



# Bifunctional Iron–Nickel Nitride Nanoparticles as Flexible and Robust Electrode for Overall Water Splitting



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## ABSTRACT

The state-of-the-art and stable electrocatalysts with non-noble metal elements are exceedingly desirable for hydrogen/oxygen production from water splitting. Herein, three-dimensional (3D) iron–nickel nitride nanoparticles grown on carbon cloth (Ni<sub>3</sub>FeN-NPs) are developed as a flexible bifunctional electrocatalyst for overall water splitting. The as-prepared Ni<sub>3</sub>FeN-NPs show outstanding electrocatalytic activities toward both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in 1 M KOH solution, with low overpotentials of 238 and 241 mV at 10 mA/cm<sup>2</sup>, Tafel slopes of 46 and 59 mV/dec, respectively. Moreover, an advanced water electrolyzer based on the Ni<sub>3</sub>FeN-NPs electrodes as anode and cathode is assembled and could achieve overall water splitting with a cell voltage of 1.81 V at 10 mA/cm<sup>2</sup>. Also, the as-fabricated water electrolyzer exhibits stable electrocatalytic performance without decreasing in 1 M KOH after 130 h even at the foldable state.

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## 1. Introduction

Electrocatalytic water splitting is emerging as a promising approach to produce renewable and clean hydrogen fuel [1–3]. The benchmark catalysts for hydrogen evolution reaction (HER) are Pt-based compounds, while Ir/Ru-based compounds represent the best catalysts for oxygen evolution reaction (OER). However, their large-scale application is precluded by their scarcity and extremely high cost [4–6]. Consequently, considerable attentions have been devoted to the development of efficient and low-cost electrocatalysts based on non-noble metal elements for HER and OER [7,8]. In the past ten years, some cost-effective electrocatalysts have been explored for HER and OER, such as MoS<sub>2</sub> [4], MoB [9], FeP [10], NiCoB [11], NiMoN<sub>x</sub> [12] for HER, and layer double hydroxides (LDHs) that containing nickel [13], iron [14,15], cobalt [16], and their mingled metal oxide nanocomposites for OER

[17–32]. Concurrently, developing bifunctional electrocatalysts for OER and HER have attracted extensively interests, which could reduce the rate and simplify the overall water splitting system [33]. The essential challenge for bifunctional electrocatalysts is simultaneously to achieve a low overall overpotential and a high current density. To accomplish this aim, electrocatalysts which based on non-noble elements have been evaluated for overall water splitting [30,34–37]. However, it is still a challenge for developing bifunctional electrocatalysts with high activity and excellent durability.

Recently, transition metal nitrides based catalysts are highly attractive for OER and HER owing to their low-cost, earth-abundant and low electrical resistance and high electrocatalytic activity [38,39]. Also, bimetallic nitrides could enhanced water splitting activity by their appropriate surface of hydride acceptor sites and proton acceptor, valence and electronic states of the elements [15]. For example, nanostructured Ni–Fe nitrides prepared from thermal ammonolysis of NiFe-LDHs nanosheets could apparently improve the overall water splitting activities [40,41]. Lately, Zhang et al. reported a synthesis of iron–nickel nitride nanoparticles on Ni foam as a bifunctional electrocatalyst for overall water splitting [42]. Despite these progresses, the

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performance of these electrocatalysts is still needed to further boost. On the other hand, to adapt the complex environment for water splitting, flexible electrocatalysts grown on conductive substrates have received increasing interests since they can provide higher electrical conductivity and better mechanical properties compared to conventional powdered electrocatalysts.

In this work, we design three-dimensional (3D) Ni<sub>3</sub>FeN-NPs on carbon cloth as a bifunctional non-noble metal electrocatalyst with improved electrocatalytic activity for overall water splitting. Due to its high electrical conductivity, light weight and good mechanical properties, carbon cloth was chosen as electrode substrate. The unique 3D nanostructures could facilitate charge transfer and afford an intimate contact between active sites and reaction medium, enabling the obtained Ni<sub>3</sub>FeN-NPs delivered good electrocatalytic performance for water splitting. Impressively, the Ni<sub>3</sub>FeN-NPs exhibited high activities for both HER and OER, with low overpotentials of 238 and 241 mV at 10 mA/cm<sup>2</sup> and Tafel slopes of 46 and 59 mV/dec, respectively. Moreover, when used the Ni<sub>3</sub>FeN-NPs electrodes as both anode and cathode for overall water splitting, the electrolyzer only needed a cell voltage of about 1.81 V to achieve 10 mA/cm<sup>2</sup> and maintained its activity for 130 h even at the foldable state. The flexible design of the catalytic electrode holds great promising application to integrate into solar cells, which fulfils the future direction of environmental-friendly solar-driven hydrogen production [43,44].

