



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 V and a high current density of 3.05 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 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 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°C in vacuum oven to remove the residual solvent and then thermally imidized to PI under 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°C for 2 h (heating rate of 5°C min^{-1}). During the carbonization process, PI nanofibers were converted into carbon nanofibers. At the same time, 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 α 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 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

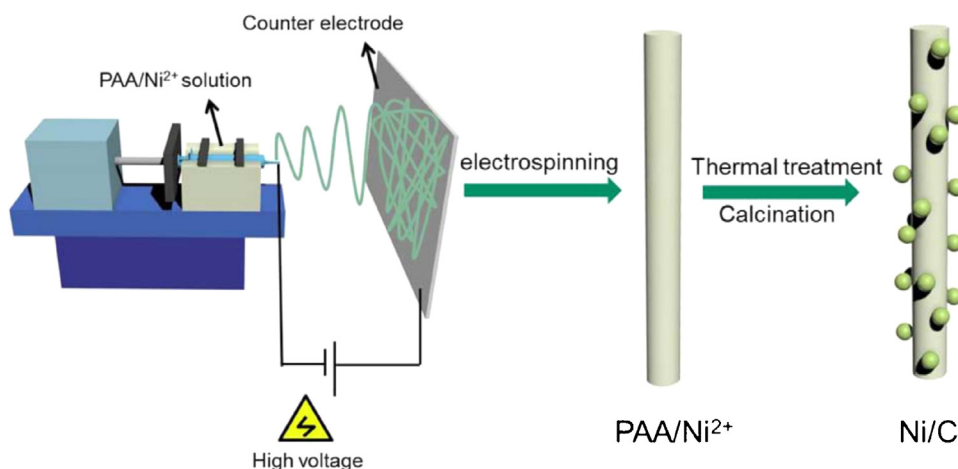


Fig. 1. Schematic of the preparation of Ni-decorated carbon nanofibers.

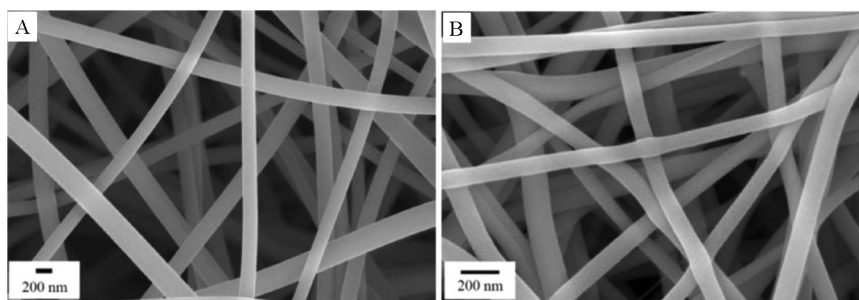


Fig. 2. FESEM images of (A) PAA nanofibers and (B) Ni²⁺/PAA nanofibers.

swept between 10^{-2} and 10^6 Hz. All these tests were carried out in oxygen free 2 M KOH solutions which were achieved by bubbling nitrogen through the solution for 20 min before the experiments.

3. Results and Discussion

3.1. Structural and morphological characterization of Ni decorated carbon nanofibers

Being mixed with DMAc containing different amount of Ni(NO₃)₂·6H₂O, the solid content of PAA solution was fixed at 15 wt%, providing an appropriate viscosity for electrospinning. Fig. 2A and B show the FESEM images of pure PAA and Ni²⁺/PAA nanofibers, respectively. It can be seen that the surface of electrospun nanofibers is smooth and almost free of beads or breakages, indicating that these precursor solutions have good spinnability. The diameter of pure PAA nanofibers is about 200–250 nm while the Ni²⁺/PAA hybrid nanofibers have a diameter of about 100–150 nm. The decrease of diameter is due to the increased surface tension of electrospun solution caused by the introduction of Ni(NO₃)₂·6H₂O, which needs a higher voltage to offset the surface tension [30]. Generally, higher voltage can also result in a smaller diameter during electrospinning process. Nevertheless, a stable jet cannot be obtained with the increase of salt content and

voltage. Therefore, the optimized solid content of Ni(NO₃)₂·6H₂O in our work was adjusted to a proper value of 8 wt %.

