

## B-NiCo<sub>2</sub>O<sub>4</sub>/NF as an efficient electrocatalyst for HER

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**Abstract.** The development of efficient catalysts for the hydrogen evolution reaction (HER) is of extreme importance for future renewable energy systems. In this work, we report on the synthesis of a novel hybrid electrode that boracic nanospheres grown on the top of some NiCo<sub>2</sub>O<sub>4</sub> nanowires with nickel foam as the baseboard (B-NiCo<sub>2</sub>O<sub>4</sub>/NF). Due to this unique structural features, the electrocatalyst has a good activity for HER, which needs overpotential of 150 mV to afford the current density of 10 mA cm<sup>-2</sup>, the catalytic activity is maintained for at least 18 h. This work provides a promising methodology for the designing and fabricating highly efficient boracic catalysts for HER.

**Keywords:** Electrocatalyst; HER; boronation;

### 1. Introduction

Nowdays, many environmental problems have been caused by burning fossil fuels, such as global warming, air pollution, and energy shortage,[1] so it is extremely urgent to develop environmentally friendly and renewable energy, which can effectively reduce environmental pollution and ease the energy crisis. Hydrogen has long been regarded as an ideal clean-burning alternative to fossil fuels.[2] Among various advanced technology for hydrogen production, electrochemical water splitting has drawn great attention due to the advantages of non-pollution, high purity and easy operation.[3-4]

As we all know, noble-metal based materials are the most effective electrocatalysts for HER (e.g. Pt/C).[5] However, the high cost, low storage, and poor stability limit their large-scale application.[6] Therefore, developing non-noble catalysts with good activity and large quantity is of great importance.

Here, we study out B-NiCo<sub>2</sub>O<sub>4</sub>/NF as a good electrocatalyst for HER by room-temperature treatment of NiCo<sub>2</sub>O<sub>4</sub>/NF in NaBH<sub>4</sub> solution, leading to the formation of boracic nanospheres on the top of some NiCo<sub>2</sub>O<sub>4</sub> nanowires. Benefiting from the deuterogetic boracic nanospheres structural, the B-NiCo<sub>2</sub>O<sub>4</sub>/NF exhibits a obviously enhanced performance for HER in comparison with NiCo<sub>2</sub>O<sub>4</sub>/NF precursor, which needs overpotential of 150 mV for HER to afford the current density of 10 mA cm<sup>-2</sup>.

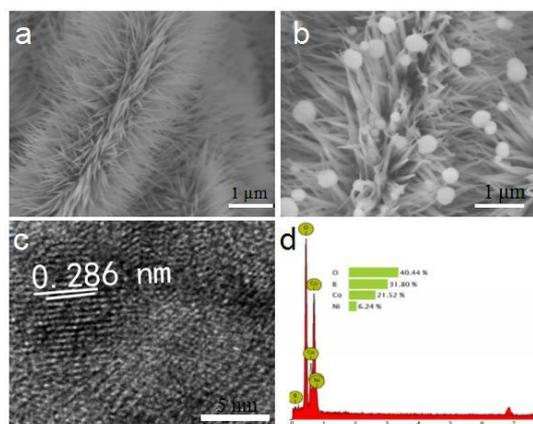
### 2. Experimental section

A piece of Ni foam (1 cm×3 cm), which was ultrasonically degreased with dilute HCl solution, ethanol and deionized water several times. Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, NH<sub>4</sub>F, and urea were dissolved in 15 mL water under stirring to form a clear solution, Then the solution was transferred into a Teflon-lined stainless autoclave (25 mL), the pre-treated Ni foam was also put in the autoclave. Then the autoclave was sealed and placed in an oven at 120°C for 6 h, after the autoclave cooled down to

room temperature naturally, the Ni foam was taken out, washed with deionized water and dried in a vacuum oven at 40 °C for 3h, and then annealed at 300 °C for 120 min in a N<sub>2</sub> atmosphere, the NiCo<sub>2</sub>O<sub>4</sub>/NF was obtained. In order to gain B-NiCo<sub>2</sub>O<sub>4</sub>/NF, the pre-prepared NiCo<sub>2</sub>O<sub>4</sub>/NF (1cm ×1cm) was immersed in 2.5 M NaBH<sub>4</sub> solution (containing 0.25 M NaOH) for 30 min.

