Electronic Supplementary information

In-situ Formation of Ni_3Se_4 Nanorod Array as a Versatile Electrocatalyst for Electrochemical Oxidation Reactions in Hybrid Water Electrolysis

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1. Material synthesis.

All chemical reagents were directly used without any further purification. The catalyst was synthesized by a one-step hydrothermal method. Specifically, 7.5 mmol selenium, 300 mg NaOH were added in a 100 mL Teflon-lined stainless autoclave, then 30 mL N,N-Dimethylformamide (DMF) and 0.28 mL 85% hydrazine hydrate was added. After stirring for 10 min, nickel foam (2 cm × 4 cm) was added. Then the mixture was heated at 180 ^{o}C for 6 h. After cooling down naturally, the product was washed with DI water and ethanol for three times respectively and dried at 60 ^{o}C for 24 hours.

2. Material Characterization.

Scanning electron microscopy (SEM) observation was carried out on JEOL JSM-7100F. Transmission electron microscopy (TEM) observation was performed on TecnaiG2 20 (Philips) at an accelerating voltage of 200 kV. The crystal phase was characterized by Empyrean (PANalytical B.V. with Cu-Kα radiation). The Raman spectroscopy was collected from LabRAM HR800. Inductively coupled plasma optical emission spectrometry (ICP-OES) was measured by Agilent ICPOES730. The X-ray photoelectron spectroscopy (XPS) experiment was implemented on a Kratos AXIS Ultra DLD-600W XPS system with a monochromatic Al Kα (1486.6 eV) X-ray source.

3. Electrochemical test.

All experiments were implemented in three-electrode system by AUTOLAB 302N electrochemistry workstation. Graphite rod and calibrated Ag/AgCl were used as counter electrode and reference electrode respectively. The following equation was used for conversion versus RHE: E (RHE) = E (Ag/AgCl) +0.195 V +0.059×pH. Linear sweep voltammetry (LSV) was tested 5 mV s^{-1} for the polarization curves. The mass loading of IrO_2 is 1 mg cm^{-2}. Electrochemical impedance spectroscopy (EIS) was collected at a frequency between 0.01 Hz and 100 KHz. Chronopotentiometry was implemented under a current density of 10 mA cm^{-2}. For electrochemically active surface area (ECSA) measurements, scan rates were 10, 20, 30, 40, 50, 60

mV s^{-1}. Oxygen evolution reaction (OER), urea oxidation reaction (UOR) and hydrazine oxidation reaction electrolysis were carried out in 1.0 M KOH, 1.0 M KOH with 0.1 M urea, 1.0 M KOH with 0.5 M hydrazine hydrate, respectively. The tested pH value (25 ^{o}C) of 1.0 M KOH, 0.1 M urea (in 1.0 M KOH), 0.5 M urea (in 1.0 M KOH), 0.1 M N_2H_4 (in 1.0 M KOH), and 0.5 M N_2H_4 (in 1.0 M KOH) was 14.02, 14.04, 14.05, 14.00, and 14.00, respectively.

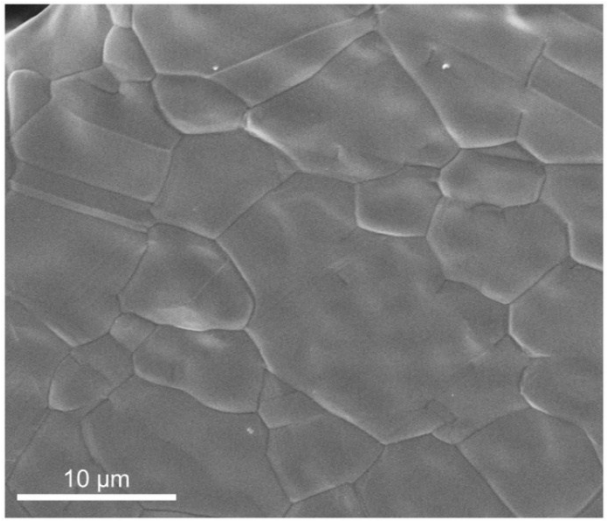

Figure S1. SEM image of nickel foam substrate.

