Supporting Information

Porous FeNi Oxides Nanosheets as Advanced Electrochemical Catalysts for Sustained Water Oxidation

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Experimental details:

1. Chemicals: The reagents of ferrous nitrate (Fe(NO₃)₃·9H₂O), nickel chloride (NiCl₂·6H₂O), urea (CH₄N₂O), trisodium citrate acid (C₆H₅Na₃O₇·2H₂O) and ethanl (AR, 100%) are bought from Sinopharm Chemical Reagent Co., Ltd, AR. 5 wt% Nafion is bought from Sigma Aldrich, AR. All chemical reagents were used as received without further purification.

2. Synthesis of FeNi LDH ultrathin nanosheet precursor

FeNi LDH nanosheets were synthesized by a one-step hydrothermal method. In detail, 0.32 ml of 1 M ferrous nitrate ($Fe(NO_3)_3$) aqueous solution, and 1.28 ml of 1 M nickel chloride ($NiCl_2$) aqueous solution, were mixed in the beaker with 70.8 ml deionized (DI) water. Then 5.6 ml of 0.5 M urea aqueous solution ad 2 ml of 0.01 M trisodium citrate (TSC) were added into the beaker in sequence with magnetic stirring.

The mixed solution was transferred to a 100 ml Teflon lined stainless steel autoclave for hydrothermal reaction at 150 °C for 48 h. The FeNi-CO₃ LDH was collected by centrifuge, washed with DI water three times and then dried before use. The yield of the as-synthesized FeNi LDH is \sim 300 mg.

3. Synthesis of FeNi oxides (FeNi-O) porous nanosheets

The FeNi LDH precursor was heated in air with a heating rate of 2 °C/min and kept at 450 °C for 3 h before it was allowed to cool down to room temperature. The formed FeNi oxides were washed with DI water and centrifuged three times and then dried before use.

4. Sample preparation for electrochemical characterizations

5 mg of catalyst was dispersed in 1 ml of water-ethanol solution ($V_{water}/V_{ethanol}=48/50$), and then 20 µl of 5 wt% Nafion was added. The mixed solution was sonicated for 30 min to make the catalyst ink. Then 10 µl of the catalyst ink (containing 50 µg of catalyst) was loaded onto a glass carbon electrode with diameter of 5 mm (the loading of catalyst was 0.254 mg/cm²)

5. Electrochemical characterizations

Electrochemical studies were carried out in a standard three electrode system controlled by a CHI 660D electrochemical workstation. Catalysts loaded on glass carbon electrode (5 mm in diameter), platinum wire and Ag/AgCl electrode were used as the working electrode, counter electrode, and reference electrode, respectively. The reference was calibrated against and converted to revisable hydrogen electrode (RHE).

Cyclic voltammetry (CV) tests were carried out at a scan rate of 10 mV/s for ~100 times until a stable CV curve was achieved before measuring the OER performance of the catalysts. The scan rates for linear sweep voltammetry (LSV) and Tafel plots were 5 mV/s and 1 mV/s, respectively. All LSV curves were 95% iR-corrected to avoid the influence of electrolyte resistance.

Chronopotentiometry (CP) tests were carried out under constant current densities of 5 mA/cm², 10 mA/cm², and 20 mA/cm², respectively.

6. Structure and morphology characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) samples were prepared by drop-drying the aqueous suspensions onto silicon wafer, and were characterized by SEM Hitachi S-4800.

Transmission electron microscopy (TEM) samples were prepared by drop-drying the catalysts suspensions onto copper grids and were analyzed by FEI Technai G20.

Atomic force microscopy (AFM) samples were prepared by drop dry the catalysts suspensions onto a silicon water and was characterized by Veeco diInnova with a Si tip.

Energy dispersive X-ray spectroscopy (EDX) analysis results were collected both in SEM Hitachi S-4800 and FET Technai G20.

7. Other characterizations

X-ray diffraction (XRD) patterns were collected on Miniflex600;

X-ray photoelectron spectroscopy (XPS) spectra were collected on Thermo ESCALAB 250XI.

Brunar-Emmett-Teller (BET) surface areas and N_2 adsorbing-desorbing isotherms were recorded on ASAP2020C+M, ASAP2020M surface area analyzer.

DFT calculations:

All of the calculations were performed with the CASTEP code in the Materials Studio, version 7.1 software package (Accelrys software Inc., San Diego, CA).^[S1] The DFT calculations were performed using a plane wave implementation^[S2] at the generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE) level.^[S3] Spin-polarized DFT + U theory was applied to correct the self-interaction errors for the strongly correlated electrons in Fe³⁺ and Ni²⁺.^{[S4-} ^{S6} The ionic cores are described by ultrasoft pseudopotentials to improve transferability and reduce the number of plane waves required in the expansion of the Kohn-Sham orbitals.^[S7,S8] The Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm is used to search the 6) supercells and exposed (200) facets were applied for the calculations. And the atomic ratio of Fe/Ni in FeNi-O model is 1/8. The atoms at the bottom two layers were kept fixed and the surface for reaction was divided by 15 Å of vacuum to avoid interactions. The structure and energy optimizations are based on the following points if not otherwise indicated: (1) an energy tolerance of 1×10^{-5} eV/atom; (2) a maximum force tolerance of 0.03 eV/Å; and (3) a maximum displacement tolerance of 1×10^{-3} Å. A Fermi smearing of 0.1 eV and Pulay mixing are used to ensure the fast convergence of the self-consistent electron density. [S10]



Figure S1. TEM (A, B) and HRTEM (C) images of FeNi LDH nanosheets. Due to the ultrathin nanosheet structure, the FeNi LDH nanosheets were twisted with lots of wrinkles (labeled with white arrows in C). The lattice fringes of 0.208 nm and 0.244 nm could be ascribed to the (018) and (015) facets of Fe-doped NiO.