### 3. Results and discussion

The morphology of the as-obtained samples were characterized by scanning electron microscopy (SEM). As shown in **Figure 1a**, the entire surface of the Ni foam is uniformly covered by NiCo<sub>2</sub>O<sub>4</sub> nanowires. After NaBH<sub>4</sub> treatment, the product becomes a mixed structure of hierarchical nanospheres and nanowires. The energy-dispersive X-ray (EDX) spectrum (**Figure 1d**) indicates the presence of Co, Ni, and B elements in the nanospheres. As shown in **Figure 1b**, the NiCo<sub>2</sub>O<sub>4</sub> nanowires maintain the original morphology after boronation, at the same time, many boracic nanospheres were produced. **Figure 1b** also proves that boracic nanospheres only grown on the top of some



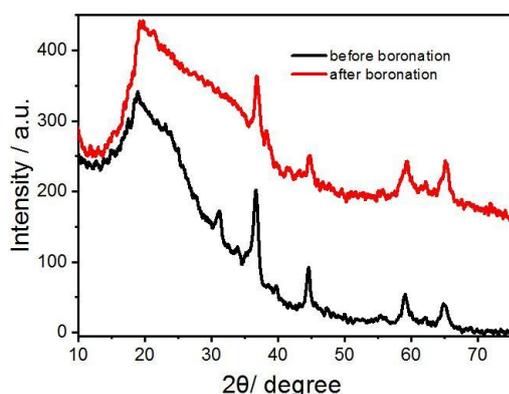
**Figure 1.** (a) The SEM image of NiCo<sub>2</sub>O<sub>4</sub>/NF; (b) the SEM image of B-NiCo<sub>2</sub>O<sub>4</sub>/NF;(c) the TEM image of B-NiCo<sub>2</sub>O<sub>4</sub>/NF; (d) EDX spectrum of boracic nanospheres.

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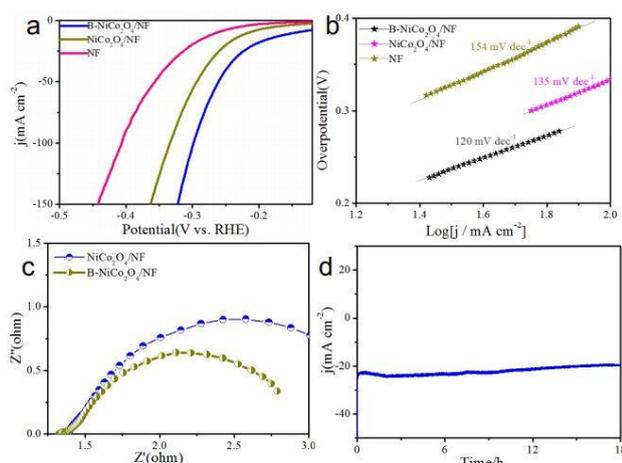
NiCo<sub>2</sub>O<sub>4</sub> nanowires, not all nanowires. **Figure 1c** exhibits the high-resolution TEM image of B-NiCo<sub>2</sub>O<sub>4</sub>/NF, where the interplanar spacing of 0.286 nm is correspond well to the (220) [7] lattice plane of NiCo<sub>2</sub>O<sub>4</sub>.