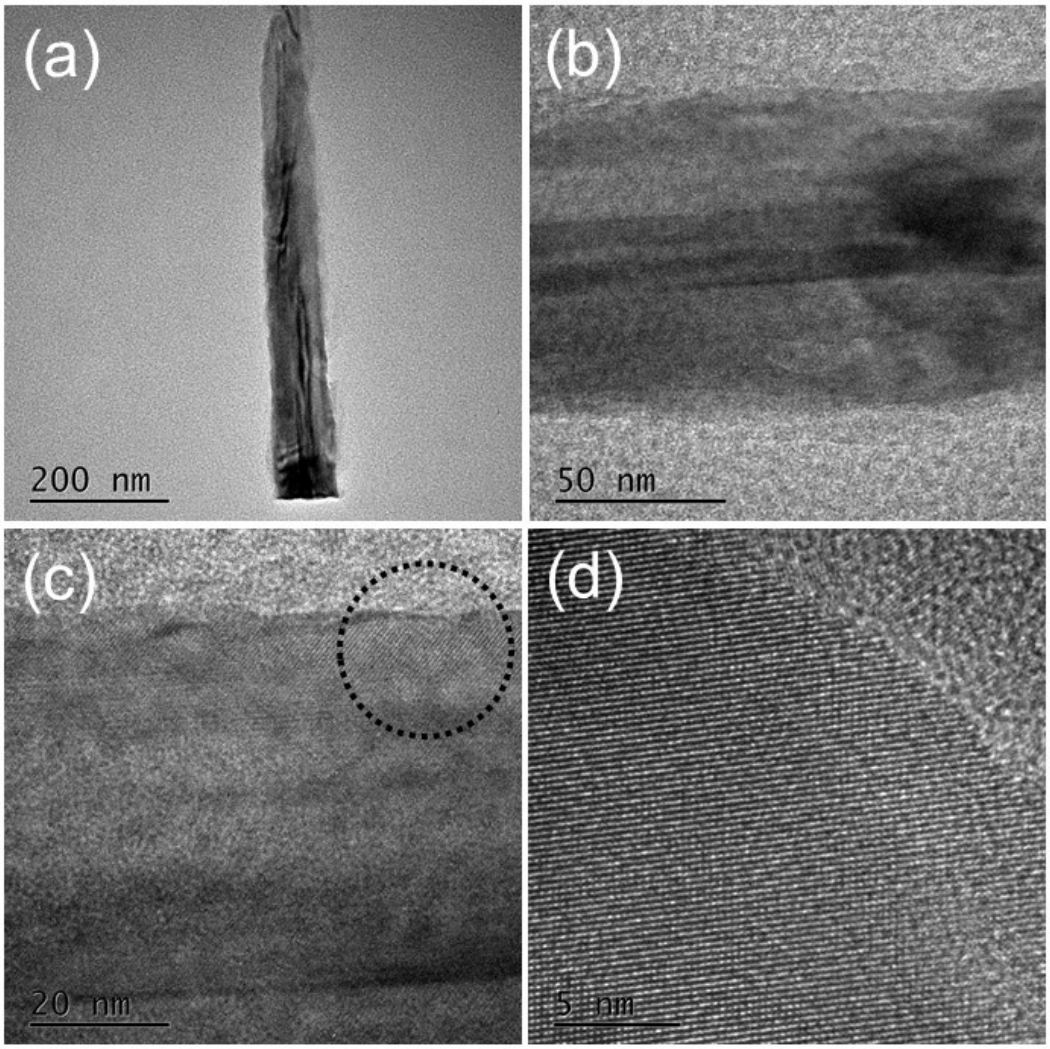

Figure S2. TEM images of Ni_3Se_4 nanorod. Figure 1e and Figure S2d is derived from the selected area (black circle) of Figure S2c.

