

# Binary Nickel-iron Nitride Nanoarrays as Bifunctional Electrocatalysts for Overall Water Splitting†

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## Experimental section

### Synthesis of Fe<sub>2</sub>Ni<sub>2</sub>N nanoplate arrays on Ni foam:

All of the chemicals were of analytical grade and used without any further purification. Fe<sub>2</sub>Ni<sub>2</sub>N nanoplate arrays was synthesized by the following steps. Firstly, a piece of nickel foam (approximately 2 cm×3 cm, the pore size of the nickel foam we used is around 0.2~0.4 mm with a Pores Per Linear Inch (PPI) value of 110) was cleaned by concentrated HCl solution, ethanol and distilled water with assistance of ultrasonication for several minutes. Afterward, the purified Ni foam was put against the wall of a Teflon lined stainless steel autoclave which contained a homogeneous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1 mmol), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (1 mmol), CO(NH<sub>2</sub>)<sub>2</sub> (10 mmol) and 36 ml distilled water. Then the autoclave was sealed and maintained at 120°C for 12 h to synthesize Ni-Fe layered double hydroxides nanoplate arrays. After the hydrothermal reaction, the sample was taken out and rinsed several times with distilled water and ethanol with the assistance of ultrasonication, and dried at 80°C for 3h. The precursor was then calcinated in a tube furnace to 380°C with a rate of 5°C min<sup>-1</sup> under a flowing NH<sub>3</sub> atmosphere. After reacting for 2 h, the sample was subsequently cooled to ambient temperature in the ammonia flow. The obtained Fe<sub>2</sub>Ni<sub>2</sub>N nanoplate arrays were denoted as Fe<sub>2</sub>Ni<sub>2</sub>N NPAs.

### Synthesis of NiFe-based oxide nanoplate arrays on Ni foam:

The NiFe-based oxide nanoplate arrays were obtained from NiFe layered double hydroxides nanoplate arrays by a calcination treatment. The NiFe-based precursor nanoplates were placed in the tube furnace. The furnace was heated to 400°C with a

rate of  $10^{\circ}\text{C min}^{-1}$  in air and maintained for 3 h. Then the final products were collected as contrast samples.

### **Synthesis of $\text{Ni}_3\text{N}$ nanoplate arrays on Ni foam:**

The  $\text{Ni}_3\text{N}$  nanoplate arrays were obtained from nickel hydroxide nanoplate arrays by a calcination treatment in a  $\text{NH}_3$  atmosphere. The nickel hydroxide nanoplate arrays were synthesized following our previous report<sup>[1]</sup>. Then the precursor was calcinated in a tube furnace to  $380^{\circ}\text{C}$  with a rate of  $5^{\circ}\text{C min}^{-1}$  under a flowing  $\text{NH}_3$  atmosphere and maintained for 2 h. The final products were also collected as contrast samples.

### **Characterizations:**

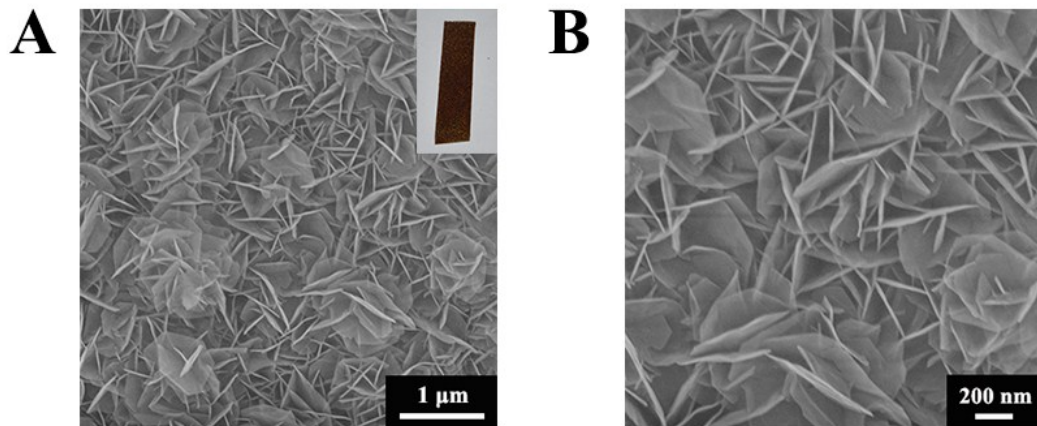
X-ray powder diffraction patterns were recorded on an X-ray diffractometer (Rigaku D/max 2500) at a scan rate of  $10 (^{\circ})/\text{min}$  in the range from  $20$  to  $90^{\circ}$ . The size and morphology of the samples were characterized using a field-emission SEM (JEOL JSM6335) operating at 20 kV and a TEM system (H800) operating at 200 kV. High resolution transmission electron microscopy (HRTEM) measurements were carried out using a JEOL JEM 2100 system operating at 200 kV. X-ray photoelectron spectra (XPS) were carried out by using a model of ESCALAB 250 and LabRAM Aramis.

