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Short communication

Electrodeposition of nickel–phosphorus nanoparticles film as a Janus electrocatalyst for electro-splitting of water

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HIGHLIGHTS

- Ni–P/CF can act as bifunctional HER and OER electrocatalyst in basic electrolytes.
- Ni–P/CF exhibits high catalytic activity towards both HER and OER.
- Ni–P/CF can achieve 10 mA cm^{-2} water-splitting current at a cell voltage of 1.68 V.

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ABSTRACT

Nickel–phosphorus nanoparticles film on copper foam (Ni–P/CF) was prepared by electrodeposition. This electrocatalyst shows high catalytic activity and durability toward both hydrogen and oxygen evolution reactions in basic electrolytes. The results show that Ni–P/CF can deliver a current density of 10 mA cm^{-2} at an overpotential of 98 mV for hydrogen production and 325 mV for oxygen generating. A two-electrode water electrolyzer using Ni–P/CF as cathode and anode produces 10 mA cm^{-2} at a cell voltage of 1.68 V with high stability.

1. Introduction

Clean, renewable and sustainable energy sources are very necessary for human society due to the depletion of fossil fuels and the increased environmental concerns [1]. Hydrogen, as the best candidate to replace fossil fuels, can be simply produced by water splitting [2]. Electro-splitting of water powered by electric energy has attracted extensive attention because this process can convert electric energy into chemical energy for easier storage and delivery. The water splitting process can be divided into two half-reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). Both reactions are crucial for the overall efficiency of water splitting. Although water splitting only needs a theoretical minimum voltage of 1.23 V, commercial electrolyzers typically operate at a much higher value of 1.8–2.0 V because it is a strongly uphill reaction with large overpotential [3,4]. Thus, efficient HER and OER electrocatalysts are of vital importance to overcome the large overpotentials. Currently, state-of-the-art HER electrocatalysts are Pt-based materials and OER electrocatalysts are Ru- or Ir-based materials, but the scarcity and high cost of such catalysts limit their mass uses. Therefore, tremendous efforts have been made to develop efficient earth-abundant HER (sulfide [5,6], phosphide [7–10], nitride [11,12], selenide [5,13–15]) and OER (oxide [16–18], hydroxide [19–22], sulfide [23,24] selenide [25]) electrocatalysts.

Water splitting should be performed in either strongly acidic or alkaline solution to minimize the overpotentials [26]. Alkaline water splitting has emerged as a strong candidate for commercialization toward mass hydrogen production [27]. Utilizing a same electrocatalyst for both HER and OER has advantages of simplifying the system and lowering the cost. It is thus highly attractive to develop non-precious metal electrocatalyst efficient for both HER

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and OER in strongly alkaline electrolytes. Although nickel (Ni) has emerged as an interesting non-noble metal for its catalytic power toward HER and OER, their performance needs to be further improved [4].

In this communication, we demonstrate nickel–phosphorus nanoparticles film electrochemically deposited on copper foam (Ni–P/CF) behaves as an efficient HER and OER electrocatalyst with good durability in strongly alkaline solutions. This electrode needs HER overpotential of 98 mV and OER overpotential of 325 mV to achieve current density of 10 mA cm^{-2}. A stable two-electrode water electrolyzer made from Ni–P/CF affords 10 mA cm^{-2} water-splitting current at a cell voltage of 1.68 V.

2. Experimental

2.1. Reagents and materials

CF was purchased from Kunshan Desco Electronics Co., Ltd. $NiSO_4 \cdot 6H_2O$, KOH and NaOAc were obtained from Beijing Chemical corporation. NaH_2PO_2 and $RuCl_3 \cdot 3H_2O$ were bought from Aladdin Co., Ltd. (Shanghai, China). Pt/C (20 wt% Pt on Vulcan XC-72R) and Nafion (5 wt%) were purchased from Sigma–Aldrich Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

2.2. Synthesis of Ni–P/CF

Electrolyte solution for electrodeposition was prepared by dissolving 1.3142 g of $NiSO_4 \cdot 6H_2O$, 0.4101 g NaOAc, and 2.1997 g NaH_2PO_2 were dissolved in 50 mL H_2O. Prior to electrodeposition, CF was washed with ethanol and water several times to remove the surface impurities. The electrodeposition was carried out in a standard three-electrode setup, with using a piece of CF, a graphite plate and a saturated calomel electrode (SCE) as work, counter and reference electrode, respectively. The CV was cycled 15 times between −1.0 and −0.3 V with a scan rate of 10 mV s^{-1}. After electrodeposition, the CF was carefully withdrawn from the electrolyte solution, rinsed with water and ethanol and dried at room temperature.