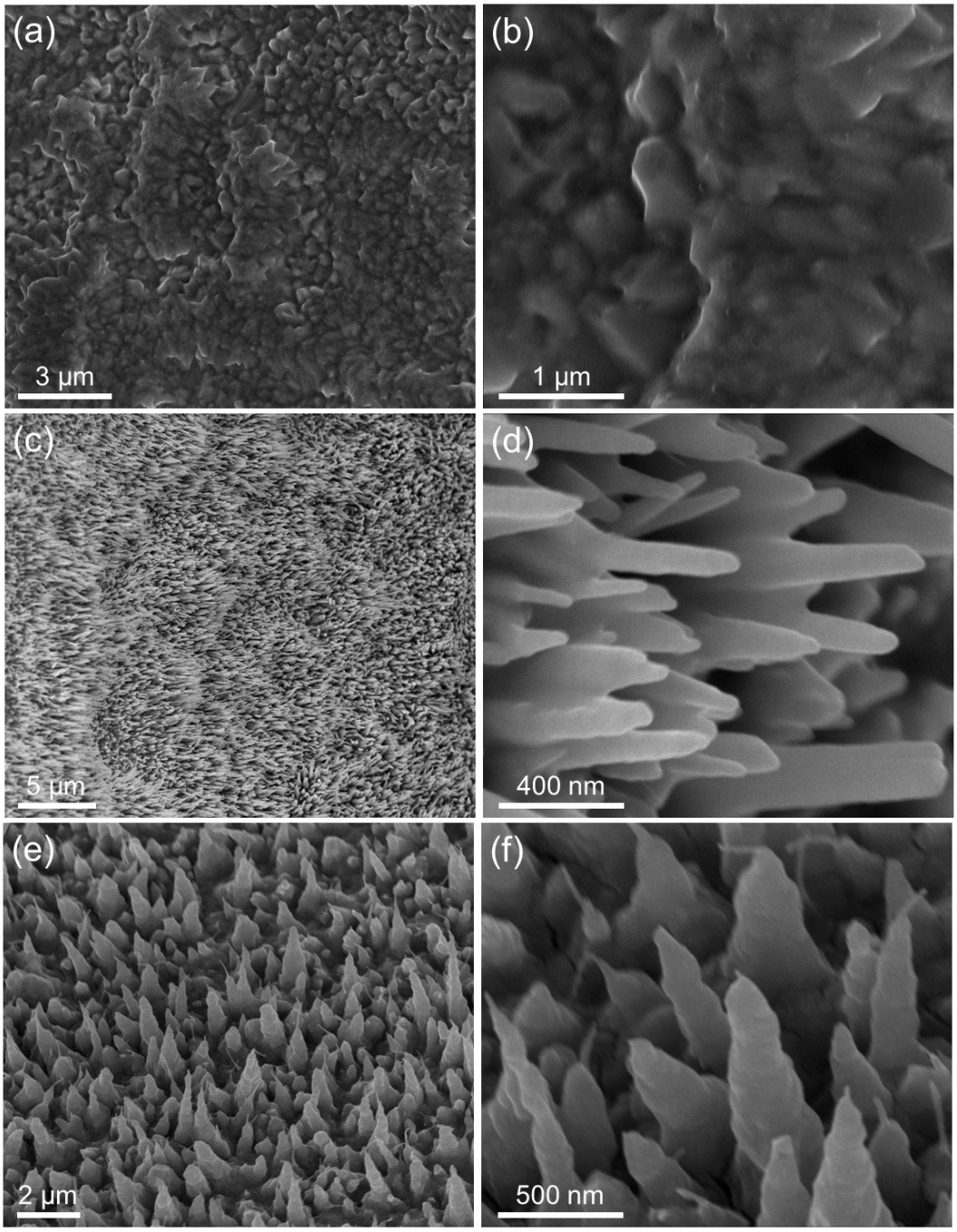

Figure S3. SEM images of different Se powder feeding ratio: a) and b) 3.75 mmol; c) and d) 7.5 mmol; e) and f) 11.25 mmol.

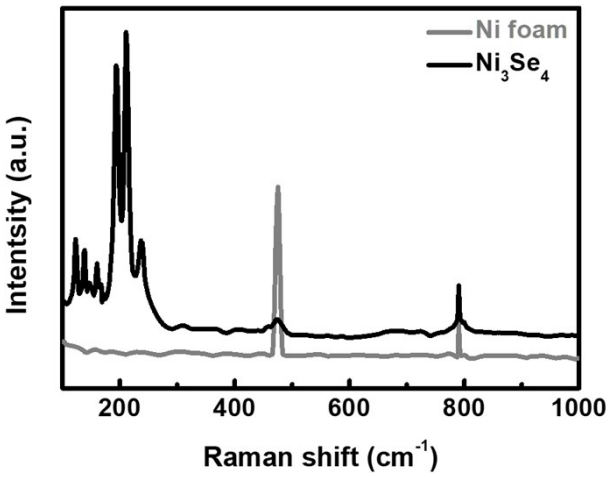

Figure S4. Raman spectrum of Ni_3Se_4 and Ni foam.

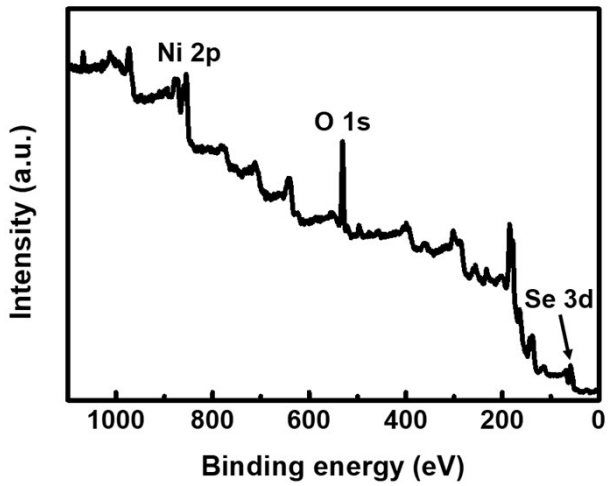

Figure S5. XPS survey spectrum of Ni_3Se_4 sample.