### **Electrochemical measurements:**

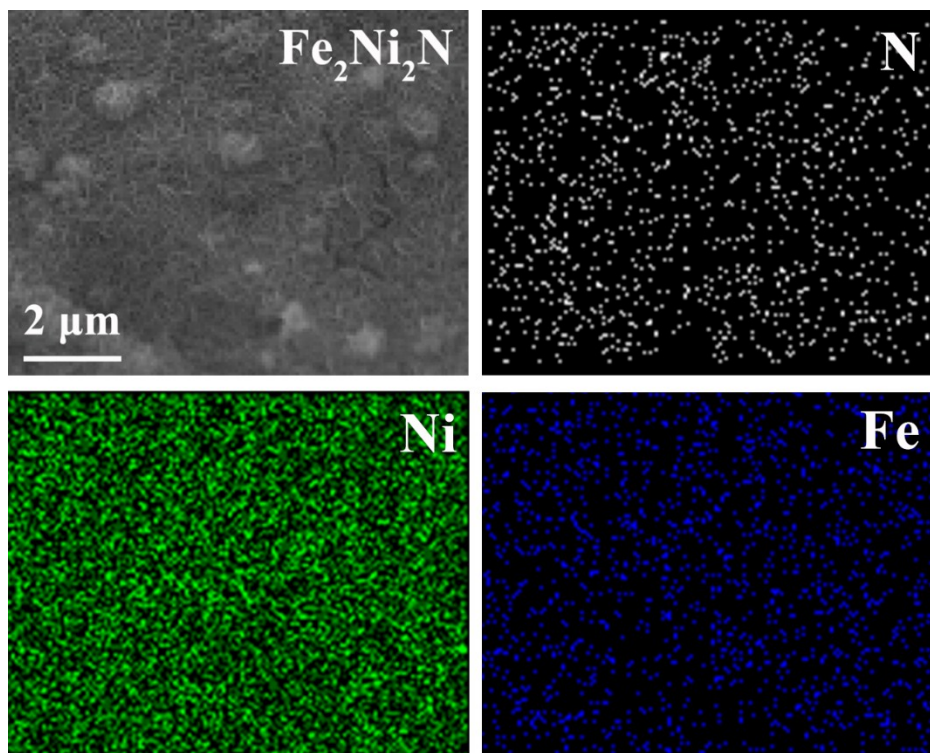
The electrochemical measurements were carried out at room temperature in a three-electrode glass cell connected to an electrochemical workstation (CHI 660D, chenghua, shanghai.). A platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Freshly prepared 1 M KOH aqueous solution was used as the electrolyte. The electrolyte was saturated by hydrogen (for HER) or oxygen bubbles (for OER) before and during the experiments. Polarization curves were obtained using LSV with a scan rate of  $1 \text{ mV/s}$ . All polarization curves were corrected for an ohmic drop tested by impedance spectroscopy. The long time durability test was performed using the controlled potential electrolysis method without  $iR$  correction. The electrochemical impedance spectroscopy was obtained by AC impedance spectroscopy in 1 M KOH solution at open circuit voltage from  $10^5$ -0.1 Hz with an AC voltage of 5 mV to measure the system resistance.

