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Small and well-dispersed Cu nanoparticles on carbon nanofibers: Self-supported electrode materials for efficient hydrogen evolution reaction



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ABSTRACT

In this study, a facile and effective approach was demonstrated for designing and preparing small Cu nanoparticles (NPs) densely and uniformly distributed on carbon nanofibers (CNFs). Self-supported hybrid CuNPs/CNFs with three-dimensional (3D) architectures were prepared via electrospinning and thermal reduction processes. The hybrid CuNPs/ CNFs were directly used as electrodes for an electrocatalytic hydrogen evolution reaction (HER), and they exhibited excellent activity, with a low onset potential of only 61 mV, an overpotential of 200 mV at 10 mA cm⁻², a small Tafel slope (152 mV dec⁻¹) and a long-term stability in acidic electrolyte. The 3D self-supported architecture exhibited a high conductivity, a large specific surface area and a high porosity, all of which are beneficial for the access of electrolyte for the CuNPs and the release of the formed H_2 , thereby reducing the overpotentials and accelerating the electrode kinetics. This work demonstrates that CuNPs/CNFs are promising candidates for the substitution of noble metal Pt-based materials in producing the HER from water.

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Introduction

Over the last several decades, environmental pollution and resource exhaustion have escalated, and more and more researchers have been paying close attention to clean and renewable energy, especially hydrogen [1]. It is known that hydrogen is the most promising clean energy because it is sustainable, free of contamination, and high in energy density [2]. There are several technologies available for producing hydrogen, such as electrocatalytic water splitting, biohydrogen production and photocatalytic water splitting. Electrocatalytic water splitting, namely, the hydrogen evolution reaction (HER), is a promising and economical method for large-scale commercial applications because of its high efficiency, simplicity and environmental friendliness [3]. Pt and Pt-based materials are the best electrocatalysts for the HER

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due to their very low overpotentials, small Tafel slopes and tremendous current density. However, their major drawbacks of high costs and insufficient resources severely restrict their practical applications in industrial production [4]. Therefore, discovering earth-abundant non-noble metal electrocatalysts, such as copper, iron, nickel and cobalt, to replace Pt-based materials is urgent for satisfying the rapidly increasing energy demand and for ameliorating environmental pollution [5].

Earth-abundant and low-cost Cu-based materials have recently attracted more attention, particularly due to their favorable electrical conductivity and excellent catalytic activity [6]. Thus, Cu-based nanomaterials play a key role in many fields, including photocatalysis, electrocatalysis and the reduction of carbon dioxide. Zhao et al. prepared hierarchical branched Cu₂O-nanowire photocatalysts that exhibited remarkable catalytic activities for photocatalytic H₂ production from water [7]. Zhang et al. reported the fabrication of an interdigitated architecture of Cu metal-organic frameworks (MOFs) using chiral ligands for enantioselective recognition and electrocatalysis [8]. Several methods can be used for the preparation of Cu-based materials, such as chemical treatment, photochemical techniques and thermal treatment. Because of their high surface energy, small Cu nanoparticles are very difficult to control and are prone to agglomeration during catalytic reactions. In addition, Cubased materials are rarely utilized as electrocatalysts for the electrocatalytic HER.

To date, carbon-based materials, such as carbon nanotubes (CNTs) and graphene, have been extensively employed as conductive supports [9,10]. These carbonaceous materials can effectively control the size, prevent the agglomeration and promote the uniform distribution of the nanocrystals, forming more active catalysts. In addition to the above carbonaceous materials, electrospun carbon nanofibers (CNFs) have attracted widespread attention due to their excellent mechanical properties, intriguing physical properties and chemical stability as well as their high electrical and thermal conductivity [11]. Recently, our groups have designed several CNFs based on hybrid noble metal and transition metal dichalcogenide (TMD) nanomaterials, serving as efficient HER catalysts [12]. The CNFs can serve as nanoreactors for the growth of nanocrystals. The control of the size, shape and dispersion of nanocrystals on CNFs is essential for the highly active HER activity [13]. To the best of our knowledge, only a few studies have focused on the preparation of HER catalysts based on Cu nanoparticles.

In this work, we describe a facile and effective method for fabricating CuNPs/CNFs hybrid nanomaterials with three-dimensional (3D) architectures, serving as highly efficient HER electrode materials. The size, morphology and dispersion of the CuNPs can be controlled by CNFs. The 3D CuNPs/CNFs nanofibrous membranes can be directly used as electrodes for the HER. The CuNPs/CNFs electrode shows an excellent HER activity and a long-term stability up to 10 h as well as a high cathodic current density. The non-noble metal CuNPs/CNFs are promising electrocatalysts to replace the Pt-based material electrocatalysts for HER.

