



Ultrafast and large scale preparation of superior catalyst for oxygen evolution reaction



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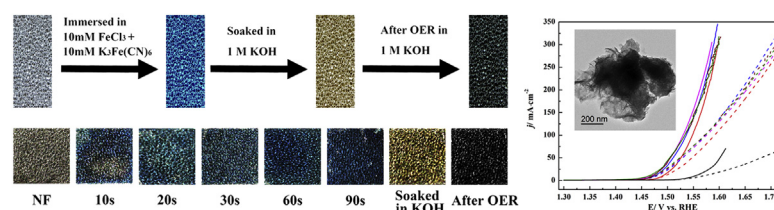
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HIGHLIGHTS

- Ultrafast synthesization of NiFe-LDHs has been derived from prussian blue analogue.
- NiFe-LDHs can be prepared in few seconds with significantly enhanced OER activity.
- It is promising for manufacture of low-cost, effective and robust OER electrodes.

GRAPHICAL ABSTRACT



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ABSTRACT

The development of efficient and earth abundant catalyst for the oxygen evolution reaction (OER) is a key challenge for the renewable energy research community. Here, we report a facile and ultrafast route to immobilize nickel-iron layered double hydroxide (NiFe-LDH) nanoparticles on nickel foam (NF) via soaking the direct electroless deposited prussian blue analogue (PBA) on NF in 1 M KOH. This NiFe-LDH/NF electrode can be prepared in a few seconds without further treatments. It has three-dimensional interpenetrating network originated from its PBA precursor which facilitate the diffusion and adsorption of the reactants and producing for OER. And further characterization of the Faradaic efficiency and forced convection tests show direct evidence to demonstrate the formation of free intermediate(s) in the OER process. This electrode (typically NiFe-LDH-20s/NF) exhibits outstanding electrocatalytic activity with low overpotential of ~ 0.240 V at 10 mA cm^{-2} , low Tafel slope of 38 mV dec^{-1} , and great stability. This feasible strategy affords a new strategy for the large scale manufacture of low-cost, effective and robust OER electrodes.

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1. Introduction

Water oxidation catalysts play an important role in the sustainable and efficient energy conversion and storage systems, such as water electrolyzers, solar water-splitting devices, and rechargeable metal-air batteries [1]. As the common anodic half-reaction in these important processes, water oxidation or the

oxygen evolution reaction (OER) holds the decisive key to their success [2–4]. So far, IrO_2 and RuO_2 are demonstrated to be the state-of-the-art OER catalysts, however, they suffer from high cost, scarcity and unstable in alkaline condition, which would seriously impede their widespread applications [3,5]. Therefore, a new and effective OER electrocatalyst, comprising low cost earth abundance, high stability, and corrosion resistance, that can substantially lower the overpotential, increase the catalyst durability, and thus enhance the energy conversion efficiency is highly desired [6]. In particular, iron-doped nickel hydroxides in the form of layered double

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hydroxides (NiFe-LDHs) have drawn special attention [7–12].

NiFe-LDHs have been established as one of the most active electrocatalysts with their activity closely approaching or even outperforming those precious metal benchmarks in alkaline media [5,7,13–16]. Many researchers have evoked to synthesis NiFe-LDHs with different methods, such as electrodeposition [17–20], hydrothermal [21,22], liquid deposition [23], etc. However, most of the as-prepared NiFe-LDHs products are fine powders, which need to be fabricated using polymer binders and other additives to coat onto conductive substrates for OER tests. The application of these electrical insulating and inactive binders can deteriorate the conductivity of the electrode and may partially block the pores and active sites of NiFe-LDHs leading to diminished electrocatalytic performances [24]. To address this, NiFe-LDHs directly grown and tightly bonded on current collector without any binders is highly desirable [17,25–28]. Electrochemical deposition and *in situ* growth (e.g. hydrothermal method) are facile and scalable manufacturing process, which has shown great potential in developing NiFe-LDHs electrodes [8,17,23,29]. Nevertheless, one main pitfall of these methods is their time and energy consuming, e.g. it generally requires hours (even the most rapid electrodeposition method requires 3–15 min [17]). This limitation prompts us to search for other simple yet effective, binder-free, energy saving approaches to prepare NiFe-LDHs with optimal electrocatalytic power. Herein, we report a novel and ultrafast approach for the synthesis of NiFe-LDHs derived from prussian blue analogue (PBA) as OER catalysts with significantly enhanced activity.

2. Experimental

2.1. Preparation of the catalyst

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$) and concentrated sulfuric acid (H_2SO_4) of analytical grade were used as received without further purification. The prussian blue analogue (PBA) was directly grown on the nickel foam (NF) via a displacement reaction under ambient condition. Typically, 0.1622 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (10 mM), 0.3292 g $\text{K}_3\text{Fe}(\text{CN})_6$ (10 mM) were dissolved in 100 mL double distill water with stirring to form a dark reddish brown homogeneous solution. Then the dilute H_2SO_4 solution (0.5 M) washed NF was immersed into the reddish brown solution to initiate the formation of PBA film. After a few seconds, the blue NF (PBA/NF) was pulled out and washed with double distilled water for several times. The PBA/NF was dried at room temperature and stored in ambient condition for further use. The catalyst for water oxidation was directly generated by putting the PBA/NF into the KOH solution.

