Supporting Information for

In-situ phosphoselenization induced heterointerface engineering endow $NiSe_2/Ni_2P/FeSe_2$ hollow nanocage with efficient water oxidation electrocatalysis

Jiongting Yin [a], Cheng Wang [a], Jie Li [a], Kewang Zhang [a], Zhengying Wu *[b], Ning Wang [b] and Yukou Du *[a]

[a] *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China*

[b] *Jiangsu Key Laboratory for Environment Functional Materials, School of Materials Science and Engineering, Suzhou University of Science and Technology, Suzhou 215009, China*

** Corresponding author: Tel: 86-512-65880967, Fax: 86-512-65880089;*

E-mail: duyk@suda.edu.cn (Y. Du); zywu@mail.usts.edu.cn (ZY. Wu)

Experimental section

Synthesis of NiFe-PBA nanocubes

0.6 mmol $Ni(NO_3)_2 \cdot 6H_2O$ and 0.8 mmol $C_6H_5Na_3O_7 \cdot 2H_2O$ were added to 20 mL of deionized water to form clear solution A. Then, 0.4 mmol $K_3[Fe(CN)]_6$ was dispersed in 30 mL of deionized water to form solution B. Afterwards, solution A is carefully poured into solution B and kept stirring for 2 minutes. The solution was aged for 24 h, and final product was obtained by centrifugation and washing.

Synthesis of NiFe-PBA nanocages

20 mg NiFe-PBA nanocubes were dissolved in 10 mL ethanol by sonicating for preparing solution C. Subsequently, 4.2 mL ammonia solution were separated into 15 mL DI water to form homogeneous solution D. Solution D was gradually added to solution C while stirring the mixture at room temperature for 30 minutes. The precipitation was collected by centrifuging and washing after settling for 12 hours. The products were achieved following an overnight drying period at 70 °C.

Synthesis of NiFePSe hollow nanocages

NiFePSe nanocages was attained through in-situ phosphoselenization process. Specifically, 20 mg NiFe-PBA nanocages, 50mg Se powder, and 100mg $NaH_2PO_2 \cdot H_2O$ were placed in three different positions at the porcelain boat of tube furnace. It is importance to ensure that $NaH_2PO_2 \cdot H_2O$ and Se powder were upstream of the tube furnace. Then, the tube furnace was heated to 350 °C at 1 °C min^{-1} and kept it for 120 minutes during the phosphoselenization process. Finally, the black product was collected and named NiFePSe.

Characterizations

The morphology and structure of all prepared samples were filmed by scanning electron microscopy (SEM; Hitachi, Regulus 8230) and transmission electron microscopy (TEM; Hitachi, HT7700, 120 kV). High-resolution TEM (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed on a FEI TecnaiG2F2 FEI Talos F200X S/TEM. Elemental analysis was determined by SEM-energy-dispersive-X-ray spectroscopy (SEM-EDX). X-ray

photoelectron spectroscopy (XPS) was conducted on a VG scientific ESCA Lab 220 XL electron spectrometer. X-ray diffraction (XRD) was detected on Bruker D8 Advanced X-ray Diffractometer.

2.5 Electrochemical tests

The electrochemical measurements of the OER were performed on a CH electrochemical workstation (CHI660, Chenhua, Shanghai) by using a three-electrode setup. To obtain the catalyst ink, 4 mg catalyst and 2 mg carbon powder were added into a mixture of 1 mL ethanol and 15 μL 5 wt% Nafion solution, after 30 min sonication, 10 μL of the as-obtained catalyst ink was deposited on the polished glassy carbon electrode (GCE) (diameter: 5 mm, area: 0.196 cm^2) which served as the working electrode. A graphite rod was employed as the counter electrode, and a saturated Ag/AgCl electrode was used as the reference electrode. The reversible hydrogen electrode (RHE) is used to calibrate all of the reference potentials displayed in these studies: E (RHE) = E (Ag/AgCl) + 0.059 pH + 0.197 V. The linear sweep voltammetry (LSV) uses a 5 mV s^{-1} scan rate and a potential range of 1.0 V to 1.7 V. The Tafel slope was extracted from the Tafel equation, $\eta = b \log j + a$. All the electrochemical tests were implemented without iR compensation.

