



# In situ growth of iron-nickel nitrides on carbon nanotubes with enhanced stability and activity for oxygen evolution reaction

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## ABSTRACT

The efficiency of energy storage technologies such as water splitting and metal-air batteries is limited by the sluggish dynamics of the oxygen evolution reaction (OER). Herein, we report a galvanic replacement-mediated method for *in-situ* growth of iron-nickel nitride on carbon nanotubes (CNTs) as a powdery catalyst for OER. This *in-situ* grown structure creates intimate interaction between the active substance of Fe<sub>2</sub>Ni<sub>2</sub>N and CNTs so as to accelerate charge transfer in the catalytical interface. First-principles calculations reveal that the Fe<sub>2</sub>Ni<sub>2</sub>N is intrinsically metallic, and the contribution mainly derives from the Fe atoms at corner sites of crystal structures. A good synergistic effect between metallic Fe<sub>2</sub>Ni<sub>2</sub>N with excellent intrinsic activity and conductive CNTs lead to outstanding electrochemical performance with a low overpotential ( $\eta_{10 \text{ mAcm}^{-2}} = 282 \text{ mV}$ ) and Tafel slope ( $38 \text{ mV dec}^{-1}$ ), as well as good long-term stability.

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## 1. Introduction

The oxygen evolution reaction (OER) plays a vital part of renewable energy techniques like water-splitting devices and metal-air batteries. As a half reaction of water-splitting, the sluggish kinetics and high overpotential of OER reduce the current efficiency, and become huge obstacles of industrialized water electrolysis and hydrogen generation. Traditionally, some metal oxides such as IrO<sub>2</sub> and RuO<sub>2</sub> exhibit considerably good OER catalytic performance. However, their resource-scarcity and high price motivate researchers from all over the world to seek candidates with abundant reserves and low cost, as well as high efficiency toward OER [1–5]. In recent years, intensive efforts have been made to transition metal-based catalysts including their oxides [6–8], sulfides [9–11], carbides [12,13], nitrides [14–16] and phosphides [17–19]. Since the first employment as non-precious-metal OER catalyst by Wu's group in 2015 [20], metal nitrides (Ni<sub>3</sub>N [21], Co<sub>4</sub>N [22,23], Fe<sub>x</sub>N [24]) are considered as one of the most promising class of OER electrocatalyst because of their metallic characteristics, excellent catalytic activity, as well as easy operation [20,25,26].

Furthermore, bimetallic nanocomposite is widely considered to be a more promising alternative catalyst due to their better electrocatalytic capacities than related monometallic [27–29]. The combination of different bimetallic materials provides ample probabilities to modulate the physico-chemical properties towards valency electron and electronic state of the metallic elements, and thus create more active sites and somehow enhance the conductivity [30]. For instance, Ni/Fe alloy nitrides consisting of the two most common metals have been identified as highly efficient electrocatalysts for water splitting particular for OER [29,31,32]. Wang's group synthesized a nanoparticle-stacked porous Ni<sub>3</sub>FeN nanosheet for electrolysis-splitting water, which provides highly active sites for OER and large specific surface area [27]. Sun's group reported a Fe<sub>2</sub>Ni<sub>2</sub>N catalyst on Ni foam for water splitting with small overpotential and fast-growing current density [26]. Our very recent work proposed a partial-sacrificial-template synthesis of Ni/Fe nitride nanostructures on Ni foam as a self-supported bifunctional water splitting electrocatalyst [33]. The catalyst exhibits extraordinarily high activities toward OER and extremely good durability with more than 400 h of consistent galvanostatic electrolysis without any visible voltage elevation. Although this galvanic replacement-mediated method for Ni/Fe alloy nitrides with significant performance advantages has been demonstrated, it is only confined to the self-supported electrode system where use

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the nickel foam substrate, and therefore their application become severely constrained [29]. Thereupon the synthesis of powdery Ni/Fe nitrides via this advanced methodology are worthy of our attention, since the powdery electrocatalysts are easily coated on carbon and other types of membrane electrodes.