Figure S2. SEM images of FeNi-O formed from the FeNi LDH nanosheet precursor in different magnifications showing the porous nanosheet structure.



Figure S3. TEM (A, B) and HRTEM (C-F) images of FeNi-O porous nanosheets. The lattice fringes of 0.239 nm, 0.146 nm, 0.204 nm could be ascribed to (111), (220), and (200) plane of Fe-doped NiO.



Figure S4. (A) Pore size distribution of FeNi-O porous nanosheets and FeNi LDH precursor. (B, C) N₂ adsorption-desorption isotherm curves of FeNi LDH precursor (B, red curve), FeNi-O porous nanosheets (B, blue curve), NiO (C, black curve) and Ni(OH)₂ (C, red curve).



Figure S5. Energy dispersive X-ray spectroscopy (EDX) analysis of the FeNi LDH precursor. (A) SEM image, (B) O mapping, (C) Ni mapping, (D) Fe mapping.



Figure S6. EDX analysis of the FeNi-O porous nanosheets. (A) SEM image, (B) O mapping, (C) Ni mapping, (D) Fe mapping.



Figure S7. AFM topological image (A) and corresponding height profile (B) showing that the thickness of FeNi-O porous nanosheet is less than 1.5 nm.



Figure S8. SEM images of NiO porous nanosheets.



Figure S9. XPS spectra of (A) FeNi-O and (B) NiO at the O 1s spin orbital region.



Figure S10. XPS spectra of Ni 2p spin orbitals in (A) FeNi LDH and (B) FeNi-O. the blue, green, and yellow fitting curves represent Ni2+, Ni3+, and satellites, respectively.



Figure S11. XPS spectra of Fe 2p spin orbitals region in (A) FeNi-O and (B) FeNi LDH, respectively.



Figure S12. Raman spectra of NiO (red spectrum) and FeNi-O (black spectrum) porous nanosheets.



Figure S13. Fitted Raman spectra of (A) NiO and (B) FeNi-O porous nanosheets.



Figure S14. ECSA tests of FeNi LDH and NiO nanosheets by a simple CV method. CV curves of (A) FeNi LDH and (B) NiO nanosheets on OER at different scan rates of 10, 20, 30, 40, and 50 mV/s.



Figure S15. EDX spectroscopy of FeNi-O porous nanosheets.



Figure S16. DFT model of FeNi-O. (A) side view, (B) perspective view, and (C) top view. The green, orange, red spheres represent nickel, iron, and oxygen atoms, respectively.

refs	catalysts	η (onset)/mV	η (j ₁)/mV	b/(mV/dec)	Working electrode
	FeNi-O	200	213	32	
This	FeNi LDH	213	227	38	CC
work	NiO	336	362	53	60
	Ni(OH) ₂	333	362	62	
S11	RuO ₂	250		69	GC
	Exfoliated CoCo LDH	353	394	45	
S12	Exfoliated NiCo LDH	334	390	41	GC
	Exfoliated NiFe LDH	302	350	40	
	IrO ₂	338		47	
S13	NiFeO _x	350			Carbon aloth
	NiCoO _x	380			Carbon cloth
S14	NiFe LDH/CNT	270	290 (5 mA/cm ²)	35	CFP (0.1 M KOH)
S15	Ni _{0.9} Fe _{0.1} O _x	297 (1mA/cm ²)	336	30	Au/Ti QCM crystal; ITO
	Ni _{0.5} Co _{0.5} O _x	$320 (1 \text{mA/cm}^2)$		35	
	Ni _{0.25} Co _{0.75} O _x	$340 (1 \text{mA/cm}^2)$		36	
	Ni _{0.75} Co _{0.25} O _x	$312 (1 \text{mA/cm}^2)$		33	
S16	NiCoO _x	260	340	39	Cr/Au coated glass
S17	FeNi ₁₀ LDH	$220 (2 \text{ mA/cm}^2)$	242	55	C
	FeNi ₉ Co LDH	$210(2 \text{ mA/cm}^2)$	232	52	Ni foam
	FeNi ₈ Co ₂ LDH	$200 (2 \text{ mA/cm}^2)$	220	42	
S18	Porous FeNi oxide		328	42	GC (0.1 M KOH)

Table S1. Summary of the catalytic performance of FeNi-O, FeNi LDH, NiO, and Ni(OH)₂ on OER in this work as well as the comparison with the previously reported Fe, Co, Ni based catalysts. η , j and b represent overpotential, current density and Tafel slope, respectively. η (onset) and η (j₁) indicate the onset overpotential and the overpotential at 10 mA/cm², and the OER performance was collected in 1M KOH if not otherwise indicated.

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