Supporting Figures and Tables

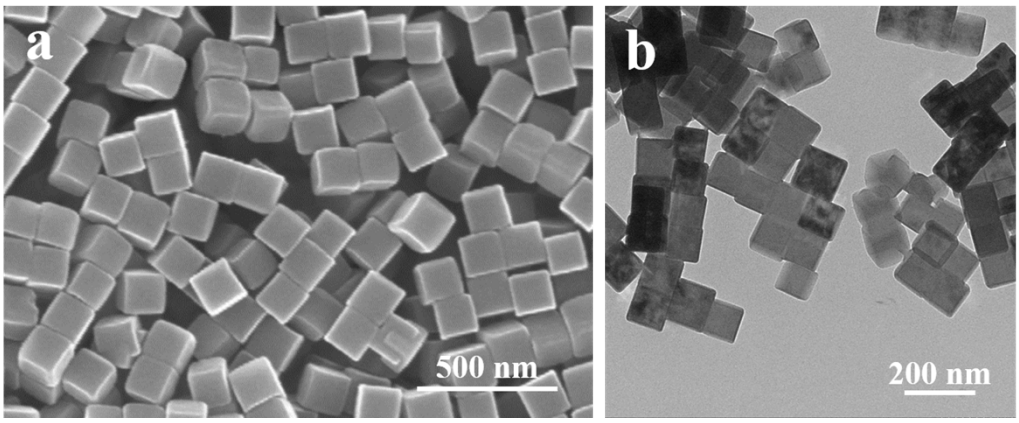

Fig. S1 (a) Representative SEM image and (b) TEM image of solid NiFe-PBA nanocubes.

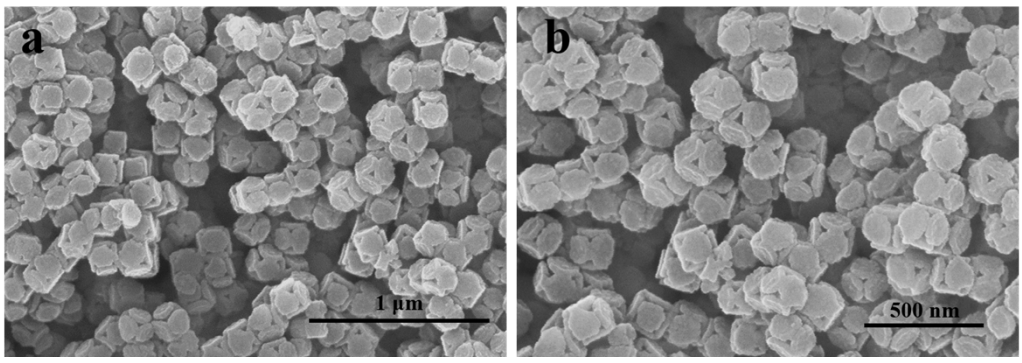

Fig. S2 (a, b) Representative SEM images of hollow NiFe-PBA nanocages.

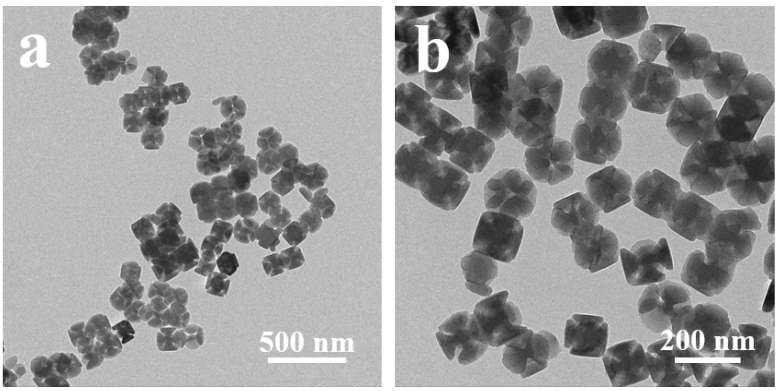

Fig. S3 (a, b) Representative TEM images of hollow NiFe-PBA nanocages.