## 2. Experimental Section

### 2.1. Preparation of Ni<sub>3</sub>FeN nanoparticles on carbon cloth

Firstly, NiFe-LDHs nanosheets grown on carbon cloth were obtained *via* a seed-assisted hydrothermal method. Typically, carbon cloth (2.0 cm × 3.0 cm) were cleaned with ethanol and dried at room temperature. 0.6 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 0.8 g Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved in ethanol (50 mL). Then, the carbon cloth was immersed into the above solution for 5 min and blow-dried with flowing air. The dried carbon cloth was further heated on a hotplate in ambient at 300 °C for 5 min, forming seeds on carbon cloth. 0.1314 g NiSO<sub>4</sub>·6H<sub>2</sub>O, 0.1390 g FeSO<sub>4</sub>·7H<sub>2</sub>O, 0.0706 g urea and 0.0196 g Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O were dissolved in distilled water (20 mL) and stirred into a pellucid solution. Then the resultant precursor solution and the seeded carbon cloth were transferred to a Teflon-lined stainless steel autoclave (25 mL). The sealed autoclave was heated and maintained at 150 °C for 12 h. After cooling down to room temperature, the carbon cloth were washed with distilled water and finally dried at 60 °C. The nitrified

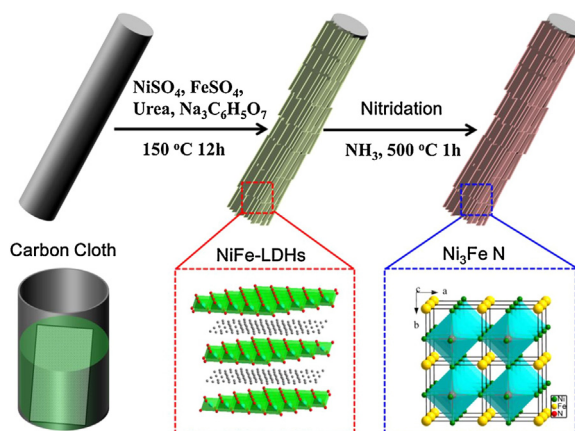
product was realized through thermal treatment of NiFe-LDHs nanosheets in ammonia atmosphere at 500 °C for 1 h. For comparison purposes after ammonia treatment of carbon cloth (CC+N) was synthesized in the same way without forming seeds and hydrothermal solution (20 ml distilled water).

### 2.2. Material characterizations

The phase compositions of the as-samples were measured by X-ray diffractometer (XRD, Rigaku, Japan) with Cu K $\alpha$  radiation and Raman Spectroscopy (Renishaw in Via). The morphologies of the samples were examined by field emission scanning electron microscope (FESEM, JSM-6330F). High resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and element-mapping images were observed by transmission electron microscopy (FEI Tecnai G<sup>2</sup> F30) equipped with energy dispersive spectroscopy. The valence states of elements of the materials were tested by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer ESCALAB 250, Thermo VG). The molar ratio of Fe and Ni elements of the Ni<sub>3</sub>FeN-NPs was detected by Inductively Coupled Plasma Optical Emission Spectrometer (ICP, Optima 8300, PerkinElmer, USA). The Brunauer Emmett Teller (BET) surface area was measured with an ASAP 2020 M (Micromeritics Instrument Corp.). For the BET measurement, carbon cloth substrates covered with NiFe-LDHs nanosheets and Ni<sub>3</sub>FeN-NPs are directly used for test.

### 2.3. Electrochemical measurements

The HER and OER electrochemical measurements were collected on a CHI 760D electrochemistry workstation. For carrying out the measurements, a typical three-electrode electrolyzer system was assembled, using Ni<sub>3</sub>FeN-NPs as the working electrode, a saturated Ag/AgCl electrode as the reference electrode and a graphite rod as the counter electrode. The overall water splitting was performed in a two-electrode system. Steady-state potential polarization curves were measured in 1 M KOH solution at 25 °C. Accelerated degradation measurement was conducted for 1000 cyclic voltammetry (CV) cycles in 1 M KOH solution at a scan rate of 100 mV/s, chronopotentiometry was also used to measure their life. Except for special command, all of the potentials and voltages are IR corrected. The impedance of the two-electrode overall cell is tested under 1.2 V to 2.5 V voltage. The electrochemical impedance spectroscopy (EIS) measurements were conducted over a frequency range 0.01–10<sup>6</sup> Hz with amplitude potential of 5 mV.



**Scheme 1.** Schematic of the synthesis process for Ni<sub>3</sub>FeN-NPs on carbon cloth.

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