The water splitting catalyst electrolyzer was fabricated with a two-electrode cell, with the same electrode ( $\text{Fe}_2\text{Ni}_2\text{N}$  NPAs) as the anode and cathode in 1 M KOH solution. Polarization curves were obtained using LSV with a scan rate of 1 mV/s. The long-time durability test was performed using controlled potential electrolysis. All data for the two electrode electrolyzer was recorded without iR correction. In all measurements, we used saturated calomel electrode (SCE) as the reference. It was calibrated with respect to reversible hydrogen electrode (RHE) by using Pt electrode as standard electrode. All the potential reported in our manuscript are against RHE.

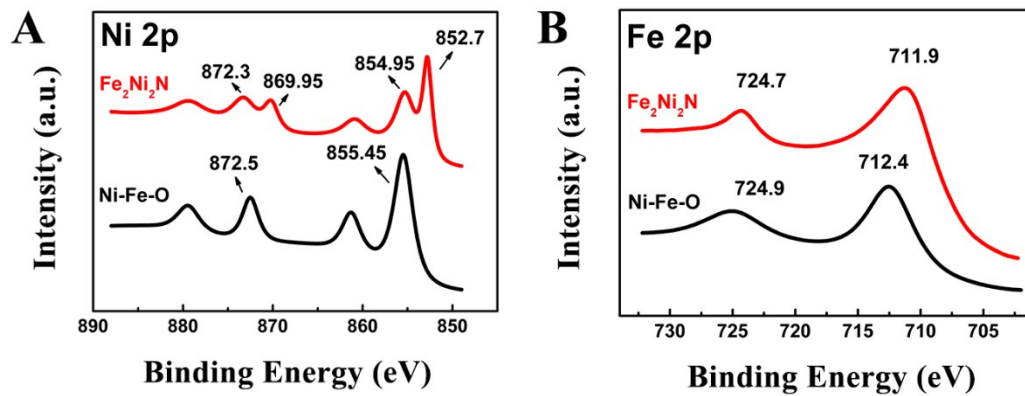
## Figures



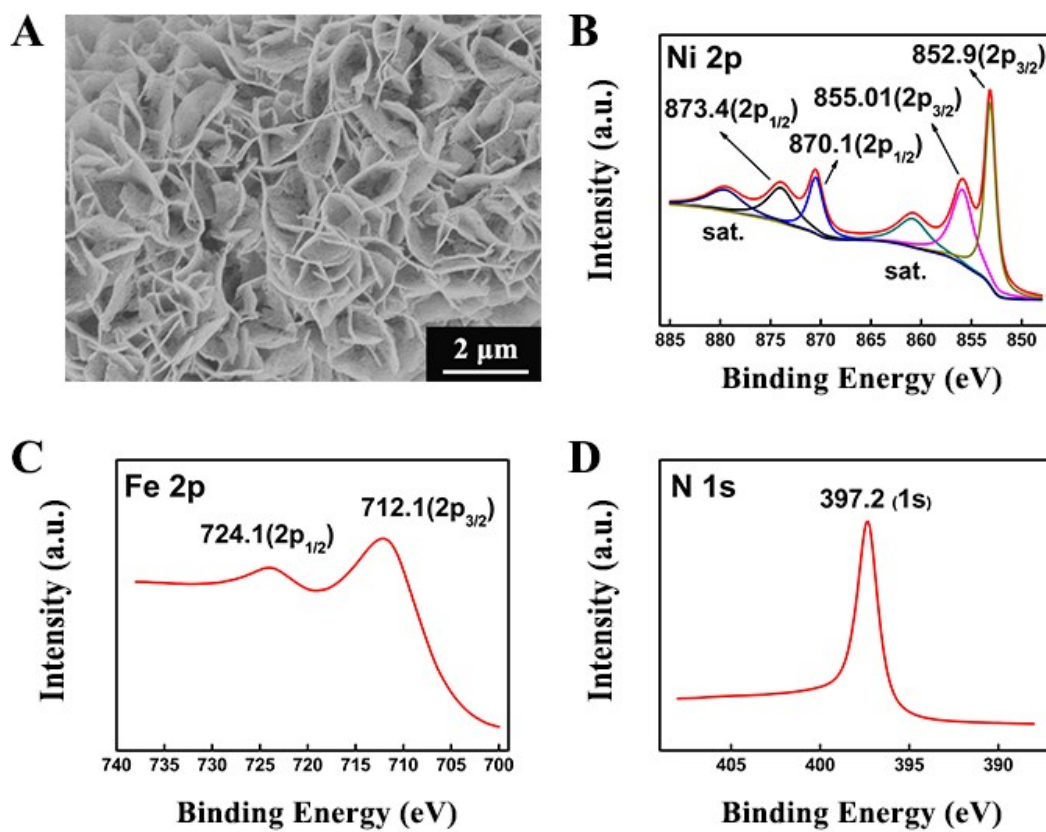
**Figure S1.** (A, B) SEM images of NiFe-based oxide nanoplates at different magnifications, the inset is the optical image.