After being imidized and carbonized under N₂ atmosphere, PAA nanofibers were converted into carbon nanofibers and Ni²⁺ in the electrospinning solution was simultaneously reduced and aggregated into Ni nanoparticles. Nanofibers were carbonized to impart the hybrid materials excellent electrical conductivity. Furthermore, a series of Ni-decorated carbon hybrid nanofiber membranes were prepared by simply adding different amount of Ni(NO₃)₂·6H₂O into the precursor solutions. Morphologies of carbon nanofibers and Ni-decorated carbon hybrid nanofibers were also investigated by FESEM, as shown in Figs. 3 and 4. From the FESEM images, it can be observed that Ni nanoparticles are directly grown and anchored on the nanofibers. The intimate contact affords efficient electron transport between the nanoparticles and carbon nanofibers, which is key to the high electrocatalytic activity of Ni-decorated carbon nanofibers. Moreover, with the increase of solid content of Ni(NO₃)₂·6H₂O, the density of Ni nanoparticles becomes higher. This is probably caused by the increase of nucleation sites during the formation of Ni nanoparticles. In addition, the formation of Ni nanoparticles on the carbon nanofibers can be explained by heat-driven process and subsequent particlization after calcination [31]. Moreover, the highly porous structures of Ni-decorated carbon hybrid nanofibers obtained by electrospinning exhibit

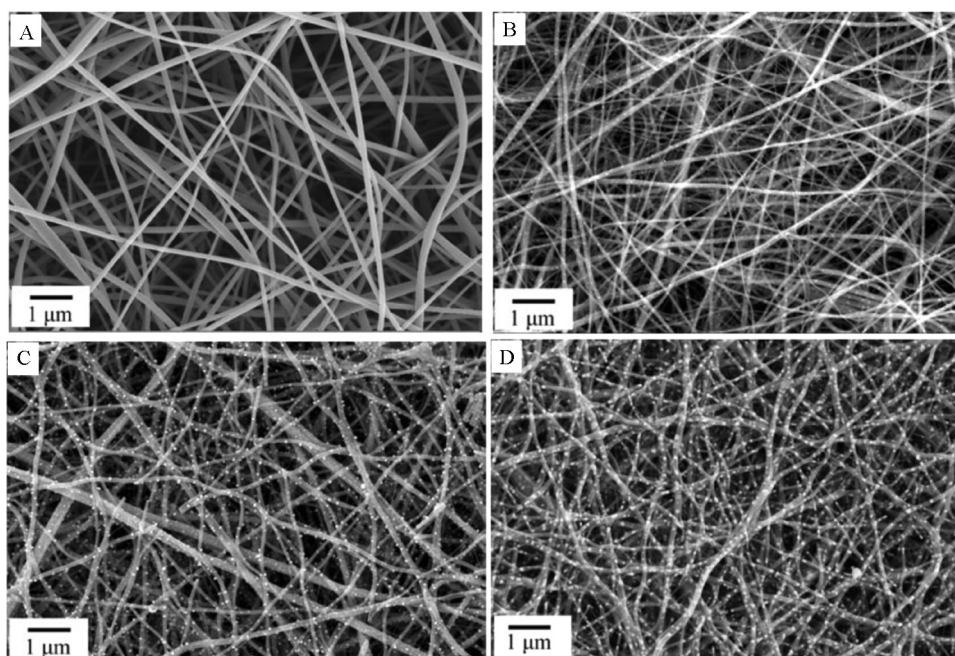


Fig. 3. Low magnification FESEM images of Ni-decorated carbon nanofibers from different Ni(NO₃)₂·6H₂O contents: (A) 0% Ni/C; (B) 3% Ni/C; (C) 5% Ni/C; (D) 8% Ni/C.

