



# Electrospun nickel-decorated carbon nanofiber membranes as efficient electrocatalysts for hydrogen evolution reaction



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## ABSTRACT

In this work, hierarchical nanostructures of nickel (Ni)-decorated carbon nanofibers have been obtained via a facile electrospinning technique and subsequent carbonization process for using as efficient catalysts of hydrogen evolution reaction (HER). During the carbonization process, nickel ions are reduced into Ni nanoparticles while polyimide nanofibers are simultaneously converted into carbon nanofibers. Moreover, the amount of Ni nanoparticles decorated on the nanofibers can be easily tuned by adjusting the content of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in the electrospinning solution. SEM and TEM characterizations of the nanocomposites show Ni nanoparticles are uniformly distributed on the surface or partly embedded in the nanofibers, ending intimate interactions and efficient charge transport between the nanoparticles and conducting carbon nanofiber network. Therefore, a low overpotential of  $-0.17\text{ V}$  and a high current density of  $3.05\text{ mA cm}^{-2}$  at  $\eta = 200\text{ mV}$  are measured for the 8% Ni-decorated carbon nanofiber membrane, suggesting a relatively high catalytic activity for HER. This versatile and low-cost method may pave a way for fabricating high-performance metal-carbon nanocomposites for various applications.

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## 1. Introduction

The industrial development in the last decades has a heavy dependency on fossil fuels. However, the gradual decline of fossil fuels reserving along with environmental pollution problems calls for urgent utilization of sustainable energy resources. Hydrogen, as a clean and fully recyclable resource with a practically unlimited supply, has been increasingly considered as the “fuel of the future” [1–4]. Currently, one effective way to prepare hydrogen is splitting of water where hydrogen can be produced using electricity obtained from renewable sources, thus making it economically and environmentally attractive [5–9]. However, the high energy consumption of water splitting hinders its large-scale application. In order to alleviate the energy consumption as well as the equipment cost, more and more efforts have been focused on lowering the overpotentials of electrode reactions, implying that electrode materials with high electrocatalytic activity are highly needed.

Actually, the activity of electrode materials is mainly based on their microstructure. Noble metals like Pt, Pd with  $d^{9s^1}$  and  $d^{10s^0}$  electronic configuration exhibit minimum overpotentials [10,11]. However, despite the high activity for hydrogen evolution reaction (HER), the high investment cost and low abundance of noble

metals are the main obstacles that limit their industrial applications. Thus, it is highly desirable to find alternative nanomaterials to replace the noble metal catalysts. Ni is one kind of transition metals, which has potential applications in many fields, such as lithium ion batteries [12], magnetic materials [13], and catalysis [14]. Moreover, Ni has been considered as a good electrocatalyst candidate for HER due to its high abundance, low cost and relatively high electrocatalytic activity [15,16]. However, the tendency of severe nanoparticle aggregation will decrease the specific surface area, yielding an inferior electrochemical activity. Thus, an effective strategy to solve these problems is to increase the surface area by loading Ni on catalyst substrates [17–20].

Carbon-based nanomaterials (e.g., graphene, carbon nanotubes and carbon nanofibers) have been widely exploited as catalyst substrates in  $\text{H}_2$  production due to their excellent resistance to corrosion, superior thermal stability and mechanical strength. Electrospinning is an efficient and versatile technique to produce nanofibers with large specific surface area, high porosity and superior mechanical properties [21,22]. Carbon nanofibers can be easily obtained from a few number of polymers, such as polyacrylonitrile, polyimide (PI), poly(vinyl alcohol), poly(vinylidene fluoride) and pitch via electrospinning technique and subsequent calcination process [23]. Among them, PI has been extensively investigated for its attractive properties such as high thermal stability, excellent mechanical property and good chemical resistance, making it a class of high-performance engineering

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plastics applied in aerospace, automobile and microelectronic industries [24,25]. Therefore, electrospun PI based carbon nanofibers can be widely employed in the substrate materials for electrochemically active catalysts.

Approaches to load electrochemical active materials on carbon materials include electrochemical reduction of metal ions by chemical vapor deposition, in situ chemical reduction of metal salts using reducing agents, and so on [26–28]. However, these approaches are complicated and energy intensive. Hence, a simple and cost-effective strategy to load electrochemical active materials on carbon materials remains a great challenge. In this work, Ni-decorated carbon nanofibers are directly produced from the precursor solution of  $\text{Ni}^{2+}$ /poly(amic acid) (PAA) (the precursor of polyimide) via a facile method by combining electrospinning and calcination process, which is simple, efficient and energy saving. Morphological characterizations show that Ni nanoparticles are uniformly distributed on the surface or partly embedded in the nanofibers. The nanofiber membranes with hierarchical nanostructures thus obtained show an efficient catalytic activity toward hydrogen evolution, making them promising candidate for electrocatalytic hydrogen production.