The chemical composition and crystal-phase structure of NiCo<sub>2</sub>O<sub>4</sub> and B-NiCo<sub>2</sub>O<sub>4</sub> powders scratched down from Ni foam were characterized by X-ray diffraction (XRD) in **Figure 2**. Before boronation, the XRD analysis proves that the nanowires can be well indexed to NiCo<sub>2</sub>O<sub>4</sub> (JCPDS card No.20-0781). After a chemical treatment of NaBH<sub>4</sub> solution, the XRD pattern have almost no change except the decrease of some peak intensity. It has been reported that Co- and Ni-based borides materials possess an unusual metal-metalloid nanostructure, which is consist of tiny metal nanocrystallites embedded in the matrix of amorphous B containing phases. In this work, the absence of the diffraction peaks of boracic material suggests its nanocrystalline or amorphous structure; similar conclusions were obtained in some other literatures. [9] So it is not surprised there is no diffraction peaks of boracic species in the XRD analysis.

The HER performance of B-NiCo<sub>2</sub>O<sub>4</sub>/NF was studied using a three electrode system in 1.0 M KOH solution. For comparison,



**Figure 2.** XRD image of NiCo<sub>2</sub>O<sub>4</sub>/NF (black) and B-NiCo<sub>2</sub>O<sub>4</sub>/NF (red).



**Figure 3.** (a) polarization curves of B-NiCo<sub>2</sub>O<sub>4</sub>/NF, NiCo<sub>2</sub>O<sub>4</sub>/NF, NF for HER; (b) corresponding Tafel plots of B-NiCo<sub>2</sub>O<sub>4</sub>/NF, NiCo<sub>2</sub>O<sub>4</sub>/NF, NF; (c) Nyquist plots of NiCo<sub>2</sub>O<sub>4</sub>/NF and B-NiCo<sub>2</sub>O<sub>4</sub>/NF at an overpotential of 1.5 V; (d) time dependent-current density of B-NiCo<sub>2</sub>O<sub>4</sub>/NF for HER at an overpotential of -0.2 V.

the same measurements of NiCo<sub>2</sub>O<sub>4</sub>/NF, and bare Ni foam were also performed. As shown in **Figure 3a**, bare NF has the worst activity. Furthermore, B- B-NiCo<sub>2</sub>O<sub>4</sub>/NF also exhibits better performance for HER, with an overpotential of 150 mV at the current density of 10 mA cm<sup>-2</sup>, B-NiCo<sub>2</sub>O<sub>4</sub>/NF needs a much higher overpotential of 223 mV to reach the same current density. The favorable performance of B- B-NiCo<sub>2</sub>O<sub>4</sub>/NF for HER should be due to its smaller charge-transfer resistance (**Figure 3c**). Form the Tafel plots in **Figure 3b**, the Tafel slope of B-NiCo<sub>2</sub>O<sub>4</sub>/NF is 120 mV dec<sup>-1</sup>, which is smaller than NiCo<sub>2</sub>O<sub>4</sub>/NF (135 mV dec<sup>-1</sup>) and bare NF (154 mV dec<sup>-1</sup>). In addition, long-term electrochemical stability is also a factor to evaluate the property of a catalyst. The stability of B-NiCo<sub>2</sub>O<sub>4</sub>/NF for HER was tested by a chronoamperometry measurement at a constant voltage for 18 h, the data in **Figure 3d** indicates there is little degradation after long time test, indicating its superior durability in the electrochemical process for HER.

## 4. Conclusion

In brief, a freestanding, noble-metal-free B-NiCo<sub>2</sub>O<sub>4</sub>/NF electrode has been developed as an efficient and robust electrocatalyst for HER. This B-NiCo<sub>2</sub>O<sub>4</sub>/NF only demands overpotentials of 150 mV to approach a current density of 10 mA cm<sup>-2</sup>, and the catalytic activity is maintained for at least 18 h, showing its great value as a low cost alternative to precious catalyst in practical applications. Such high catalytic activity can be attributed to the high surface area, relatively large thickness and interconnected nanoarray configuration of this electrode. These study results highlight the potential of boracic catalysts for HER.

## Acknowledgements

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