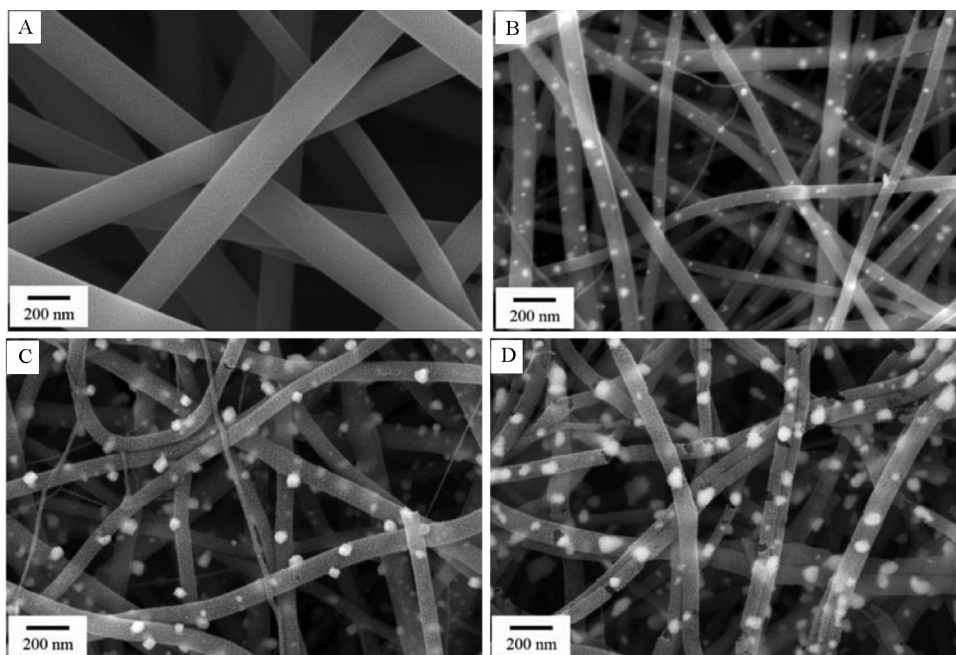


Fig. 4. High magnification FESEM images of Ni-decorated carbon nanofibers from different $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ contents: (A) 0% Ni/C; (B) 3% Ni/C; (C) 5% Ni/C; (D) 8% Ni/C.

large specific surface area, which is beneficial for the hydrogen production process from water splitting.

The EDX characterization is used to investigate the elemental distribution in the hybrid nanofibrous membranes as shown in Fig. 5. The results indicate that the membranes are mainly composed of C, Ni and O, with the carbonaceous framework uniformly decorated with Ni. Moreover, the trace amounts of oxygen can be ascribed to the residual oxygen functional groups remaining on the membranes after calcination [32].

To further investigate the morphology of samples, TEM images of Ni-decorated carbon nanofibers (8% Ni/C) are shown in Fig. 6. It reveals that Ni nanoparticles are distributed on the surface or partly embedded in the nanofibers after the calcination process.

According to the TEM images, the average diameter of Ni nanoparticles is estimated to be about 60 nm. As Ni nanoparticles are partly embedded in the nanofibers, they are difficult to peel off from the carbon nanofibers, enabling a good stability of the hybrid materials. Moreover, it also provides a large interface area between the two components, through which charge and electrolyte transfer processes can work synergistically.

The corresponding XRD patterns of the samples are presented in Fig. 7 to confirm the structure of Ni nanoparticles decorated on the nanofibers. Compared to the XRD curve of pure carbon nanofiber membrane in Fig. 7A, the additional diffraction peaks at $2\theta = 44.6^\circ$, 51.9° and 76.4° in Fig. 7B–D can be indexed as (111), (200) and (220) crystal planes of the face-centered cubic