## 2. Experimental

### 2.1. Reagents

Pyromellitic dianhydride (PMDA), 4,4'-oxydianiline (ODA), nickel (II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and N,N-dimethylacetamide (DMAc) were commercially purchased from Sino-pharm Chemical Reagent Co. Ltd. All other reagents were purchased from Aladdin Chemical Reagent Co. Ltd. and used without any further treatment.

### 2.2. Preparation of Ni decorated carbon nanofibers

PAA precursors were synthesized from the polycondensation of amic acid. After reaction for 5 h under intense mechanical stirring, a yellow viscous solution was obtained. Then, the PAA solution was mixed with DMAc containing different amount of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and the final mass content of PAA was fixed at 15 wt %. The electrospinning solution was loaded into a 5 mL syringe equipped with a stainless spinneret in diameter of 0.5 mm. The spinneret simultaneously served as an electrode, to which a high voltage was attached. Then, electrospun fibers were collected onto a flat aluminum foil, which is positioned 15 cm away from the needle

typically connected with the counter electrode. The electrospun nanofiber membranes were dried overnight at  $80^\circ\text{C}$  in vacuum oven to remove the residual solvent and then thermally imidized to PI under  $\text{N}_2$  atmosphere under the program as previously reported [29].

Calcination process was conducted in a ceramic tube furnace under a high purity nitrogen atmosphere at  $800^\circ\text{C}$  for 2 h (heating rate of  $5^\circ\text{C min}^{-1}$ ). During the carbonization process, PI nanofibers were converted into carbon nanofibers. At the same time,  $\text{Ni}^{2+}$  ions were converted into Ni nanoparticles and thus partly embedded in the nanofibrous hybrid membranes. The whole preparation procedure of the hybrid nanofiber membranes was shown in Fig. 1. Here, Ni/C nanofiber hybrid membranes with different  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  contents (3%, 5%, 8%) are labelled as 3% Ni/C, 5% Ni/C, 8% Ni/C, respectively.

### 2.3. Characterization of Ni decorated carbon nanofibers

Surface morphology of the samples was characterized by field emission scanning electron microscopy (FESEM, Zeiss) at an acceleration voltage of 5 kV. All samples were coated with a layer of gold before FESEM observation. Energy dispersive X-ray (EDX) spectroscopy was performed to investigate the chemical composition. Transmission electron microscopy (TEM) observation was performed using a JEOL JEM 2100 TEM operating at 200 kV. Phase structure of the samples was examined by X-ray diffraction (XRD) with Cu-K $\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ ) under a voltage of 40 kV and a current of 40 mA.

### 2.4. Electrochemical studies

All electrochemical studies were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua Instrument Co., China) using a standard three-electrode testing system. The as-prepared Ni-decorated carbon nanofibrous membranes were directly cut into small pieces and then pasted on the glass carbon electrode with Nafion as a working electrode. Ag/AgCl electrode was used as the reference electrode and the potential was calibrated to the reversible hydrogen electrode (RHE) at the end. Platinum (Pt) wire was used as the counter electrode. The electrocatalytic activity of Ni-decorated carbon nanofiber membranes for HER was studied using liner sweep voltammetry (LSV), which was carried out at a scan rate of  $2 \text{ mV/s}$  at room temperature. Polarization curves were recorded in nitrogen purged 2 M KOH solution for Tafel analysis. For AC impedance measurements, the generator provided an amplitude of 5 mV in the frequency range

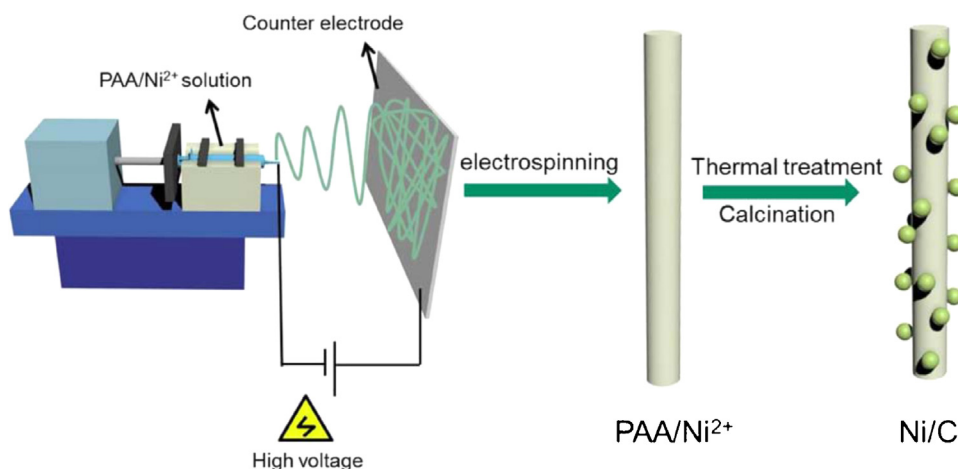


Fig. 1. Schematic of the preparation of Ni-decorated carbon nanofibers.

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