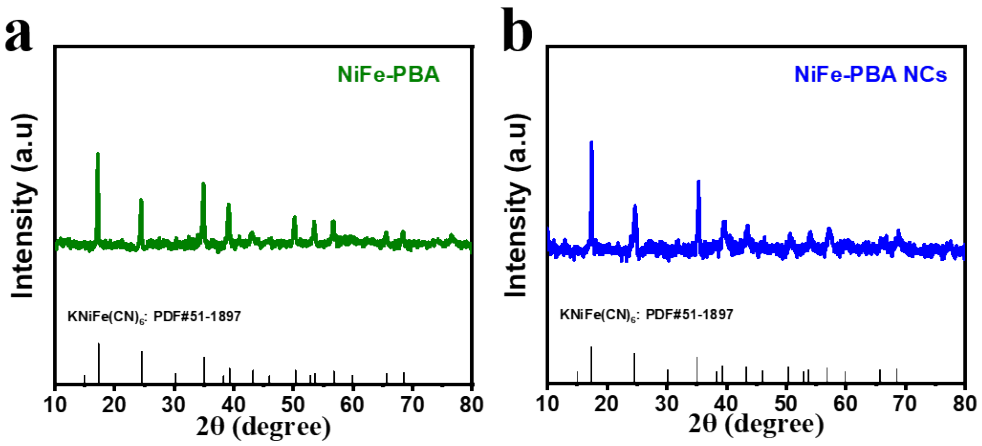

Fig. S4 XRD patterns of the (a) NiFe-PBA and (b) NiFe-PBA NCs.

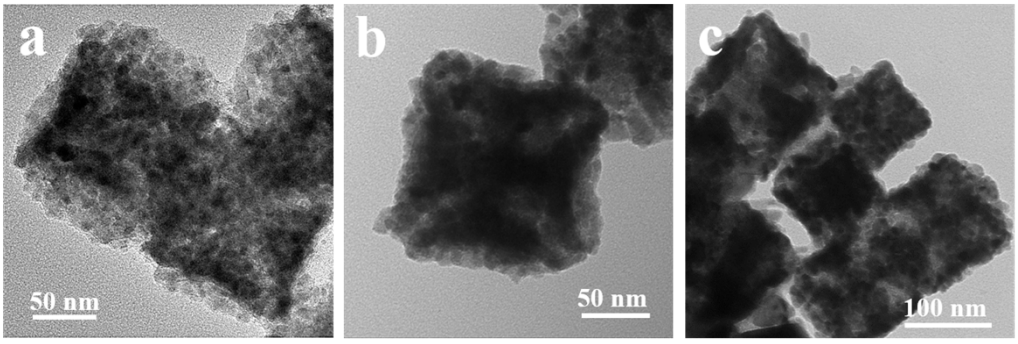

Fig. S5 (a-c) Additional TEM images of the NiFePSe hollow nanocages.

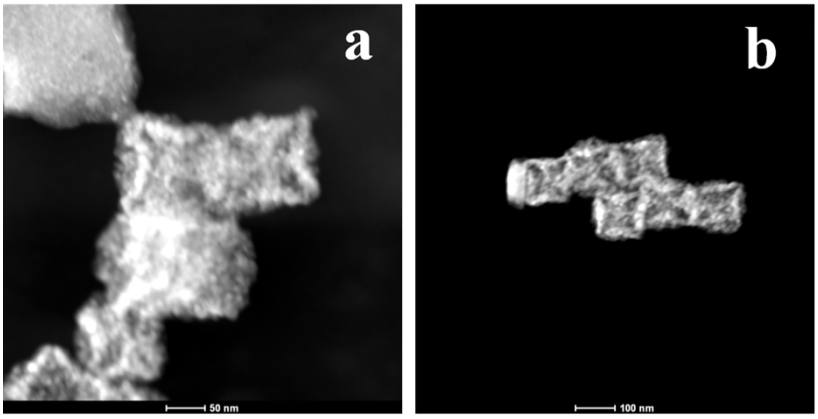

Fig. S6 (a, b) HAADF-STEM images of the unique NiFePSe hollow nanocages.

