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Nitrogen-doped carbon nanotube supported iron phosphide nanocomposites for highly active electrocatalysis of the hydrogen evolution reaction

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ABSTRACT

Design: ng efficient hydrogen evolution reaction (HER) electrocatalyst made from earth-abundant elements is essential to the development of water-splitting devices. In this communication, we described our recent effort to develop N-doped carbon nanotube supported FeP nanocomposites (FeP/NCNT) for HER. Experiments demonstrated that the FeP/NCNT is highly active toward the HER with onset overpotential of 66 mV, a Tafel slope of 59 mV dec^{-1}, and a Faradaic efficiency close to 100% in acidic solutions. It needs overpotentials of 113 and 195 mV to afford current densities of 10 and 100 mA cm^{-2}, respectively.

1. Introduction

Hydrogen is considered to be an ideal energy carrier in the hydrogen-economy paradigm [1,2]. Electrochemical reduction of water for hydrogen production is an important component of several developing clean-energy technologies, but an efficient electrocatalyst for the hydrogen evolution reaction (HER) is needed to afford high current at low overpotential [3]. Currently, Pt-based compounds are the best HER catalysts, but the high cost of Pt hinders their wide use. Water electrolysis units based on proton exchange membrane (PEM) technology operate under strongly acidic conditions and thus require using acid-stable HER catalysts [4]. As such, it is highly attractive to design cost-effective acid-stable HER catalysts. Among such catalysts, compounds based on molybdenum, tungsten, and iron-group elements have received considerable attention with great success, including MoS_2 [5–8], MoSe [9], MoB [10], Mo_2C [10,11], $NiMoN_x$ [12], $Co_{0.6}Mo_{1.4}N_2$ [13], WS_2 [14,15], $CoSe_2$ [16,17], CoP [18–20], and Ni_2P [21,22], etc.

Iron is the cheapest and one of the most abundant of all transition metals. Recently, Xu et al. have reported anion-exchange synthesis of FeP nanosheets as a HER catalyst in acidic solutions [23], but this work suffers from the involvement of several kinds of organic solvents and this catalyst needs a large overpotential (η) of ~240 mV to afford current density of 10 mA cm^{-2}. Electrocatalytic efficiency is affected by the electrical conductivity [24] and the use of conductive carbon as support leads to improved conductivity of the composite and increased dispersion of the active phases [25]. It is also shown that N doping of carbon alters electron-donating character of the support facilitating the immobilization of the catalyst [26]. In this communication, we described our recent effort in developing N-doped carbon nanotube supported FeP nanocomposites (FeP/NCNT) derived from low-temperature phosphidation of corresponding Fe_2O_3/NCNT precursor. As a novel HER electrocatalyst, the FeP/NCNT shows activity with an onset overpotential of 66 mV, a Tafel slope of 59 mV dec^{-1}, nearly 100% Faradaic efficiency (FE), and good durability. It needs over-optentials of 113 and 195 mV to afford current densities of 10 and 100 mA cm^{-2}, respectively.

2. Experimental

2.1. Reagents and materials

Methyl orange (MO), $FeCl_3.6H_2O$ $Co(NO_3)_2.6H_2O$, H_2SO_4, and HNO_3 was purchased from Tianjin Fuyu Chemical Reagent Co. Ltd. (Tianjin, China). Anhydrous $FeCl_3$ and pyrrole were purchased

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from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Nafion (5 wt%) was purchased from Sigma-Aldrich. Pt/C (20 wt% Pt/XC-72) and Fe_2O_3 (~30 nm) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

2.2. Synthesis of N-doped carbon nanotubes (NCNT)

Functional polypyrrole (PPy) nanotubes were prepared according previous work [16]. In brief: MO (50 mg) was dissolved in deionized water (90 mL). Anhydrous $FeCl_3$ (0.729 g) was added into above solution and a large of amount of precipitates occurred. Pyrrole (315 μL) was added and the mixture was stirred at room temperature for 24 h. The resulting products were washed with deionized water/ethanol several times until filtrate was colorless and neutral, and then dried at 80 °C in oven. Then functional PPy nanotubes were pyrolyzed in N_2 flow at 800 °C for 2 h.

