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Nitrogen and gold nanoparticles co-doped carbon nanofiber hierarchical structures for efficient hydrogen evolution reactions

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ABSTRACT

A novel hierarchical structure was fabricated by integrating gold nanoparticles (AuNPs) on nitrogen-doped carbon nanorods encapsulating carbon nanofibers (AuNPs@NCNRs/CNFs), and the composite was demonstrated as an electrocatalyst for the hydrogen evolution reaction (HER). First, polyaniline nanorods (PNRs) were grown on the surfaces of the CNFs, and the PNR/CNF hybrids were then decorated with small, well-dispersed and size-controlled AuNPs. The morphology, structure and chemical states of the AuNPs@NCNRs/CNFs hybrids were characterized by field emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The AuNPs@NCNRs/CNFs can be used directly as an electrode and exhibit good HER activity with a relatively low onset potential of 126 mV, a Tafel slope of 93 mV dec^{-1} and remarkable durability in 0.5 M H_2SO_4. The enhancement of the HER activity could be attributed to the synergetic effect between the nitrogen-doped carbon fibers and the AuNPs.

1. Introduction

Developing new electrocatalysts to produce renewable and clean energy from abundant and easily accessible resources is among the most challenging and demanding tasks for today's scientists and engineers. Due to its high calorific value and the fact that it is clean, pollution-free, environmentally friendly, and produces low-carbon energy, hydrogen is considered one of the most promising green energy sources of the 21st century [1,2]. Thus, the ability to effectively produce hydrogen has become one of the most active research areas [3]. The ability to electrochemically split water into hydrogen and oxygen has been realized for over 200 years. Nonetheless, highly effective, earth-abundant catalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are still in high demand [4]. Thus far, noble metal catalysts, which are comprised of industrial and platinum group metals, have been the most widely used electrocatalytic materials and remain the most efficient catalysts for the HER, capable of driving significant currents close to their thermodynamic potentials.

To enhance the electrocatalytic activity of carbon-based materials, many heteroatom-doped carbon-based materials have been extensively studied. For example, Nitrogen and phosphorus dual-doped graphene has been discovered to be an efficient HER catalyst, which showed significantly improved electrochemical performance compared with single doped counterparts [5]. Cobalt and nitrogen co-doped nanocarbons were also studied and found that it exhibited a remarkable electrocatalytic activity toward HER and stability at all pH value (pH 0–14) [6,7]. Typically, rich reserves of 3d transition metals (TMs) on the earth such as Fe, Co and Ni have been proven to be promising catalytic materials for HER in alkaline conditions [8–12]. However, 3d TMs are unstable in acidic conditions, thus limiting their application [13]. Due to the good catalytic activity and stability, AuNPs have proven to be a good catalyst for HER [14,15].

For a long time, the applicability of non-metallic catalysts to water splitting was overlooked. Zou et al. have summarized some noble metal-free catalysts for HER and indicate that the non-precious-metal catalysts exhibit promising and appealing applications in water splitting [16]. In recent studies, nitrogen-containing carbon materials have received increasing attention because nitrogen incorporation enhances the electron-donor or basic capacities of the carbon material, thereby enhancing its electrocatalytic activity [17]. According to previous reports, the electrocatalytic performance of the nitrogen-doped carbon materials based on different nitrogen sources is obviously diverse [18]. The enhanced catalytic activity of these materials can be associated with lone electron pairs of the pyridinic Ns and the presence of

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more electrons in the delocalized π-orbitals of the carbon framework (due to the higher number of electrons from the nitrogen atoms*) [19]. Nitrogen-doped carbon materials are widely used in the oxygen reduced reaction (ORR) but rarely for the hydrogen evolution reaction (HER). [20–22] We propose modifying nitrogen-doped carbon materials with a metal to improve the overall current density of the HER. Due to the advantages of fine particle and size controllability, AuNPs have been widely used in sensors [23], electrochemical biorecognition-signaling systems [24], Fenton reactions by light, [25] the ORR [26], etc., but rarely for the HER.

Herein, we attempted to design a new structure by integrating AuNPs on nitrogen-doped carbon nanorods encapsulating carbon nanofibers (AuNPs@NCNRs/CNFs) as the electrode material for the HER. In the present investigation, polyaniline nanorods (PNRs) were first grown on the surfaces of CNFs, and the PNR/CNF hybrid were then decorated with small, well-dispersed and size-controlled AuNPs. The AuNPs@NCNRs/CNFs were prepared through chemical complexation followed by a carbonization process. The associated morphology, microstructure and electrocatalytic performance were further investigated and are discussed below.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN), perchloric acid ($HClO_4$), aniline, dimethyl formamide (DMF), and thioglycolic acid (TA) were all purchased from Aladdin Chemistry Co., Ltd. Ammonium persulfate (APS) and chloroauric acid ($HAuCl \cdot 4H_2O$, 99.9%) were purchased from Shanghai Civi Chemical Technology Co., Ltd. All of the reagents were used without further purification. Deionized water (DIW, 18.2 MΩ) was used for all solution preparations.