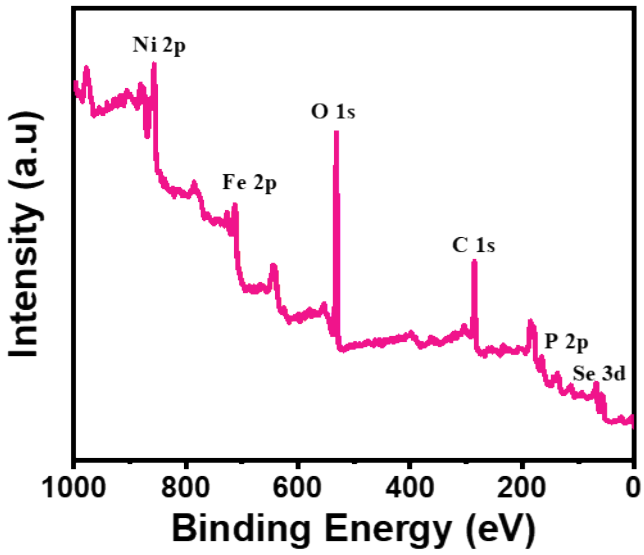

Fig. S7 XPS survey spectrum of the NiFePSe hollow nanocages.

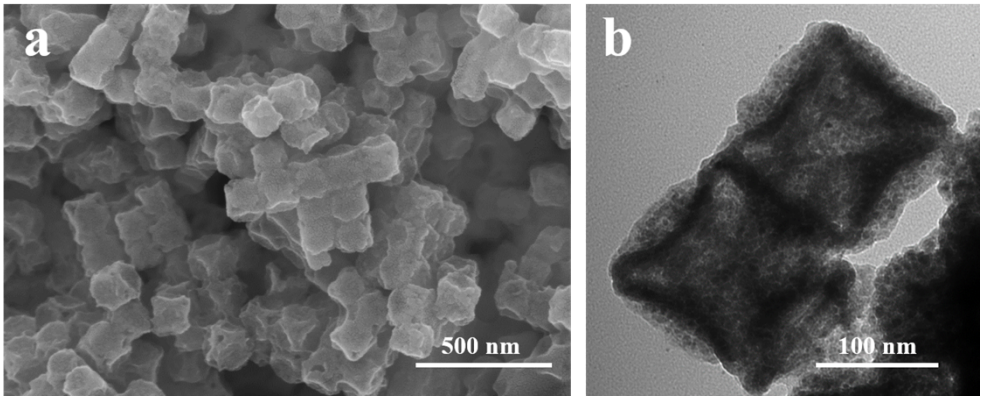

Fig. S8 (a) Representative SEM image and (b) TEM image of porous NiFeP nanocages.

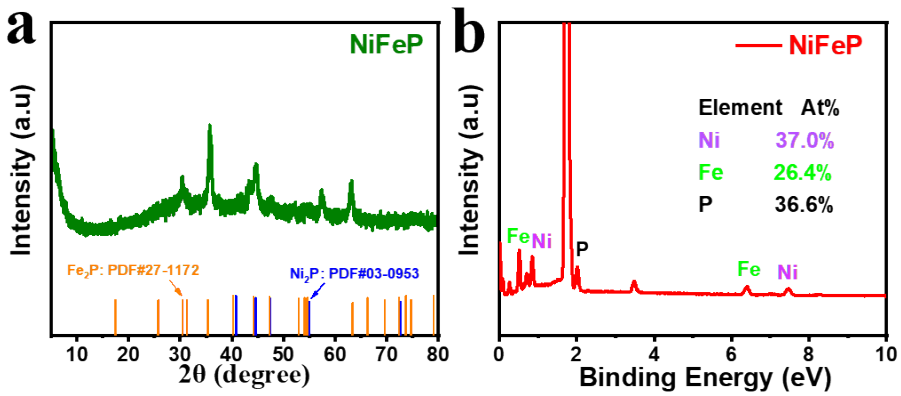

Fig. S9 (a) The XRD pattern and (b) the SEM-EDS spectrum of porous NiFeP nanocages.

