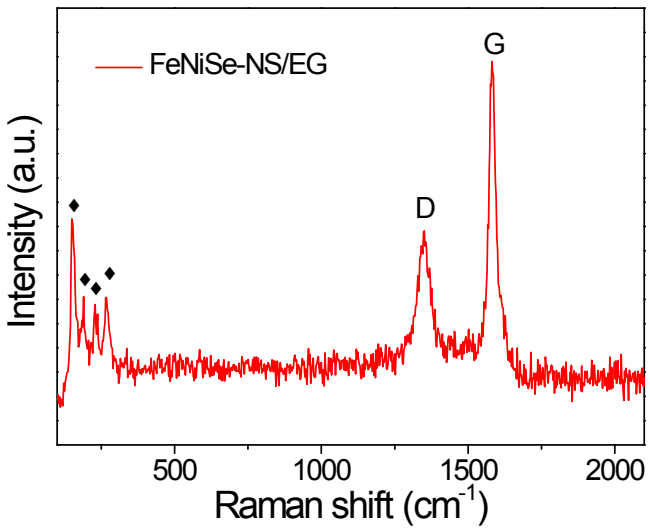

Figure S10. Raman spectrum of FeNiSe-NS/EG. Two characteristic peaks of the D and G bands are observed at about 1,350 and 1,581 cm^{-1}, with an I_D/I_G ratio of 0.51, indicating a low degree of defects in the EG.

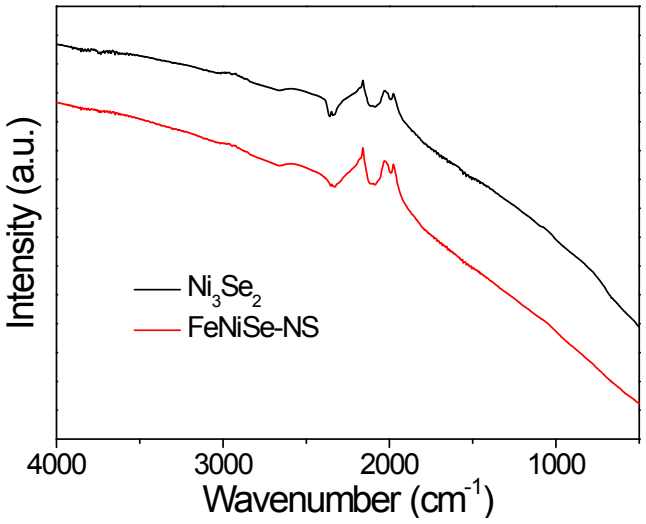

Figure S11. FTIR spectra of Ni_3Se_2 and FeNiSe-NS.

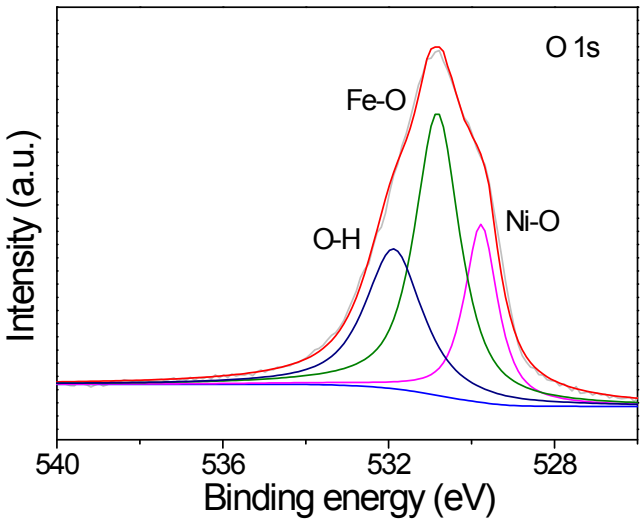

Figure S12. High-resolution O 1s XPS spectrum of FeNiSe-NS/EG.

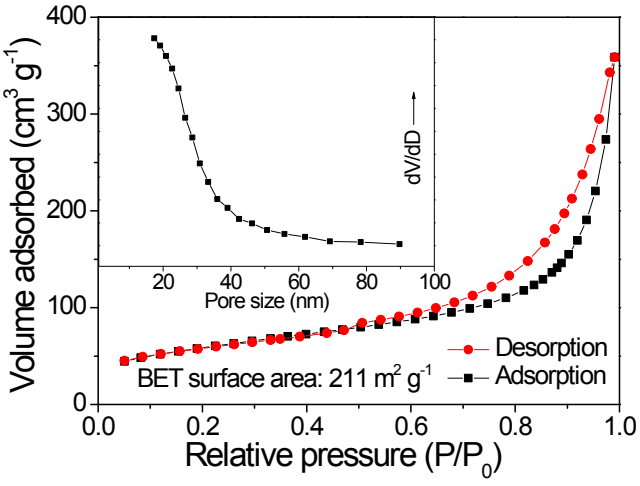

Figure S13. N_2 adsorption isotherm and the corresponding pore size distribution (inset) of NiFe-LDH.

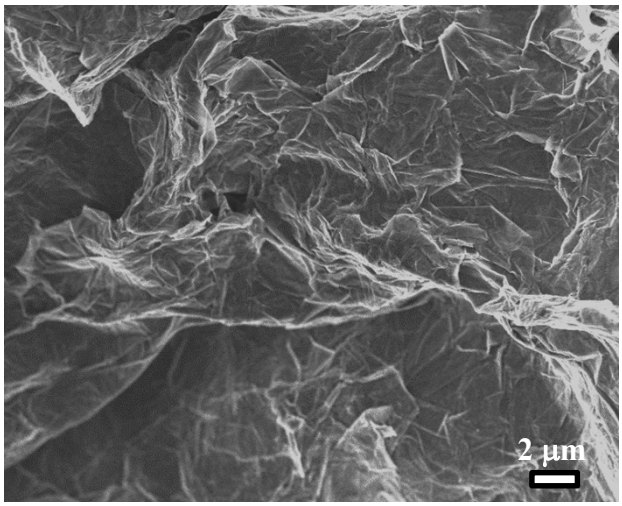

Figure S14. FESEM image of EG.

Reference

[1] K. Parvez, Z.-S. Wu, R. Li, X. Liu, R. Graf, X. Feng, K. Müllen, *Journal of the American Chemical Society* **2014**, *136*, 6083.