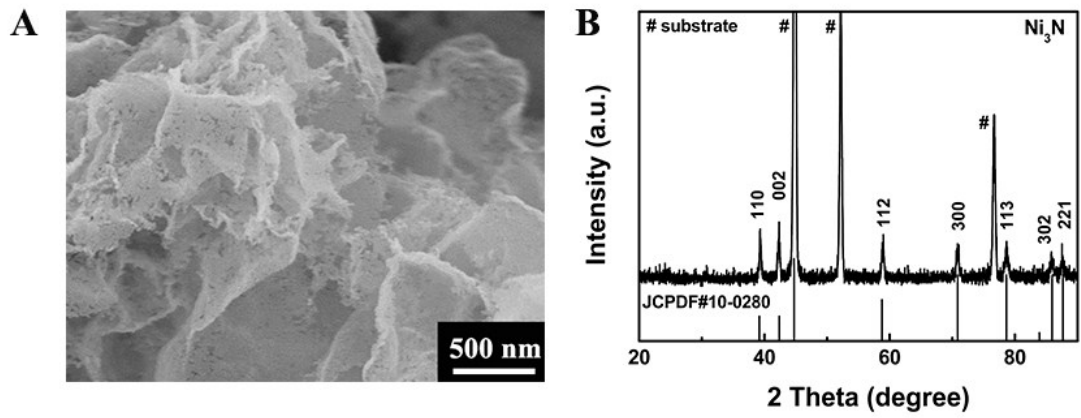
**Figure S2.** EDX mapping results of  $\text{Fe}_2\text{Ni}_2\text{N}$  NPAs film.



**Figure S3.** XPS spectra of the (A) Ni 2p (peaks at 872.3eV, 869.95eV, 872.5eV represent Ni 2p<sub>1/2</sub> in Fe<sub>2</sub>Ni<sub>2</sub>N and Ni-Fe-O, respectively; peaks at 854.95eV, 852.7eV, 855.45eV represent Ni 2p<sub>3/2</sub> in Fe<sub>2</sub>Ni<sub>2</sub>N and Ni-Fe-O, respectively). (B) Fe 2p regions of the Fe<sub>2</sub>Ni<sub>2</sub>N NPAs and NiFe-based oxide nanoplates (peaks at 724.7eV, 724.9eV represent Fe 2p<sub>1/2</sub> in Fe<sub>2</sub>Ni<sub>2</sub>N and Ni-Fe-O, respectively; peaks at 711.9eV, 712.4eV represent Fe 2p<sub>3/2</sub> in Fe<sub>2</sub>Ni<sub>2</sub>N and Ni-Fe-O, respectively).