2.3. Synthesis of RuO_2

1.037 g of $RuCl_3 \cdot 3H_2O$ was dissolved in 50 mL H_2O and heated at 100 °C under air atmosphere. After 10 min, 0.5 mL of 1.0 M KOH solution was added and kept stirring for 45 min. Then the precipitates were collected by centrifugation, washed with water and ethanol repeatedly for several times. This product was dried at 80 °C for 5 h and then calcined in air at 300 °C for 3 h.

2.4. Characterization

Scanning electron microscopy measurements were made on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. X-ray powder diffraction data were acquired by a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

2.5. Electrochemical measurements

The HER and OER electrochemical measurements were performed with a CHI 660E electrochemistry workstation (CH Instruments, Inc., Shanghai) in a standard three-electrode setup. The Ni–P/CF was directly used as work electrode, and a graphite plate as counter electrode and a SCE as reference electrode. In all measurements, the SCE reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). In 1.0 M KOH solution, E (RHE) = 0.242 + 0.059 pH. For overall water splitting, electrochemical measurements were carried out in a two-electrode setup in 1.0 M KOH solution with using Ni–P/CF as anode and cathode, respectively.

Pt/C and RuO_2 ink were prepared by dispersing 10 mg of Pt/C or RuO_2 in 480 μL of water/ethanol (v/v = 1:1) with 20 μL of 5 wt % Nafion solution. Then 37.5 μL of the Pt/C or RuO_2 ink was loaded onto a piece of CF and air-dried at room temperature for HER or OER measurements.

3. Results and discussion

The CF changed in color from brick-red to dark grey after electrodeposition (Fig. S1a). The X-ray powder diffraction (XRD) pattern of this product is similar to bare CF (Fig. S1b), indicating Ni–P nanoparticles film is amorphous. Scanning electron microscopy (SEM) images of the Ni–P/CF (Fig. 1a and b) reveal that the skeleton of CF is fully covered with smooth-surface Ni–P nanoparticles film. The corresponding energy dispersive X-ray (EDX) spectrum (Fig. S2) indicates the existence of Ni, P, O, and Cu elements (Cu signal arising from the CF substrate). EDX elemental mapping analysis (Fig. 1c) suggests that Ni and P elements are uniformly distributed in the Ni–P film. X-ray photoelectron spectroscopy (XPS) survey spectrum of Ni–P/CF indicates the presence of Ni, P, O, Cu, and C elements (Fig. S3a). The existence of C and O element is attributed to the contamination of the product and oxidized Ni and P species formed at the surface exposed to atmosphere (Fig. S3a and S3b) [28]. The XPS spectrum in Ni 2p region (Fig. 1d) shows two peaks at 852.1 and 869.1 eV, which can be assigned to metallic Ni. The binding energies (BEs) of 856.4 and 874.2 eV correspond to Ni (II). The P 2p region (Fig. 1e) exhibits two peaks at 128.9 and 129.8 eV reflecting the BEs of P $2p_{3/2}$ and P $2p_{1/2}$, respectively. The BE at 128.9 eV suggests the formation of phosphide [29] and the broad peak at about 133.1 eV is assigned to phosphate [30]. All these results suggest that as-prepared film consisting of metallic Ni and nickel phosphide [31].

The HER activity of Ni–P/CF (Ni–P loading: ~5 mg cm^{-2}) was measured in a standard three-electrode setup in 1.0 M KOH solution. For reference purposes, bare CF and commercial Pt/C (20 wt% Pt/XC-72) deposited on CF were also tested. Because as-measured reaction currents cannot reflect the intrinsic behavior of electrocatalysts due to the effect of ohmic resistance, resistance tests were made for *iR* correction of all initial data for further analysis [32]. Fig. 2a presents the polarization curves on the reversible hydrogen electrode (RHE) scale. As can be seen, the commercial Pt/C reveals excellent activity with negligible HER overpotentials. Bare CF almost has no HER activity. In contrast, the hydrogen evolution on Ni–P/CF electrode begins at a low overpotential about 55 mV, beyond which the cathodic current dramatically increases, and this electrode only needs overpotential of 98 mV to achieve current density of 10 mA cm^{-2}. This overpotential compares favorably to behavior of reported Ni-based HER electrocatalysts including $Ni(OH)_2$ on Ni foam ($Ni(OH)_2$/NF, ~250 mV) and NiFe LDH on Ni foam (NiFe LDH/NF, ~210 mV) [4] and HER electrocatalysts like crystalline NiP_2 (102 mV) [33] in 1.0 M KOH. The Tafel slope for Ni–P/CF is 55 mV dec^{-1} (Fig. 2b), which is smaller than that of crystalline NiP_2 (64 mV dec^{-1}) [33]. Because good durability is an important criterion for electrocatalyst assessment, we measured the durability of Ni–P/CF. The Ni–P/CF electrode was continuously cycled between −0.4 V and 0 V versus RHE with a scan rate of 100 mV s^{-1} in 1.0 M KOH solution for 1000 cycles. After cycling,