2.2. Characterization of the catalyst

The crystallographic structure of the sample on the ceramic tube was analyzed by a Bruker D8 Avance X-ray powder diffractometer (XRD) with Cu-K α radiation operating at 30.0 kV and 20.0 mA. The high resolution transmission electron microscopy (HRTEM) images and Energy Dispersive X-ray (EDX) spectra and EDX-mapping images were captured from CarlZeiss Libra 200FE HRTEM equipped with EDX detector. A scanning electron microscopic (SEM) image was obtained from a CamScan Apollo 300 SEM. The X-ray photoelectron spectrum (XPS) was acquired on the Kratos XSAM 800 spectrometer with a Mg K α X-ray (1253.6 eV) excitation source running at 15 kV, a hemi-spherical electron energy analyzer and a multichannel detector. The Raman spectra were recorded using Thermo Scientific DXR Raman Spectroscopy.

2.3. Electrochemical characterization

All the electrochemical measurements were performed on an electrochemical workstation (Ivium CompactStat e. 10800, Ivium Technologies B. V., The Netherlands) using a typical 3-electrode mode equipped with a Pt mesh as the counter electrode, an Hg/HgO (1 M NaOH) electrode as the reference electrode, and the as-made NiFe-LDH/NF (or PBA/NF) as the working electrode. All potentials measured were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.059 \text{ pH}$. The linear sweep voltammetry curves (LSV) were obtained by sweeping the potential from 0.2 V to 0.8 V (vs. Hg/HgO) with scan rate of 0.5 mV s^{-1} . Electrochemical impedance measurements were carried out at overpotential of 0.55 V (vs. Hg/HgO) in 1 M KOH from 0.1 Hz to 0.1 MHz with an AC amplitude of 5 mV. Chronoamperometric and chronopotentiometric responses were obtained at different potentials and current densities in 1 M KOH, respectively. A volume displacement method was used to measure the OER Faradaic efficiency of the typical NiFe-LDH-20s/NF electrode in 1 M KOH under saturated O_2 atmosphere. The forced convection effect on the OER performance of the NiFe-LDH/NF electrode was conducted in 0.1 M KOH with stirring at 1000 rpm. All the experiments were carried out at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$).

3. Results and discussion

The nanoporous PBA film was directly electroless grown on nickel foam (NF) through the precipitation of the Ni^{2+} , Fe^{2+} (generated from the replacement reaction between NF and Fe^{3+} ions) and $[\text{Fe}(\text{CN})_6]^{3-}$. Then the raw PBA/NF was washed with double distilled water and assembled into an electrochemical cell for further electrochemical characterization. Once the PBA contacted with 1 M KOH solution, the color of PBA film will rapidly change from blue to light yellow and eventually turned to black after OER test. Schematic illustration of the experimental process and the related photo images is demonstrated in Scheme 1.

The self-assembly of PBA film on NF is simple and fast, and can be done in few seconds (See in supplementary video). The key step to obtain uniform PBA/NF is infiltrating the NF using weak acidic water prior to soaking in the grown bath. With the incensement of soaking duration in the grown bath, the color of the PBA film will rapidly change from wathet blue to dark blue (even with some insoluble matters around the NF) indicating the fast augment of the PBA film. The morphology of the PBA film was characterized by the SEM and HRTEM. As showed in Fig. S1(A) and Fig. 1(A), the blue film was constructed by nanoflakes and uniformly covered the NF substance. Unfortunately, due to the low mass loading rate of blue film and high diffraction intensity of the bulk NF, no useful information about the as-made blue film was obtained from the XRD spectra (Fig. S2). Hence, further characterizations of Raman, XPS and EDX were carried out to identify the composition of the blue film. The Raman band (Fig. S3) recorded at $\sim 2131 \text{ cm}^{-1}$ is characteristic of cyanide stretching in Fe(II)-CN-Fe(III) or Ni(II)-CN-Fe(III) complexes, while the single high wavenumber peak ($\sim 2155 \text{ cm}^{-1}$) is characteristic of cyanide stretching near ferric iron [30,31]. This implies that the blue film is an iron and/or nickel hexacyanoferrate compound. In the meantime, the Fe $2p_{3/2}$ and Ni $2p_{3/2}$ XPS curves were deconvoluted to peaks with binding energies of 706.8 eV (Fe^{2+}), 712.4 eV (Fe^{3+}), 854.1 eV (Ni^{2+} -CN) and 855.9 eV (Ni^{2+} -OH) [32], respectively, indicate that the blue film is a mixture of Ni^{2+} doped Prussian blue (namely prussian blue analogue, PBA) and $\text{Ni}(\text{OH})_2$. The presence of $\text{Ni}(\text{OH})_2$ in the PBA film is probably derived from the hydration of PBA or precipitation of Ni^{2+} in neutral solution. The corresponding EDX spectrum (Fig. 1(B)) also

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