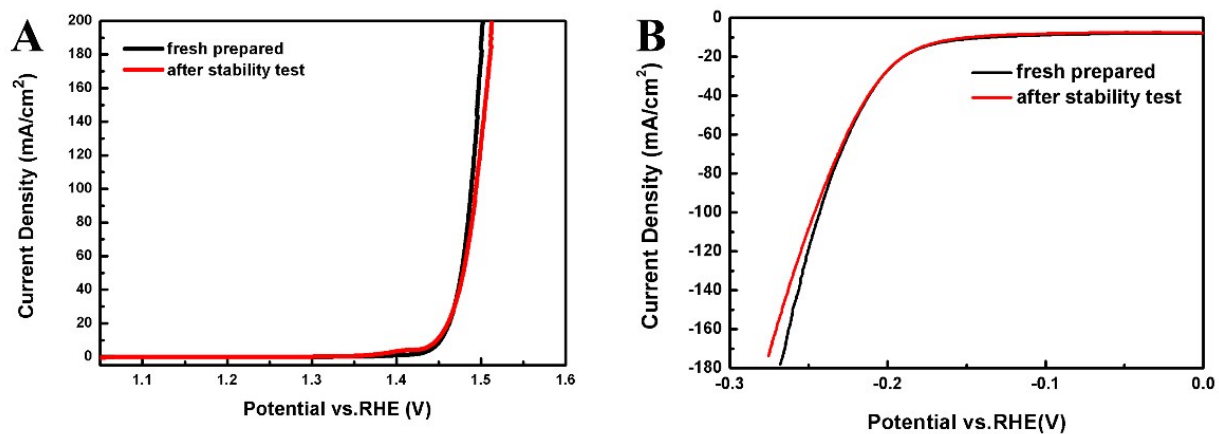


**Figure S4.** (A) SEM image and XPS spectra of the (B) Ni 2p, (C) Fe 2p, (D) N 1s peaks of the Fe<sub>2</sub>Ni<sub>2</sub>N NPAs grown on carbon fiber paper.