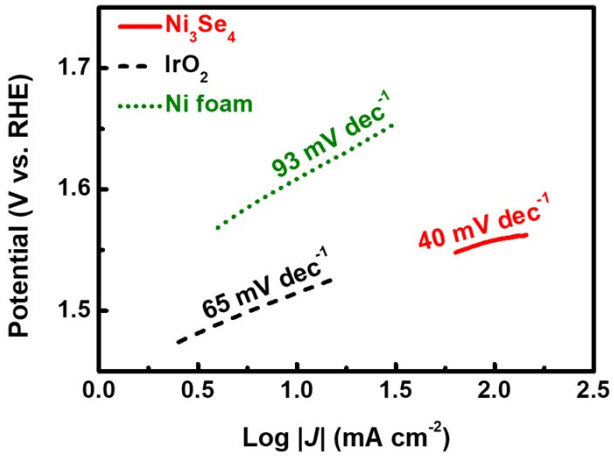

Figure S6. The corresponding OER Tafel slopes of Ni_3Se_4, Ni foam and IrO_2.

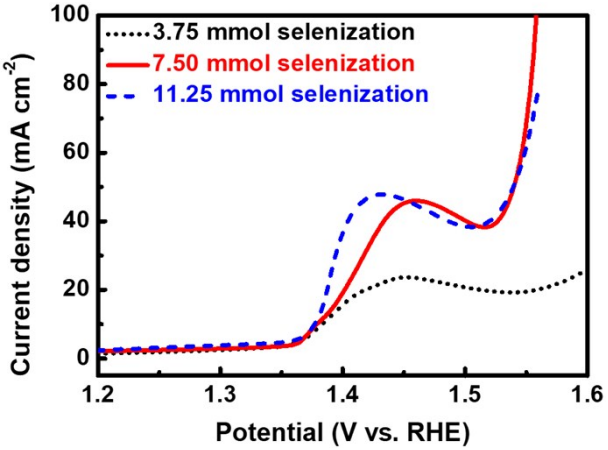

Figure S7. LSV curves of different production obtained with different selenium ratios.

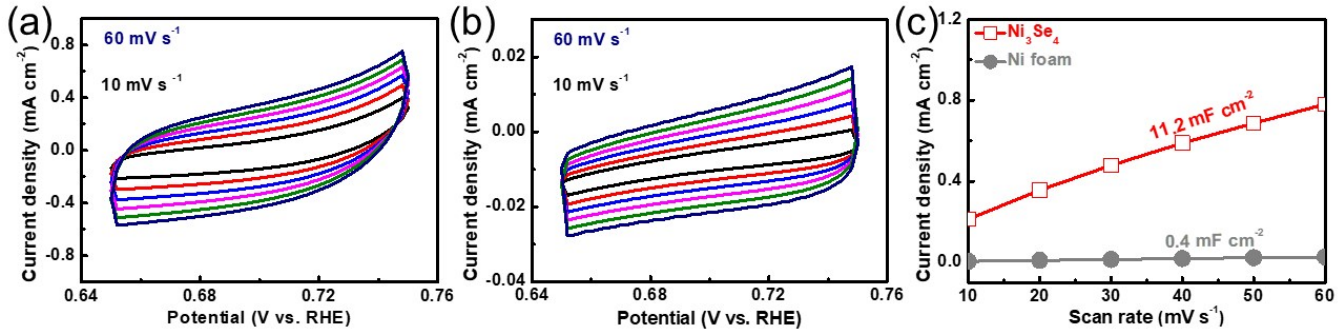

Figure S8. CV curves of (a) Ni_3Se_4 and (b) Ni foam from 10 mV s^{-1} to 60 mV s^{-1}, (c) Cdl comparison of Ni_3Se_4 and Ni foam.

