Supporting information

for

Nickel doped iridium echinus-like nanosheets for stable acidic water splitting

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Experimental section

Materials: All reagents mentioned were obtained directly without further processing: Iridium trichloride(IrCl₃, 99%) was supplied by Shanxi KaiDa chemical engineering Co., Ltd, Polyvinyl-pyrrolidone(PVP, K29~K32, Average Mw~58000) was purchased directly from MACKLIN reagent Company, Citric acid (CA, 99%), Nickel chloride(NiCl₂, 98%), benzyl alcohol (C₇H₈O, 99%) and glyoxal (C₂H₂O₂, 99%) were all obtained from Sinopharm reagents. Deionized water used in the experiment (resistivity \geq 18.25 MΩ) was obtained from ULUPURE.

Synthesis of Ir-ENS and NiIr-ENS: The samples in the experiment were obtained by a one-step liquid-phase reduction method. Firstly, IrCl₃ (7.5 mg), PVP (100 mg), CA (48 mg) were weighed and transferred to benzyl alcohol (6 mL) containing glyoxal (0.2 mL) at room temperature with a stirring rate of 1000 rpm s-1 for more than 30 min and then transferred to an autoclave of polytetrafluoroethylene (10 mL), which was heated up from room temperature to 200 °C within 60 min and held for 5 h. Ir-NS was obtained by centrifugation after cooling to room temperature and washing with a mixture of ethanol and water (3/7 vol.) for more than 3 times. The preparation method of NiIr-ENS is identical to that of Ir-ENS, except for the addition of NiCl₂ (3 mg) as a precursor. In particular, the XRD and XPS project tests were characterized by mixing the obtained sample with carbon black (XC72).

Fundamental characterizations: Material surface morphology and crystal structure were obtained by field emission scanning electron microscopy (SEM, HitachiSU8010) and transmission electron microscopy (TEM, Thermo Fisher Scientific F200x, United States). The physical phases of the electrocatalysts synthesized by X-ray diffraction (XRD, Bruker AXS D8-Focus, Germany) in the range of 5-90° were examined using Cu-K α radiation. X-ray photoelectron spectroscopy (XPS) was performed using Thermo-Scientific K- α equipment.

Electrochemical measurements: Ink was obtained by ultrasonicating the freshly synthesized catalyst (2 mg) and carbon black (2 mg) dispersed in solution (780 μ L deionized water, 200 μ L isopropanol and 20 μ L Nafion (5 wt%)) for more than 0.5 h. The 10 μ L of ink was coated on a glassy carbon electrode (GCE, d=3 mm) to obtain a working electrode, and electrochemical tests were performed at room temperature (25 °C) using a Gamry (Interface 1000E, USA) equipment using a three-electrode system (a carbon rod as the counter electrode and an Hg/HgCl as the reference electrode).

The 0.5 M H₂SO₄ solution was used for the electrochemical electrolyte and the solutions were saturated with N₂ for 30 min prior to the HER or overall water-splitting test or with O₂ prior to the OER test. The linear sweep voltammetry (LSV) curves were recorded with a scan rate of 5 mV s⁻¹, Cyclic Voltammetry (CV) was carried out with a scan rate of 50 mV s⁻¹. The electrochemical double-layer capacitance was measured at different scan rates from 10 to 100 mV s⁻¹, EIS was measured from 100 kHz to 0.01 Hz under AC voltage amplitude of 5 mV and DC voltage based at a given potential at 10 mA cm⁻². The long-term stability was measured by chronoamperometric (i-t) stability examination at a given potential. A two-electrode system for the water-splitting with the catalysts loading of 0.285 mg cm⁻² onto GCE

and used as both the anode and cathode. All potential were converted to the reversible hydrogen electrode (RHE) based on the equation: E (RHE)=E (Hg/HgCl) + 0.241 + 0.0591*pH.

DFT calculations: All DFT calculations were performed using Vienna Ab Initio Simulation Package (VASP) in a spin-polarized mode. The exchange–correlation effect was estimated by Generalized Gradient Approximation Perdew–Burke– Ernzerhof (GGA-PBE) functionals. A plane wave basis with a cut off energy of 550 eV was used to expand the Kohn-Sham wave functions. Convergence criteria for geometry structures were set to be that residual energy and force were below 10⁻⁵ eV and -0.02 eV/ Å respectively. 3×3×1 gamma centered k-point grid was used to sample (111) surfaces. The top two layers of the surfaces were fully relaxed during structural optimization.