Experiments

Preparation of CuNPs/CNFs hybrid membrane

In brief, 1.5 g of PVA powder and 0.075 g of CuCl₂ were both dissolved in 11 mL deionized water at 80 °C under magnetic stirring to form a homogenous solution. Then, the prepared CuCl₂/PVA precursor solution was directly transferred into a syringe with a stainless copper needle at the tip. The applied voltage was 15 kV and the distance between the needle tip and the collector was 12 cm. The feeding rate was 0.3 mL/h. The electrospun CuCl₂/PVA nanofibrous membranes were collected on a parallel plate apparatus covered by a piece of aluminum foil. The obtained CuCl₂/PVA nanofibrous membranes were placed into a home-built chemical vapor deposition (CVD) system for graphitization. The CuCl₂/PVA nanofibers were carbonized at 900 °C for 3 h under Ar/NH₃ atmosphere and then cooled down to room temperature.

Instruments

Field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan), transmission electron microscopy (TEM, JSM-2100, JEOL, Japan), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Tecnai G2 F30S-Twin, Philips-FEI), X-ray photoelectron spectrometry (XPS) (Kratos Axis Ultra DLD) and X-ray diffraction (XRD, Breker AXSD8 DISCOVER) were performed to characterize the as-obtained samples.

Electrochemical characterization

All electrochemical experiments were carried out using the CHI660C electrochemical workstation (Shanghai Chenhua Instrument Company, China) with a standard three-electrode cell testing system at room temperature. The CuNPs/CNFs membranes were cut into a square of 1×1 cm⁻² and directly used as the working electrode. A platinum mesh and a saturated calomel electrode were used as the counter and reference electrodes, respectively. The electrochemical characterization was performed in an aqueous solution of 0.5 M H₂SO₄. Prior to the data collection, the working electrodes were preprocessed under a continuous Ar flow by cyclic voltammetry to bubble away the surface contaminants. The potentials were calibrated against a reversible hydrogen electrode (RHE).

Results and discussion

In the present investigation, the CuCl₂ was mixed with a PVA solution and then electrospun into CuCl₂/PVA nanofibers. After graphitization at 900 °C for 3 h with a heating rate of 5 °C/ min in a home-built CVD system under Ar/NH₃ atmosphere, small CuNPs formed across the PVA-derived CNFs surfaces. As shown in Fig. 1a, the PVA-derived CNFs with smooth surfaces exhibit three-dimensional (3D) conductive networks, which were synthesized by a graphitization process. The average



Fig. 1 – FE-SEM images of the (a) CNFs and (d) CuNPs/CNFs. (b) TEM and (e) HRTEM of CuNPs/CNFs. (c) The HAADF-STEM image and (f) STEM-EDS mapping images of CuNPs/CNFs. (g) The line-scan EDX spectra of the CuNPs/CNFs and inset in Fig. 1g is the SAED pattern of the CuNPs/CNFs. (h) The XRD patterns of CNFs and CuNPs/CNFs.

diameter of the CNFs ranged from 100 to 400 nm. The electrospun CNFs possess high electrical conductivities, large surface areas and superior length to diameter ratios; these networks were employed as a well-suited support frame and reaction vessel to load the CuNPs.

Compared with pure CNFs, a large number of small CuNPs were densely and homogeneously immobilized on the external surface of the CNFs with nearly no aggregation when the CuCl₂/PVA was treated at 900 °C (Fig. 1d). As shown in Fig. 1b, the TEM image further confirms the existence of CuNPs on the CNFs. It can be observed that small and uniform CuNPs were immobilized on the CNFs, and the size of the CuNPs was approximately 5 nm-20 nm. The HRTEM image of CuNPs/CNFs (Fig. 1e) shows two significantly different lattice spacings on the small CuNPs. And the lattice spacing values are approximately 2.1 Å and 1.8 Å, corresponding to the (111) and (200) planes of Cu, respectively. In addition, the CuNPs were surrounded by several graphitic carbon layers and the interlayer distance of the surrounded carbon was approximately 3.6 Å, corresponding to the (002) plane of carbon. The formed CuNPs on the CNFs can be protected from agglomeration and corrosion, which is beneficial to the catalytic activity for the HER. These images show that the CuNPs were successfully synthesized after thermal treatment at 900 °C. Fig. 1c displays the HAADF-STEM images of the typical CuNPs/CNFs

morphology. Most of the CuNPs are indeed located at the surface of the CNFs. In addition, the STEM-EDS mapping images clearly illustrate the elemental distribution. Carbon signals confirm that the CNF substrates are constructed from evenly distributed carbon elements. The bright sky-blue and green spots of the Cu signals align with the bright spots in the red rectangle of the CuNPs, thus confirming the successful synthesis of the CuNPs/CNFs.