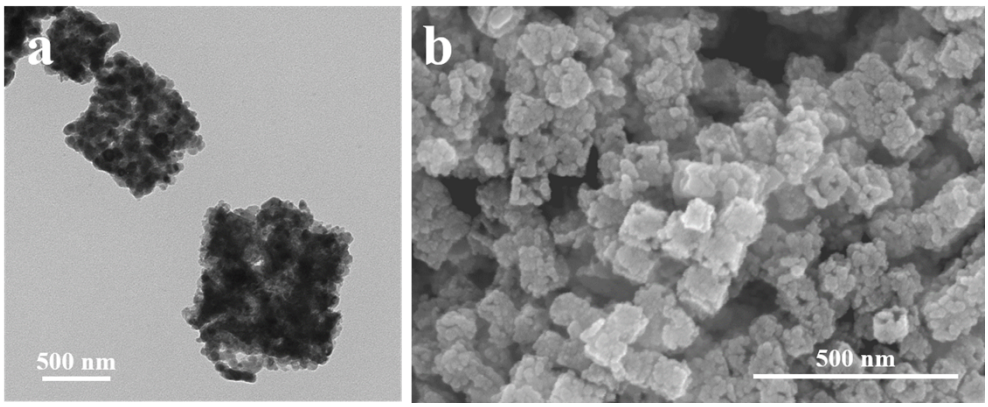

Fig. S10 (a) Representative TEM image and (b) SEM image of porous NiFeSe nanocages.

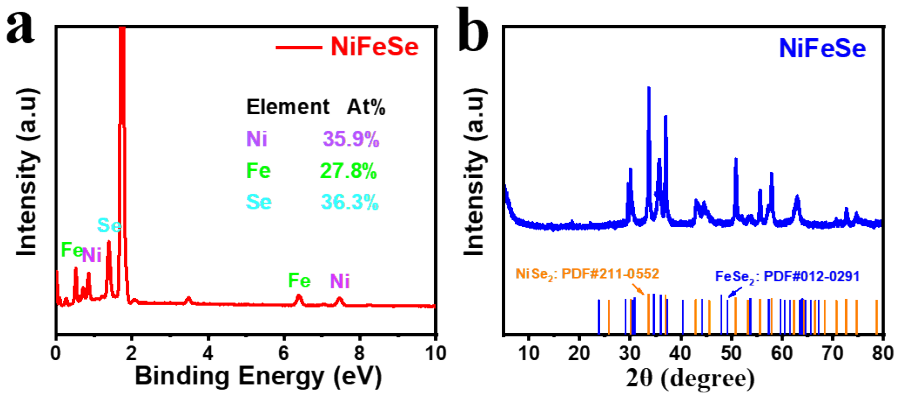

Fig. S11 (a) The SEM-EDS spectrum and the XRD pattern of porous NiFeSe nanocages.