In this paper, we report an *in situ* growth of iron-nickel nitrides on carbon nanotubes (CNTs) for OER. Carbon nanotubes (CNTs) are chosen as the powdery electrocatalyst support because of their abundant catalytic sites with its unique lumen structure and good conductivity, as well as strong stability [34,35]. Firstly, CNTs coated by Ni metal (Ni/CNTs) we used are readily available. Secondly, the  $\text{Ni}^{2+}$  is released by the galvanic replacement reaction between the Ni metal and  $\text{Fe}^{3+}$  in solution, and then coprecipitated with Fe species to form  $\text{FeNi}(\text{OH})_x/\text{CNTs}$  composite. The last step is heating-treatment of  $\text{FeNi}(\text{OH})_x/\text{CNTs}$  under ammonia atmosphere to obtain the final product of  $\text{Fe}_2\text{Ni}_2\text{N}/\text{CNTs}$ . The preparation routine is shown in Scheme 1. Benefiting from synergistic superiorities of bimetallic compounds and unique architecture, the  $\text{Fe}_2\text{Ni}_2\text{N}/\text{CNTs}$  catalysts exhibit extraordinary behaviors with an onset potential of 1.47 V (vs. RHE) and low overpotential (282 mV) at  $10 \text{ mA cm}^{-2}$  with the Tafel slope of  $38 \text{ eV dec}^{-1}$ , as well as excellent durability in alkaline solution. The excellent electrocatalytic performance can be attributed to the strong interaction between the  $\text{Fe}_2\text{Ni}_2\text{N}$  and CNTs, and the intrinsic metallic character of  $\text{Fe}_2\text{Ni}_2\text{N}$  that is confirmed by density-function theory (DFT) calculations.

## 2. Experimental section

**Material Characterization:** The Ni/CNTs were obtained from TIMES NANO (China). Trisodium citrate and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were acquired from Tianjin Zhiyuan Chemical Reagent Company (China).  $\text{RuO}_2$  was purchased from Alfa Aesar (China). All aqueous solutions were configured with ultrapure water ( $>18 \text{ M}\Omega \text{ cm}^{-1}$ ) through Millipore equipment.

Specimen Morphology was recorded using JEOL JSM-7000F FESEM (field-emission scanning electron microscope) and JEOL JEM-2100F TEM (transmission electron microscope). Crystalline data was collected by X-ray diffraction (SHIMADZU, Lab X XRD-6000, Japan). Thermogravimetric analysis (TGA) was performed on a Luxx STA 409 PC of  $10 \text{ K min}^{-1}$  heating rate with nitrogen flowing. X-ray photoelectron spectroscopy (XPS) were carried with Kratos Axis Ultra using monochromatic Al K  $\alpha$  source (150 W, 15 kV), and the binding energies were calibrated via referring C 1s peak to 284.6 eV. The accurate amounts of nickel and iron were

measured by ICP-OES (AGILENT 730).

**Preparation of  $\text{Fe}_2\text{Ni}_2\text{N}/\text{CNTs}$ :** The Ni/CNTs were transferred into a 100 mL flask containing of  $\text{FeCl}_2$  (0.8, 1.2 and 1.6 mmol) and trisodium citrate (0.075 mmol). After that, ultrapure water was added to form 40 mL homogenous suspension. The aforementioned solutions were then put in oil bath maintained  $90^\circ\text{C}$  for 6 h with magnetic stirring. Dark precipitates ( $\text{FeNi}(\text{OH})_x/\text{CNTs}$ ) were collected by centrifugation (6000 rpm for 3 min), washed with ultrapure water to remove tan supernatant, and then kept at  $60^\circ\text{C}$  in vacuum dried overnight. Afterwards, the final electrocatalysts were obtained by annealing process under ammonia atmosphere at  $350^\circ\text{C}$ ,  $450^\circ\text{C}$  and  $550^\circ\text{C}$  for 2 h with heating rate of  $10^\circ\text{C min}^{-1}$ . Unless otherwise specified, the  $\text{Fe}_2\text{Ni}_2\text{N}/\text{CNTs}$  is specified to the sample that are prepared under optimal condition with 1.2 mmol  $\text{FeCl}_2$  and annealing temperature of  $450^\circ\text{C}$ . For the control sample, the  $\text{FeNiO}_x/\text{CNTs}$  was obtained by calcined  $\text{FeNi}(\text{OH})_x/\text{CNTs}$  at  $450^\circ\text{C}$  for 2 h under nitrogen atmosphere. The preparation of  $\text{Fe}_2\text{Ni}_2\text{N}$  was similar with  $\text{Fe}_2\text{Ni}_2\text{N}/\text{CNTs}$ , but calcined on muffle oven at  $450^\circ\text{C}$  for 2 h to remove CNTs before final nitridation.