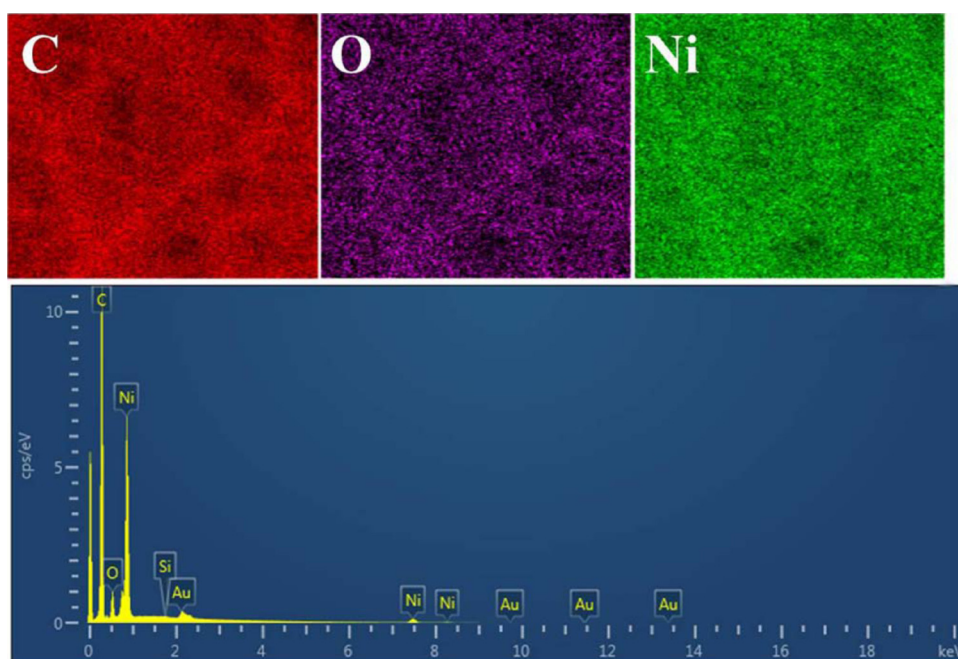


Fig. 5. (A) FESEM image of 8% Ni/C nanofibers and its corresponding elemental mappings for (B) C, (C) Ni, and (D) O. (E) The corresponding EDX spectrum.

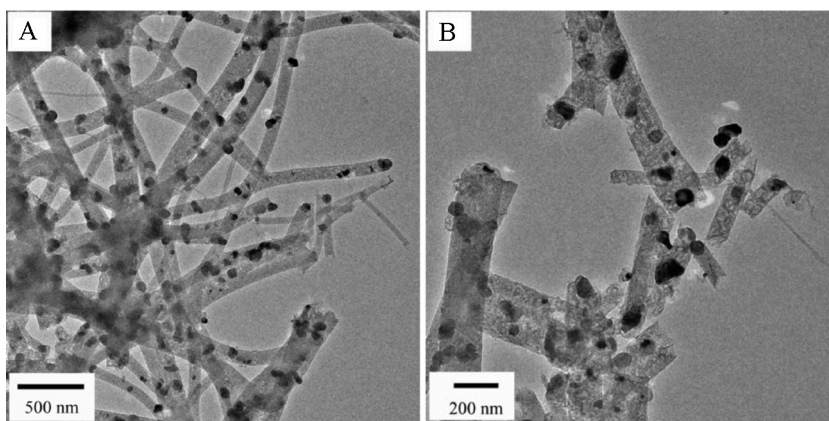


Fig. 6. TEM images of 8% Ni/C nanofibers at low (A) and high (B) magnifications.

Ni (JCPDS 65-2865). Therefore, the XRD results indicate that Ni^{2+} ions were reduced to Ni after calcination. Moreover, the intensity of the diffraction peaks was enhanced as the solid content of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ increased, which was ascribed to the the degree of crystallinity.

3.2. Electrocatalytic activity of the electrodes for hydrogen evolution reaction

The electrocatalytic activity of Ni-decorated carbon nanofibers toward HER was investigated in 2 M KOH solution using a standard three-electrode testing system. LSV polarization curves of 0% Ni/C, 3% Ni/C, 5% Ni/C and 8% Ni/C nanofiber membranes are shown in Fig. 8A. For a better comparison of the HER activity of all the samples, the current densities at overpotentials of -0.15 V and -0.2 V are recorded from the LSV curves and are presented in Fig. 8B. It can be seen that pure carbon nanofiber membrane exhibits little activity for HER. However, Ni-decorated carbon nanofiber membranes show significant enhancement in current density and obvious potential shift compared to the pure carbon nanofiber membrane, which clearly demonstrates the inherent catalytic activity of Ni nanoparticles for HER. However, carbon nanofibers also play an important role in the HER process as the excellent conducting nature facilitates fast and efficient electron transport from Ni nanoparticles to the charge collector via the conducting network of carbon nanofibers. Besides, it also suggests that the number and size of nanoparticles are contributing factors to the different electrocatalytic performance exhibited by the series of hybrid materials. With the increase of the density of Ni nanoparticles, larger interfacial area between the two components