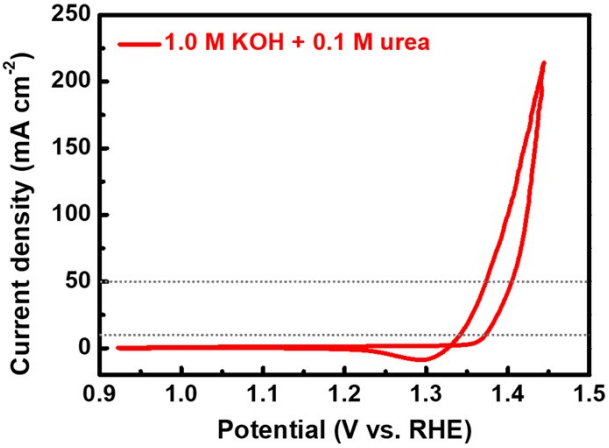

Figure S9. CV curve of UOR in 1.0 M KOH with 0.1 M urea.

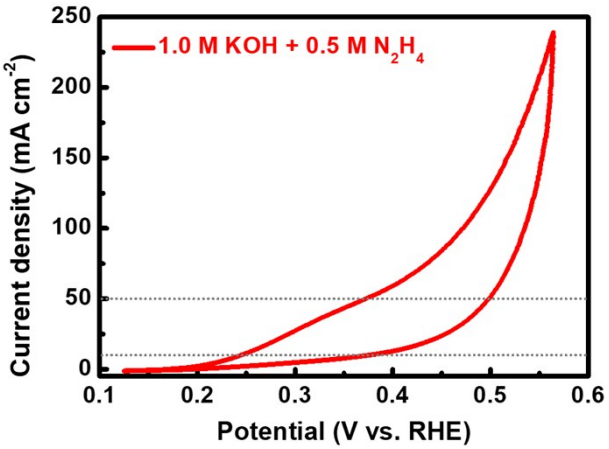

Figure S10. CV curve of HzOR in 1.0 M KOH with 0.5 M N_2H_4.

Table S1. OER activity of recent reported catalysts.

Catalysts	Electrolyte	Overpotential (η_{10})（mV）	Overpotential (η_{50})（mV）	Tafel slope (mV dec^{-1})	Reference
Ni_3Se_4 nanorod	**1 M KOH**	**243**	**309**	**40**	**This work**
NF@NC‐$CoFe_2O_4$/C NRAs	1 M KOH	240	--	45	*Adv. Mater.* **2017**, *29*, 1604437
Mn-Co oxyphosphide	1 M KOH	320	--	52	*Angew.Chem. Int. Ed.* **2017**, *56*, 2386
Fe_1Co_1-ONS	0.1 M KOH	308	--	36.8	*Adv. Mater.* **2017**, *29*, 1606793
A-$CoS_{4.6}O_{0.6}$-PNCs	1 M KOH	290	--	67	*Angew.Chem.Int .Ed.* **2017**, *56*,4858
$Ni_3FeAl_{0.91}$–LDH/NF	1 M KOH	304	--	57	*Nano Energy* **2017**, *35*, 350
CuO	1 M NaOH	290	--	64	*Angew.Chem.* **2017**, *129*,4870
N-CoFe LDHs	1 M KOH	281	--	40.03	*Adv. Funct. Mater.* **2018**, *28*, 1703363
Fe-doped NiOx	1 M KOH	310	--	49	*Nano Energy* **2017**, *38*, 167
Co/VN	1 M KOH	320	--	55	*Nano Energy* **2017**, *34*, 1

Table S2. UOR activity of different catalysts.

Catalysts	Electrolyte	Current density (mA cm^{-2})	Potential （V vs. RHE）	Durability (hours)	Reference
Ni_3Se_4 nanorod	**1 M KOH +0.1 M urea**	**10**	**~1.38**	**24**	**Present work**
$NiCo_2O_4$	1 M KOH + 0.33 M urea	136	~1.77	--	*Nanoscale*, **2014**, *6*, 1369
$Zn_{0.08}Co_{0.92}P$/TM	1 M KOH + 0.5 M urea	115	~1.62	--	*Adv. Energy Mater.* **2017**, *7*, 1700020
$Fe_{11.1\%}$–Ni_3S_2/Ni foam	1 M KOH + 0.33 M urea	10	~1.44	20	*J. Mater. Chem. A,* **2018**, *6*, 4346
M-$Ni(OH)_2$	1 M KOH + 0.33 M urea	~18	~1.48	18	*Angew. Chem. Int. Ed.* **2016**, *55*, 12465
NF-G-Mn	1 M KOH + 0.5 M urea	~8	~1.37	16	*Angew. Chem. Int. Ed.* **2016**, *55*, 3804
r-$NiMoO_4$	1 M KOH + 0.5 M urea	249.5	~1.62	--	*ACS Catal.* **2018***, 8,* 1
MnO_2/$MnCo_2O_4$@ Ni	1 M KOH + 0.5 M urea	10	~1.43	15	*J. Mater. Chem. A,* **2017**, *5*, 7825