2.3. Synthesis of Fe_2O_3/NCNT:

The Fe_2O_3/NCNT was synthesized using a hydrothermal method reported before. In a typical synthesis, NCNT (24 mg) and $FeCl_3.6H_2O$ (0.25 mmol) were added into deionized water (30 mL) and sonicated for 0.5 h. Then the mixture was transferred to a 50 mL Teflon-lined autoclave and heated at 90 °C for 5 h. Then the as-prepared product was washed with deionized water and dried at 80 °C, followed by calcination at 350 °Cin air for 2.5 h.

2.4. Synthesis of FeP/NCNT and FeP nanoparticles

Fe_2O_3/NCNT (20 mg) and sodium hypophosphite (100 mg) were mixed together and grind to a fine powder by using a mortar. Then, the mixture was calcined at 350 °C under N_2 flow for 2 h with a heating speed of 2 °C/min. The same procedure was performed to prepare FeP nanoparticles with the commercial Fe_2O_3 as precursor. The obtained samples were washed with deionized water and dried at 80 °C overnight.

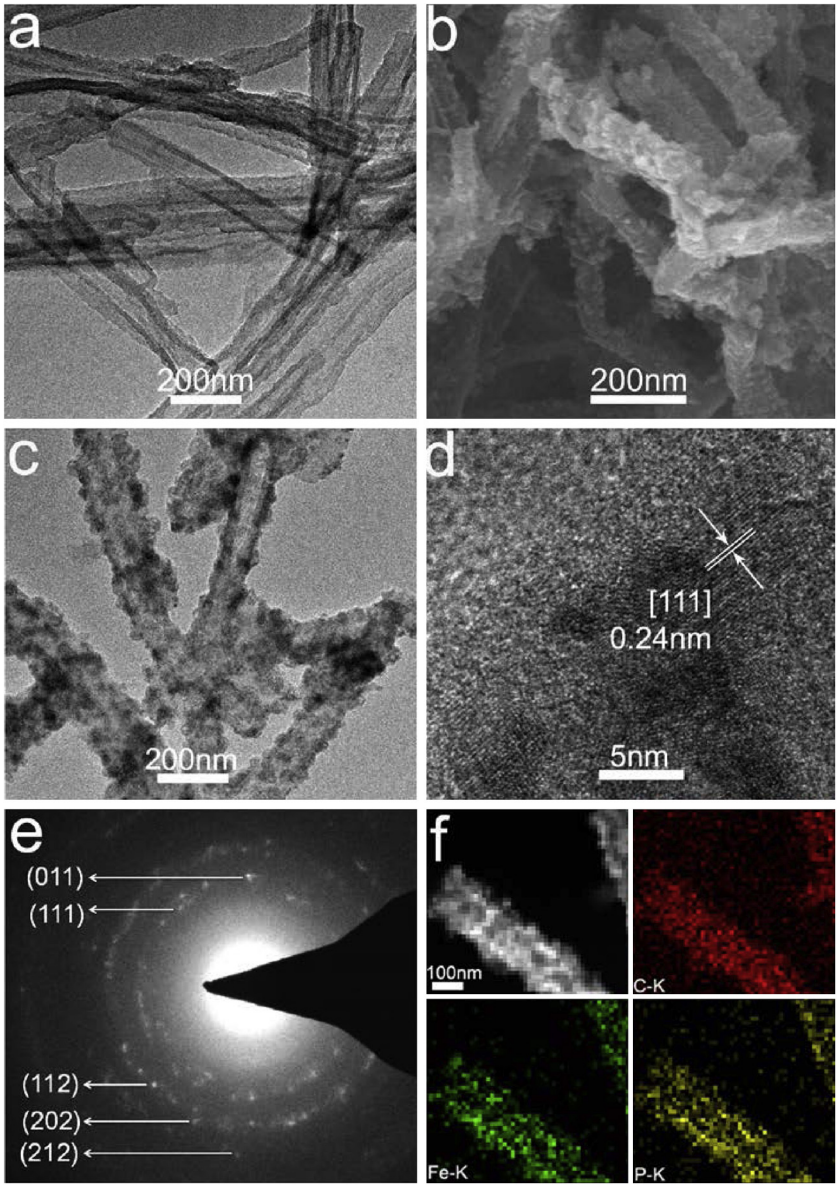

Fig. 1. (a) TEM image of NCNT. (b) SEM and (c) TEM images of FeP/CNT. (d) HRTEM image and (e) SAED pattern of FeP nanoparticles. (f) STEM image and EDX elemental mapping of C, Fe, and P for the FeP/NCNT.