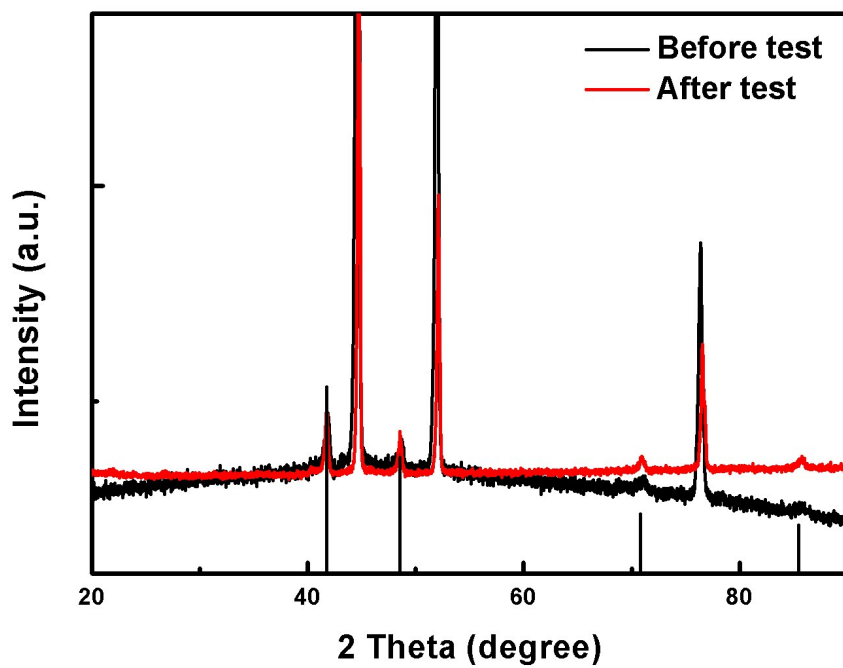


**Figure S5.** (A) SEM image and (B) XRD patterns of Ni<sub>3</sub>N nanoplate arrays on Ni foam.

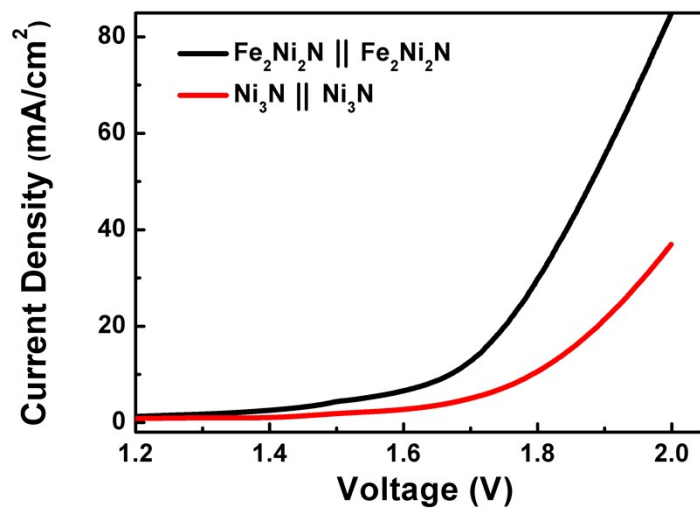




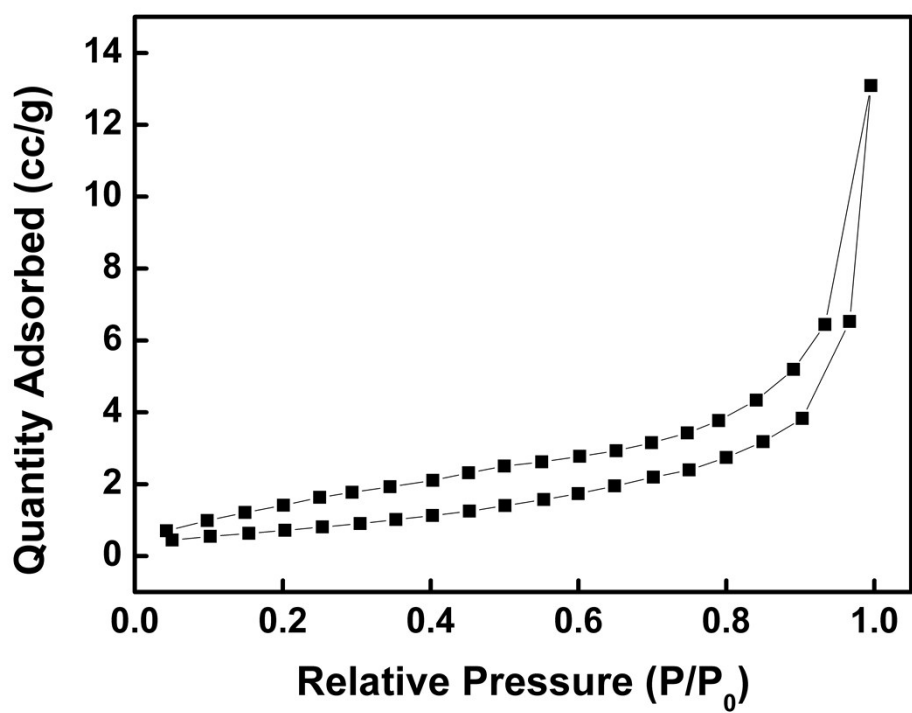
**Figure S6.** Polarization curves of Fe<sub>2</sub>Ni<sub>2</sub>N NPAs initially and after 10h stability test.



**Figure S7.** XRD patterns of Fe<sub>2</sub>Ni<sub>2</sub>N NPAs before and after test.



**Figure S8.** Polarization curve of Fe<sub>2</sub>Ni<sub>2</sub>N and Ni<sub>3</sub>N electrodes for the overall water-splitting reaction in 1 M KOH at 5 mV s<sup>-1</sup> (not iR corrected).



**Figure S9.** BET data of the Fe<sub>2</sub>Ni<sub>2</sub>N NPAs.

**Table S1.** Specific surface areas of pure Ni foam and Fe<sub>2</sub>Ni<sub>2</sub>N NPAs grown on Ni

foam, respectively.

| <b>Samples</b>                                    | <b>Specific Surface Area</b>         |
|---|--------------------------------------|
| Pure Ni foam                                      | 0.06 m <sup>2</sup> /cm <sup>2</sup> |
| Fe <sub>2</sub> Ni <sub>2</sub> N NPAs on Ni foam | 0.21 m <sup>2</sup> /cm <sup>2</sup> |

### **Reference:**

[S1] Z. Lu, Z. Chang, W. Zhu and X. Sun, *Chem. Commun.*, 2011, **47**, 9651–9653.