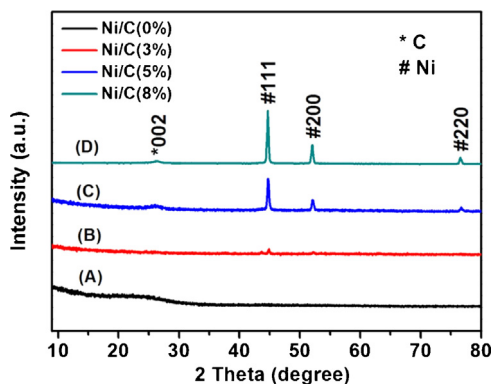


Fig. 7. XRD curves of Ni-decorated carbon nanofibers from different $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ contents: (A) 0% Ni/C; (B) 3% Ni/C; (C) 5% Ni/C; (D) 8% Ni/C.

and more reactive sites are provided, affording a superior electrocatalytic activity compared to the other samples [33].

The Tafel plots for pure carbon nanofibers and Ni-decorated carbon nanofibers are shown in Fig. 9. The linear portions of the Tafel plots follow a typical Tafel behavior (following equation: $\eta = b \log(j) + a$, where η is the overpotential, j is the steady-state current density and b is the Tafel slope), yielding Tafel slopes of 286, 120, 111 and 105 mV/decade for 0% Ni/C, 3% Ni/C, 5% Ni/C and 8% Ni/C

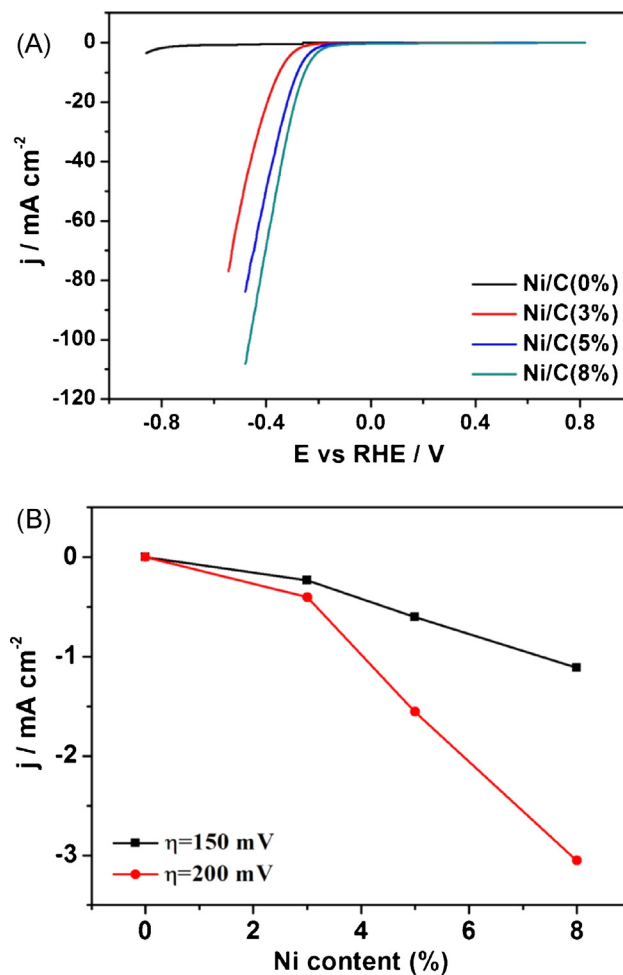


Fig. 8. (A) LSV polarization curves of Ni-decorated carbon nanofiber electrodes in nitrogen purged 2 M KOH solution. Scan rate: 2 mV/s. (B) Current densities for Ni-decorated carbon nanofiber electrodes with various Ni contents at overpotentials of 150 and 200 mV, respectively.

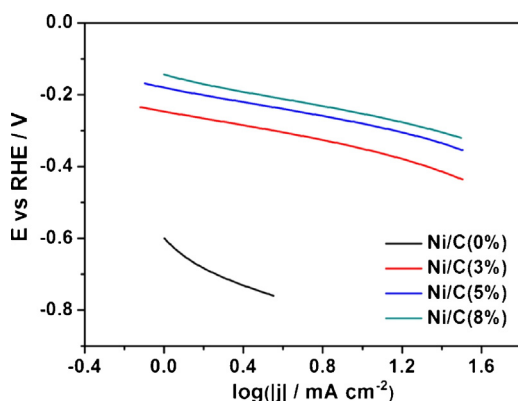
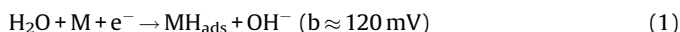


Fig. 9. Tafel plots for Ni-decorated carbon nanofibers.