The energy (E (ads)) of each primitive step is defined as:

$$\Delta G (ads) = \Delta E_{DFT} + \Delta E_{ZPE} + T * \Delta S$$

among ΔE_{DFT} is the binding energy obtained by DFT, and the zero-energy correction difference ΔE_{ZPE} and T* ΔS is calculated by vibration analysis.

| Electrocatalyst | $\mathbf{\eta}_{10}$ | Potential@10 | Stability | Referenc |
|------------------------------------------------------|----------------------|--------------|-----------|-----------|
| | (mV, OER) | (V, WS) | (h, WS) | e |
| NiIr-ENS | 224 | 1.548 | >40 | this work |
| P-IrCu _{1.4} NCs | 311 | 1.55 | 10 | 1 |
| np-IrCr | 252 | 1.56 | 24 | 2 |
| SrRu _{0.5} Ir _{0.5} O ₃ | 1185 | 1.50 | 24 | 3 |
| IrOx/ATO | 440 | 1.73 | 15 | 4 |
| Ir-Co ₃ O ₄ | 236 | - | 30 | 5 |
| IrM NPNWs | 283,295,302 | - | 3.3 | 6 |
| 3%IrOx/NCNT | 241 | 1.487 | 12 | 7 |
| Ir WNWs | 270 | 1.62 | 11 | 8 |
| IrNi NCs | 280 | 1.58 | 1 | 9 |
| IrNi TL/C | 348 | - | 13 | 10 |
| 67%Ni-Ir | 310 | 1.63 | - | 11 |
| Co-IrCu ONC/C | 293 | 1.59 | 16 | 12 |
| Co-RuIr | 235 | 1.52 | 25 | 13 |

Table S1 Comparison of electrochemical performance of Ir-basedelectrocatalysts tested in acidic electrolyte.



Figure S1. XPS survey scan of NiIr-ENS and Ir-ENS.



Figure S2. Mass activities of Ir-ENS, NiIr-ENS and IrO_2 (@1.55 V vs. RHE).



Figure S3. OER performance of single active of Ir-ENS, NiIr-ENS and IrO_2 (@1.53 V vs. RHE).



Figure S4. Double-layer capacitance of Ir-ENS and NiIr-ENS.



Figure S5. EIS spectrum of Ir-ENS and NiIr-ENS (OER).



Figure S6. Tafel slopes of commercial lrO₂, Ir-ENS and NiIr-ENS.



Figure S7. Electrochemical impedance spectroscopy and related doublelayer capacitance of NiIr-ENS electrocatalyst before and after OER cycle stability test (3k).



Figure S8. Tafel slopes of NiIr-ENS before and after 3000 cycles.



Figure S9. OER performance of Ir-ENS electrocatalyst before and after OER cycle stability test (1k).



Figure S10. OER performance of commercial IrO_2 electrocatalyst before and after OER cycle stability test (1k).



Figure S11. OER performance of NiIr-ENS before and after CA test.



Figure S12. Mass activities of Ir-ENS, NiIr-ENS and commercial Pt/C (20%) (@-0.1 V vs. RHE).



Figure S13. CV curves and related double-layer capacitances of Ir-ENS, NiIr-ENS and commercial Pt/C.



Figure S14. EIS spectrum of of Ir-ENS and NiIr-ENS (HER).



Figure S15. HER performance of single active and Tafel slopes of Ir-ENS, NiIr-ENS and Pt/C.



Figure S16. CV curves and double-layer capacitance of NiIr-ENS electrocatalyst before and after HER cycle stability test (5k).



Figure S17. EIS spectrum of NiIr-ENS electrocatalyst before and after HER cycle stability test (5k).



Figure S18. Tafel slope of NiIr-ENS before and after 5000 cycles.



Figure S19. HER performance of Ir-ENS electrocatalyst before and after HER cycle stability test (5k).



Figure S20. EIS spectrum and C_{dl} of Ir-ENS electrocatalyst before and after HER cycle stability test (5k).



Figure S21. HER performance of commercial Pt/C electrocatalyst before

and after HER cycle stability test (2k).



Figure S22. HER performance of NiIr-ENS before and after CA test.



Figure S23. XRD patterns and TEM images of NiIr-ENS electrocatalyst after WS-CA test (40 h).



Figure S24. Deconvoluted Ir 4f, Ni 2p, surface element content of NiIr-ENS electrocatalyst after WS-CA test (40 h).



Figure S25. Chemical structure states of intermediates during the adsorption of OER by Ir(111) and NiIr.

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