Additionally, the line-scan EDX spectra over two CuNPs in the selected region are shown in Fig. 1g. It is indicated that the Cu signals are mainly centered at the bright spots area and further indicate that the small particles (bright spots) were CuNPs. The selected-area electron diffraction of the CuNPs/ CNFs demonstrates the polycrystallinity of the CuNPs. To further investigate the surface structure of the CuNPs/CNFs, the XRD patterns were employed to study the crystal structure of the CuNPs/CNFs and CNFs. As illustrated in Fig. 1g, the CuNPs/CNFs and CNFs both exhibit strong and broad peaks at 24.1°, which can be assigned to the (002) planes of graphitic carbon [14]. The calculated d₀₀₂ value is approximately 3.4 Å, which is close to the lattice spacing of graphitic carbon, as shown in Fig. 1e (3.6 Å). The slight change may be attributed to the influence of the CuNPs. Compared with pure CNFs, the CuNPs/CNFs clearly indicate two new diffraction peaks appearing at 43.3° and 50.4° , which are indexed to the (111)

and (200) planes of the Cu crystals [15]. The calculated d111 and d200 values of the CuNPs are in accordance with the lattice spacings of 2.1 Å and 1.8 Å, as shown in the HRTEM images. The XRD results verify that the former Cu^{2+} ions in the PVA nanofibers were successfully reduced to metallic-state CuNPs and were tightly grown on the surface of the CNFs after the graphitization process.

The XPS spectra were taken to investigate the surface oxidation states and chemical composition of the Cu/CNFs, which are shown in Fig. 2. The survey XPS spectrum of the CuNPs/CNFs presented in Fig. 2a reveals the corresponding peaks of copper, carbon and oxygen, confirming the presence of CuNPs in the CNFs. The Cu 2p XPS spectrum of the CuNPs/ CNFs can be deconvoluted into two distinct peaks located at approximately 932.7 eV and 952.0 eV, which can be ascribed to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively [16,17]. In addition, there are no separate satellite peaks of CuO and Cu₂O observed, and all the peaks of the Cu 2p are in accordance with the peaks of metallic Cu. As shown in Fig. 2c, the C 1s XPS spectrum exhibits three different types of peaks located at 284.9 eV, 286.2 eV and 289.7 eV, which were assigned to the C atoms in the C–C or C–H, C–O or C=C and C=O bonds, respectively. Meanwhile, the distinct peak of the C-C or C-H bond located at 284.9 eV corresponds to the graphitized carbon converted from PVA. The C=O groups originate from the PVA polymer. As demonstrated in Fig. 2d, the O 1s spectrum of the CuNPs/CNFs shows two peaks located at 531.6 eV and 532.8 eV, which are attributed to C=O and C-OH originating from the hydroxyl group in the original PVA. The XPS analysis confirms that the main composition of the catalyst is metallic Cu, which is in accordance with the results of the XRD analysis.

Based on the above results, it is possible that the novel CuNPs/CNFs can be used as excellent catalysts for the HER. Subsequently, the electrochemical performance of the CuNPs/ CNF membrane electrode (Fig. 3) towards HER has been investigated using a typical three-electrode cell testing system in an aqueous 0.5 M H₂SO₄ solution. The CuNPs/CNF membranes were cut into $1 \times 1 \text{ cm}^{-2}$ squares and directly used as the working electrode. A platinum mesh and a saturated calomel electrode were used as the counter and reference electrodes, respectively. Fig. 3a shows the linear sweep voltammetric (LSV) of commercial Pt/C, CuNPs/CNFs and pure CNFs. Apparently, the Pt/C possesses excellent HER activity with nearly zero onset potential, the smallest Tafel slope and a prominent current density. The pure CNF electrode exhibits negligible HER activity with a high onset potential and a very low current density. Compared with pure CNFs, the CuNPs/ CNF membrane electrode exhibits robust HER activity with a lower onset potential of 61 mV and a lower overpotential of 200 mV at a cathodic current density (j) = 10 mA cm⁻². The overpotential at 10 mA cm⁻² of the CuNPs/CNFs only requires 200 mV, and the overpotential at 10 mA cm⁻² approaches to the precious metal electrocatalysts of PtNPs/CNFs according to previous report [18].