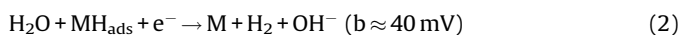
samples, respectively. The 8% Ni/C sample shows the lowest overpotential at -0.17 V (vs. RHE) and Tafel slope of 105 mV/decade in the series, indicating a higher electrocatalytic activity for HER. The characters of high density and large size of Ni nanoparticles decorated on the nanofibers are all critical to higher electrocatalytic activity. Larger interfacial area between carbon nanofibers and Ni nanoparticles leads to higher apparent current density at a specified overpotential.

Three possible reaction steps have previously been suggested for HER in alkaline media [17].

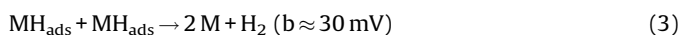
Discharge reaction (Volmer step):



Electrochemical desorption reaction (Heyrovsky step):



Combination reaction (Tafel step):



On the basis of the Tafel slope value, the result is close to 120 mV/decade, which is in good line with the typical values obtained for HER with nickel electrodes in alkaline solutions in the previous work [34]. Therefore, here the Volmer step is considered as the rate determining step of the HER with Ni-decorated carbon nanofiber electrocatalyst. Namely, the adsorption of H_2 onto the active Ni nanoparticle sites is a slow step in the HER. Moreover, a smaller Tafel slope is preferred in HER as a smaller change in electrode overpotential can generate a larger increase in current, resulting in a faster hydrogen gas production. Compared to the Ni catalysts reported previously [17,35,36], our materials show a

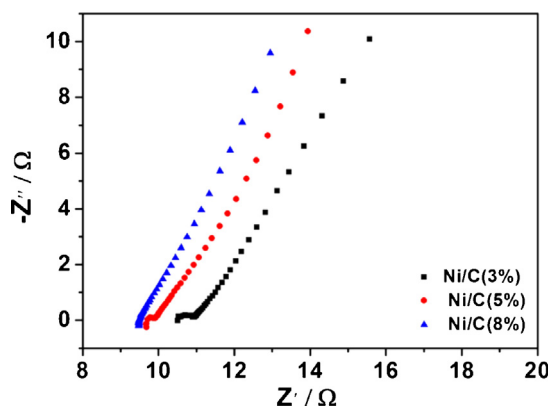


Fig. 10. AC impedance spectroscopy of Ni-decorated carbon nanofibers in 2 M KOH from 10^{-2} to 10^6 Hz with an AC amplitude of 5 mV.

superior electrochemical activity with a low overpotential and Tafel slope. Besides, the preparation process is facile and energy-saving compared to the conventional electrochemical deposition method.

AC impedance measurements of the Ni/C nanofiber membranes were conducted to further investigate the catalytic activity, in the frequency range of 10^{-2} to 10^6 Hz at open-circuit voltage with an AC amplitude of 5 mV in a 2 M KOH aqueous solution. It can be seen in Fig. 10 that, 8% Ni/C nanofiber membrane shows a lower charge-transfer resistance compared to other samples, which can be attributed to more active sites provided by Ni nanoparticles decorated in the nanofibers. Besides, the lower charge-transfer resistance indicates an easier electrochemical reaction, which is in accordance with the results shown in Fig. 8.

4. Conclusions

In summary, Ni-decorated carbon nanofibers have been prepared from earth-abundant and inexpensive components via a facile fabrication method combining electrospinning technique and subsequent calcination process. Both the well distribution of Ni nanoparticles and the three-dimensional carbon nanofiber network are important to their high electrocatalytic activity toward hydrogen evolution reaction. With a larger interfacial area between the two components and more reactive sites, the 8% Ni-decorated carbon nanofiber membrane exhibits a relatively high catalytic activity for HER with a low overpotential of -0.17 V and a high current density of 3.05 mA cm^{-2} at $\eta = 200$ mV. Furthermore, the as-prepared Ni-decorated carbon nanofiber membranes show superior advantages, such as low cost, easy preparation and energy-saving compared to those materials previously prepared via electrodeposition, thus making it promising for widespread employment in hydrogen production applications.

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