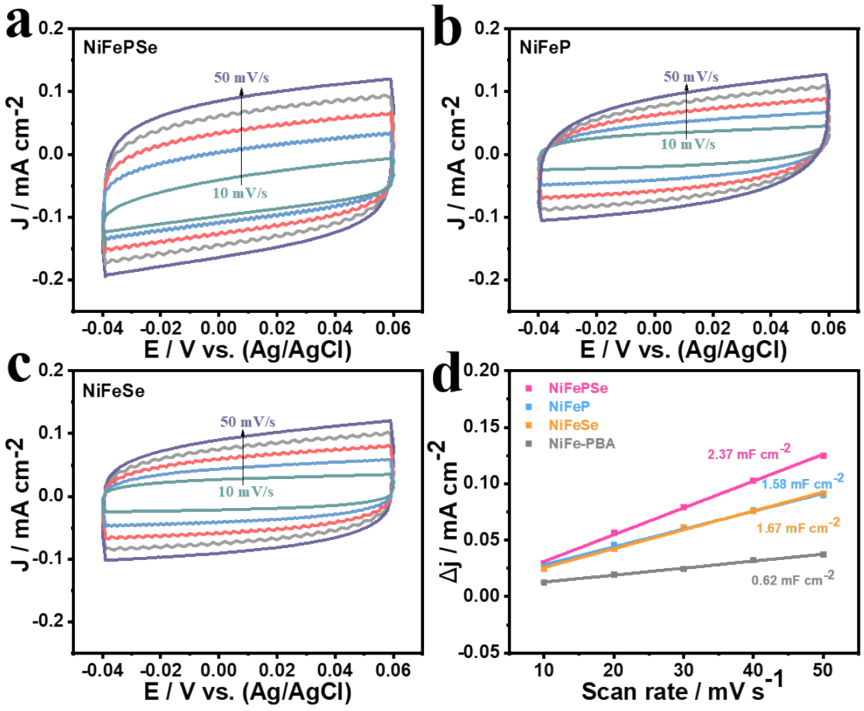

Fig. S12 CV curves of (a) NiFePSe, (b) NiFeP, and (c) NiFeSe in 1 M KOH electrolyte

at different scan rates. (d) Double layer currents of different catalysts versus scan rate.

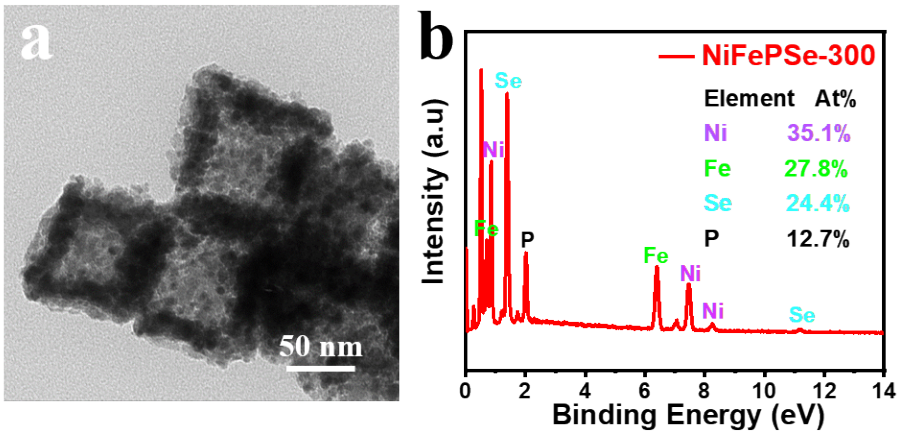

Fig. S13 (a) Representative TEM image and (b) the SEM-EDS spectrum of hollow NiFePSe-300 nanocages.

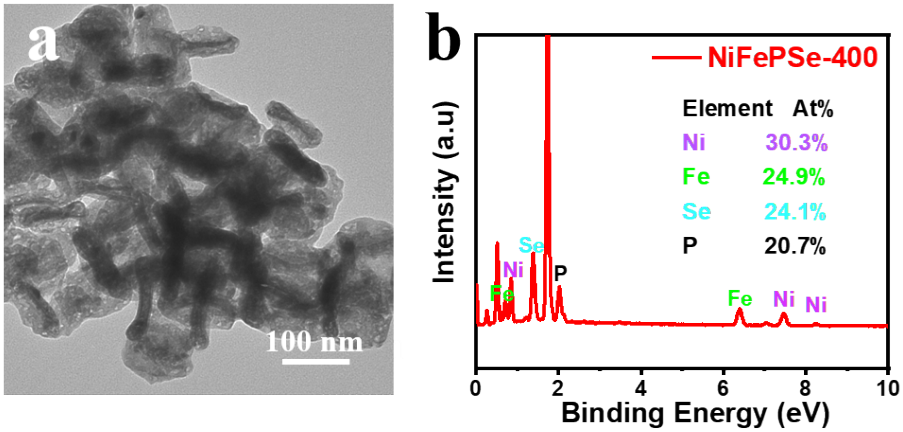

Fig. S14 (a) Representative TEM image and (b) the SEM-EDS spectrum of hollow NiFePSe-400 nanocages.