**Electrochemical Measurements:** Electrochemical tests were performed on a CHI 660D electrochemical workstation by a traditional three-electrode cell. Platinum foil and Ag/AgCl were adopted respectively as auxiliary and reference electrodes. Working electrodes were prepared by casting catalyst on the glass carbon with loading of  $0.408 \text{ mg cm}^{-2}$  (4 mg/mL catalyst in mixture of water and ethanol (4:1 v/v) with  $35 \mu\text{L}$  5% Nafion). Ohmic drop ( $iR$ ) measured by electrochemical impedance spectroscopy (EIS) have been compensated for all electrochemical tests. EIS measurements were set at 1.5 V (vs. RHE) with amplitude of 5 mV and a frequency range of 100 K–0.1 Hz. The rotation rate of the Rotating Disk Electrode (RDE) measurements was set at 900 rpm. Long-term durability test was carried at  $10 \text{ mA cm}^{-2}$  with the loading of  $0.200 \text{ mg cm}^{-2}$  on carbon cloths ( $1 \times 2 \text{ cm}^2$ ).

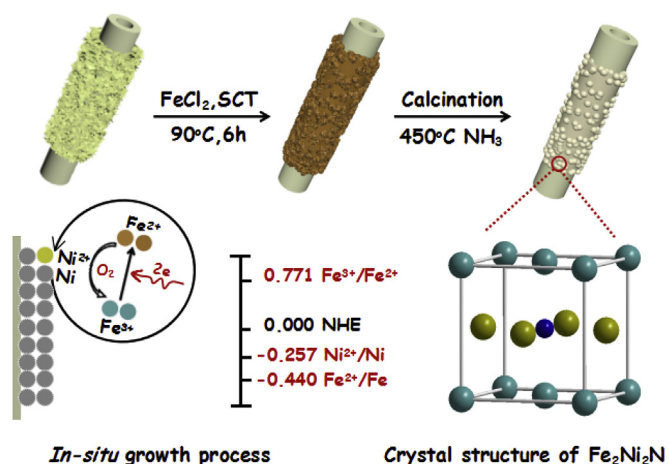
In order to ensure the gas saturation, 200 sccm  $\text{O}_2$  was bubbled into 1 M KOH solution at least 20 min prior to experiments and kept above the liquid level during the whole testing. The Ag/AgCl electrode was standardized with reversible hydrogen electrode (RHE) based on procedure reported in literature [36]. In a 1 M KOH solution,  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 1.0945 \text{ V}$ .

**Calculation Method:** First-principle calculations were started out using density-functional theory (DFT) [37,38] applied in VASP [39,40] package. The generalized-gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) [41] form and the projector augmented wave (PAW) [42] approach are employed. The valence electrons of all atoms were depicted using a plane wave basis set with a kinetic-energy cut-off of 520 eV. During geometric optimization, the Brillouin zones are sampled with  $15 \times 15 \times 15$  and  $9 \times 9 \times 1$  mesh for bulk and surfaces of  $\text{Fe}_2\text{Ni}_2\text{N}$ , respectively. A denser k-points grid of  $19 \times 19 \times 19$  and  $15 \times 15 \times 1$  are used for calculating the density of states (DOS). The thickness of vacuum space is set to be 15 Å. All calculations were carried out with full relaxation of ionic locations in a spin unlimited state until the energy difference between the two successive relaxations was less than 0.1 meV.

## 3. Results and discussion

### 3.1. Material characterization

The preparation process of  $\text{Fe}_2\text{Ni}_2\text{N}/\text{CNTs}$  was monitored by transmission electron microscopy (TEM). Fig. 1A shows the initial typical microstructure of CNTs with diameter of 30–50 nm, on which irregularity wrinkles were twined owing to the loading of Ni metal (50.27 wt %) (Table S1). Afterwards, Ni metal on the CNTs was etched by the newly generated  $\text{Fe}^{3+}$  from the  $\text{FeCl}_2$  solution due to



Scheme 1. Schematic illustration of the formation of  $\text{Fe}_2\text{Ni}_2\text{N}/\text{CNTs}$ .

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