The Tafel slope is an important parameter for the HER because it can be used as a simple way to discern the kinetics of a reaction including the Volmer reaction, Heyrovsky



Fig. 2 – The XPS spectra of (a) survey, (b) Cu 2p, (c) C1s and (d) O 1s of the CuNPs/CNFs.



Fig. 3 – (a) The polarization curves of the CNFs, CuNPs/CNFs and Pt/C catalysts obtained in 0.5 M H_2SO_4 with a scan rate of 2 mV s⁻¹. (b) The corresponding Tafel slopes of CNFs, CuNPs/CNFs and Pt/C catalysts. (c) The Nyquist plots of CuNPs/CNFs and CNFs catalysts performed at -0.25 V vs. RHE. (d) The time-dependent current density of the CuNPs/CNFs at a constant voltage of -0.2 V vs. RHE. The insets in Fig. 3d are the enlarged time-dependent current density curve and the photograph of the H_2 bubbles formed on the CuNPs/CNFs membrane at the electrocatalytic process.

reaction or Tafel reaction. From the calculation of the Tafel equation ($\eta = a + blog |J|$, where J, b and η are the current density, the Tafel slope and the onset potential, respectively), the Tafel slope of commercial Pt/C catalysts is 32 mV dec $^{-1}$. For Cu/CNFs, the Tafel slope is 152 mV dec⁻¹, and it is far smaller than the CNFs (335 mV dec^{-1}) and close to that of the commercial Pt/C catalysts (32 mV dec⁻¹). As smaller Tafel slope means that only a small increase in potential can generate a larger catalytic current density. These results indicate the Volmer-Hyrovsky mechanism for the CuNP/CNF electrode. In addition, electrochemical impedance spectroscopy (EIS) is another essential method to evaluate the catalytic properties of the electrode materials for HER. Fig. 3c displays the corresponding Nyquist plots of CuNPs/CNFs and pure CNFs. Obviously, the resistance of the CuNPs/CNFs is much smaller than that of pure CNFs, and the charge transfer resistance (R_{ct}) value of the CuNPs/CNFs is approximately 150 Ω , which can be clearly seen from the inset in Fig. 3c. It is well known that a smaller resistance leads to a faster electron transfer rate for the HER [19].

Thus, with the incorporation of CuNPs into the CNFs, the conductivity of the materials significantly improved. To further evaluate the catalytic activity and stability of the assynthesized Cu/CNFs catalyst in the acidic conditions, a time-dependent current density analysis is performed (Fig. 3d). The CuNPs/CNFs membrane electrode remains

stable in the long-term electrochemical process for 10 continuous hours. Only a small degradation in the current density after 10 h is observed, indicating the strong stability of the CuNPs/CNFs membrane electrodes. As shown in the inset in Fig. 3d, a photograph of the H₂ bubbles formed on the CuNPs/CNFs membrane and a large number of the H₂ bubbles released can be clearly observed during the electrocatalytic process. In addition, the enlarged time-dependent current density curve exhibits zigzag shapes, which are caused by the alternating processes of bubble accumulation and bubble release process. The obtained CuNPs/CNFs exhibit superior HER activity for several reasons. Small and well-dispersed CuNPs grow on the surfaces of the CNFs, which expose more active sites for the HER. The 3D self-support architecture exhibits high conductivity, specific surface area and porosity, which are beneficial for accessing the electrolyte in the CuNPs and for releasing formed H₂, reducing the overpotentials and accelerating the electrode kinetics process. The CNF vessel can protect the CuNPs from agglomeration, corrosion and catalyst poisoning under the reaction conditions, promoting the dispersion of active CuNPs and improving the HER performance of the CuNPs/CNF electrode. The low-cost CuNPs/CNFs electrode material with a low overpotential, a small Tafel slope and a fast electron transfer rate is a promising HER catalyst in large-scale commercial applications.

Conclusions

In summary, we have successfully designed and synthesized3D and self-supported CuNPs/CNFs nanomaterials that can serve as efficient HER electrocatalysts in acidic media. The hybrid CuNPs/CNFs were prepared by combining electrospinning and thermal reduction processes. The Cu²⁺ ions from CuCl₂ in the PVA nanofibers were reduced to Cu nanoparticles because of the reduction of carbon. The obtained CuNPs/CNFs show excellent HER activity in acidic electrolyte with an onset potential of 61 mV, an overpotential of 200 mV at 10 mA cm⁻², a small Tafel slope of approximately 152 mV dec⁻¹ and long-term stability up to 10 h as well as a high cathodic current density. This work demonstrates that Cu or Cu-based catalysts are promising candidates for substituting noble metal Pt-based materials for large-scale HER applications using water.

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