2.2. Preparation of PAN-based carbon nanofibers (CNFs)

Typically, 5 g of PAN powder was dissolved in 45 ml DMF under magnetic stirring at 65 °C and then electrospun into PAN nanofibers. The voltage, distance and fluid flow rate were 15 kV, 20 cm and 0.6 ml h^{-1}, respectively. Subsequently, the CNFs were prepared by pre-oxidation at 280 °C in air and subsequent carbonization of the PAN nanofibers under Ar atmosphere at 1000 °C. The heating rate was 5 °C min^{-1} in both cases.

2.3. Fabrication of NCNRs/CNFs

The PANI nanorod (PNR)/CNF nanostructures were first synthesized through an *in situ* reaction between the CNFs and an aniline solution under nitrogen protection. The typical steps of this process are as follows: 50 mg CNFs were added to a 0.01 M aniline monomer solution under mild stirring, after which 4 ml of perchloric acid was added to the unreacted suspension. After stirring for 20 min, 1 ml of anhydrous ethanol was dropped slowly into the mixture. Next, 40 ml of 0.04 M APS solution was added to the suspension drop by drop, and polymerization was accomplished via an ice bath. When the solution became blackish green, the mixture was stirred mildly for another 5–6 h. Finally, the resulting PNRs/CNFs were washed with deionized water and anhydrous ethanol three times and dried for 36 h at 30 °C. The nitrogen-doped carbon nanorods (NCNRs)/CNFs were obtained by calcining the PNRs/CNFs under the protection of Ar gas.

2.4. Fabrication of AuNPs@NCNRs/CNFs

First, 200 mg of PNRs/CNFs was added to 1 M ammonia for 30 min and then washed with deionized water and ethanol several times. The resulting samples were mixed with 0.6 g TA solution under mild stirring for 1 h. The mixture was then re-dispersed in

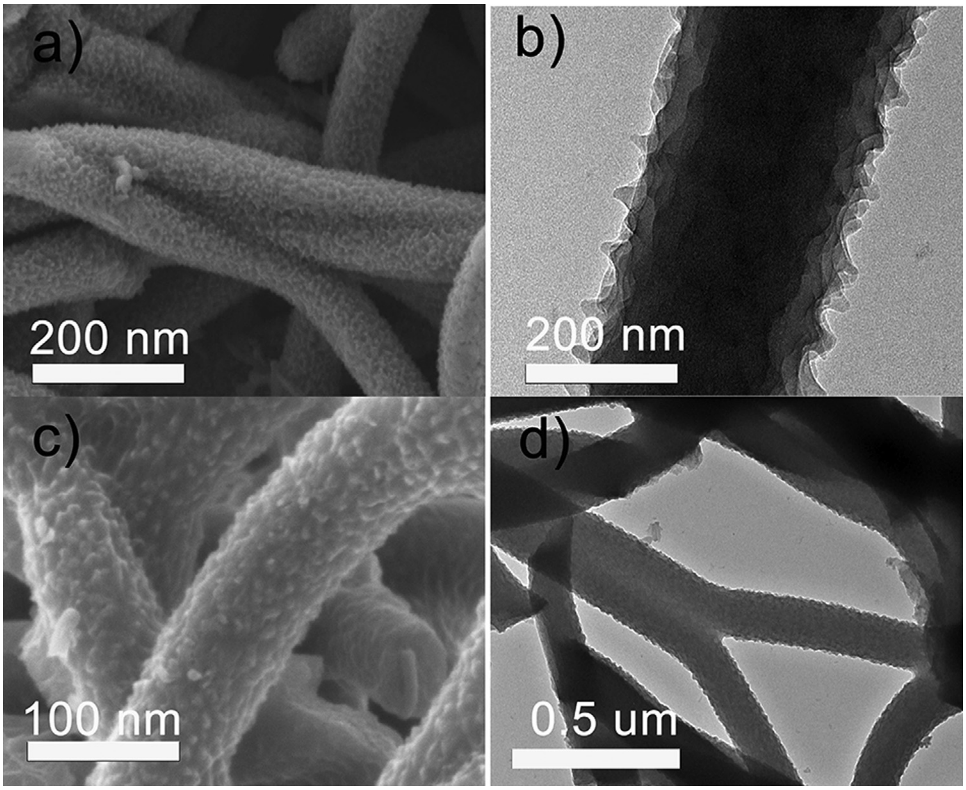

Fig. 1. FE-SEM and TEM images of (a, b) PNRs/CNFs, and (c, d) NCNRs/CNFs.