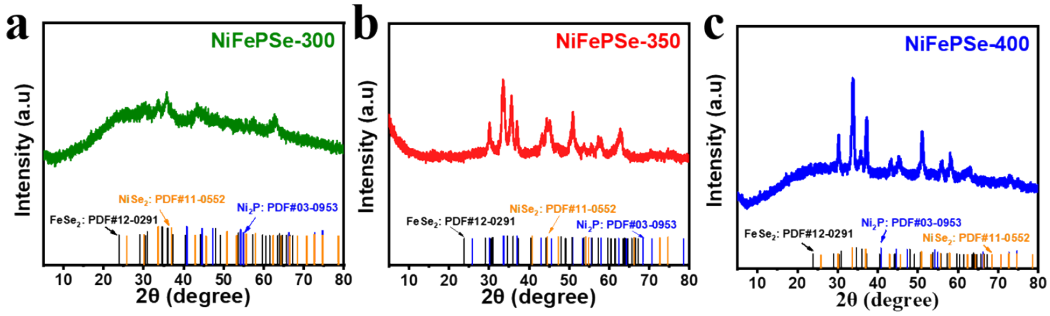

Fig. S15 XRD patterns of the (a) NiFePSe-300, (b) NiFePSe-350, and (c) NiFePSe-400.

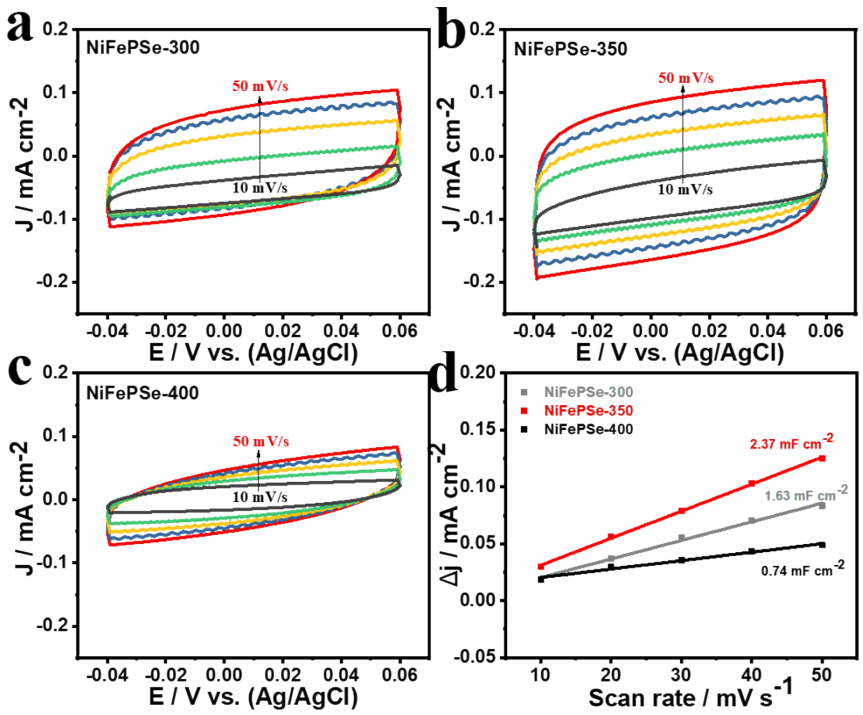

Fig. S16 CV curves of (a) NiFePSe-300, (b) NiFePSe-350, and (c) NiFePSe-400 in 1 M KOH electrolyte at different scan rates. (d) Double layer currents of different catalysts versus scan rate.

Tab. S1 EIS fitting parameters from equivalent circuits of samples during electrocatalytic process.

Samples	R_s / Ω cm^{-2}	R_1 / Ω cm^{-2}	CPE1 / S s^{-n}	n / 0<n<1	R_{ct} / Ω cm^{-2}	CPE2 / S s^{-n}	n / 0<n<1
NiFePSe	6.39	9.31	1.29E-2	0.95	1.14	4.50E-2	0.52
NiFeP	6.39	17.78	6.59E-3	0.95	3.17	2.62E-2	0.52
NiFeSe	6.09	30.20	3.10E-3	0.96	1.54	4.07E-3	0.64
NiFe-PBA	6.42	102.60	9.18E-3	0.82	5.38	7.67E-4	0.84