Electrocatalysis



Designed Synthesis of Size-Controlled Pt—Cu Alloy Nanoparticles Encapsulated in Carbon Nanofibers and Their High Efficient Electrocatalytic Activity Toward Hydrogen Evolution Reaction

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Well-dispersed Pt—Cu alloy nanoparticles (NPs) with a diameter of only \approx 2 nm encapsulated in carbon nanofibers (CNFs) are synthesized using electrospinning technology followed by a graphitization process in a chemical vapor deposition furnace. Distinctly, even with a small amount of Pt, the Pt—Cu/CNFs-1:2 catalyst possesses outstanding hydrogen evolution reaction (HER) activity, including small overpotential, long-term stability, and a high exchange current density as well as large double layer capacitance (C_{dl}). The excellent HER performance of the Pt—Cu/CNFs-1:2 catalyst is attributed to the synergistic interaction between Pt and Cu, the uniform distribution of the alloy NPs and the use of CNFs with 3D architectures. This development may provide a simple, efficient, and green synthesis method to design bi- or multimetal alloys for use as the cathode electrocatalysts for the HER or other electrocatalytic devices.

1. Introduction

The awareness of energy use has risen considerably during the past several decades due to the fossil fuel crisis and the pollution of the environment.^[1] Therefore, hydrogen, as a clean, efficient, and sustainable energy carrier, may become the most promising candidate to replace fossil fuels.^[2] Among the technologies for producing hydrogen, the electrochemical hydrogen evolution reaction (HER), which is the reduction half-reaction of electrochemical water splitting, has to be economical if electrochemical water splitting is to achieve large-scale commercial application.^[3] The noble metal platinum (Pt), which has been identified as the best electrocatalyst for the HER, has a high catalytic activity and fast reduction kinetics in acidic media.^[4] Ding et al. synthesized a ternary electrocatalyst of CuPdPt/C with high activity and durability for HER, which exhibited superior mass activity.^[5] Huang et al. prepared Pt nanostructures on dispersible single-layer MoS2 nanosheets by solutionphase epitaxial growth, which exhibited much better HER

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performance than commercial Pt/C.^[6] However, the exorbitant price and low abundance of Pt heavily impedes its extensive utilization on a large scale.^[7] Thus, the ultimate goal is to reduce the usage of the precious metal Pt by substituting lowcost and earth-abundant non-noble metals for Pt to design a novel electrocatalyst for the HER.

Currently, the combination of Pt with a transition metal such as iron, cobalt, nickel, Cu or their alloys has been considered as efficient HER catalysts due to their structure and unique properties, which can enhance their catalytic activities.^[8,9] Among all of the options, Cu, which is well-known as an earth-abundant and inexpensive 3d transition metal, has been

used for many years in the fields of optics, electronics, machine manufacture, etc.^[10] Although bulk Cu has been applied in various fields, its poor resistance to oxidation has restricted its wider and efficient use.^[11] Over the past few decades, with the rapid development of nanoscience and nanotechnology, Cu NPs have attracted more attention by many researchers due to their unique physical and chemical properties, especially in the field of nanometer materials and catalysis.^[12,13] Therefore, there are many efforts to design a novel structure or supporting materials, including core/shell Cu NPs, alloys, and metal organic framework materials, which would enhance the stability of the Cu NPs to avoid oxidization under atmosphere conditions.^[14,15] However, as far as we know, there are few reports regarding the use of nanoscale alloys of Cu and Pt as a catalyst for the HER.

Recently, a great number of studies have focused on nanoscale catalysts with high activity, stability, and repeatability based on the low-cost and earth-abundant elements and their compounds, including transition metal dichalcogenides (MX₂, such as MoS₂, WS₂, and CoSe₂; metal phosphides (NiP and FeP); and metal carbides (WC and Mo₂C).^[16,17] For instance, Zhang et al. reported a highly efficient catalyst of polymorphic CoSe₂ with mixed orthorhombic and cubic phases for the HER, with an overpotential for significant H₂ evolution of ~150 mV.^[18] Pan et al. prepared different phases and monodispersed nanocrystals of nickel phosphide with an overpotential of 118 mV at a 10 mA cm⁻² current density.^[19]





In addition, Alhajri et al. have synthesized a new molybdenum carbide-carbon nanocomposite with a sufficiently small average particle size of 8 nm,^[20] using a reactive template of mesoporous graphitic carbon nitride (mpg- C_3N_4) at different temperature that exhibits a lower onset potential of 100 mV versus RHE. Although, the HER performances of catalysts have greatly improved using the various approaches, in general, most of these catalysts have a low intrinsic activity compared to Pt for the HER in acidic medium.^[21,22]

In this study, we report a facile method to design an alloy of Pt with the inexpensive 3d transition metal Cu via in situ reduction and electrospinning with polyvinyl alcohol (PVA) as well as chemical vapor deposition (CVD) furnace. First, we use $CuCl_2$ and $H_2PtCl_6 \cdot 6H_2O$ as well as PVA to prepare a precursor solution, and then use an electrospinning technology under constant conditions to obtain electrospun nanofibers (NFs) with different Pt-Cu mass ratios. Next, the obtained Pt-Cu/PVA NFs were heated to different temperature and kept under an Ar atmosphere for graphitization. Notably, there are no other oxidants or reductants added in the entire preparation process and the synthesized Pt-Cu alloy exhibits a high catalytic efficiency toward the HER. Furthermore, we also studied the effect of the graphitization temperature (600, 800, and 1000 °C) and the mass ratio of Pt-Cu NPs (0:1, 1:3, 1:2, 1:1, 1:0) on the HER performance. The results indicated that the Pt-Cu catalyst with a mass ratio of 1:2, graphitized at 1000 °C, exhibited an outstanding HER catalytic activity and long-term stability. This method may pave the way to synthesize other new structure of bi- or multimetal nanoparticles/ carbon nanofibers (CNFs) with a small size and excellent activity for use as HER catalysts.

2. Results and Discussion

The surface morphology and interior structure of Cu/CNFs, Pt/ CNFs, and Pt-Cu/CNFs-1:2 prepared with the carbonization temperature of 1000 °C, recorded by field-emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM) as well as high-resolution (HRTEM), are shown in Figure 1. It is observed from Figure 1a,b that there are many Cu NPs dispersed in the CNFs with an average diameter of ≈15 nm. The HRTEM image in Figure 1c shows that the lattice fringes of the Cu/CNFs are 2.1 and 1.8 Å, which corresponds to the (111) and (200) planes of Cu metal, respectively. Figure 1d,e exhibits the FE-SEM image and TEM image of the Pt/CNFs, respectively, and those images suggest that the small Pt NPs are extremely uniformly embedded in the surface of the CNFs with diameters of ≈2 nm. Further insight into the internal structure of the Pt/CNFs was obtained from the HRTEM image in Figure 1f, where the lattice distance of the Pt (111) and (200) planes are 2.3 and 2.0 Å, respectively. The morphology and interior structure of Pt-Cu/CNFs-1:2 are shown in Figure 1g,h. A large number of small Pt-Cu NPs with an average diameter as small as the diameter of the Pt NPs of ≈2 nm are evenly immobilized on the surface of the CNFs. In addition, Figure 1i shows an HRTEM image of a Pt-Cu NPs and the crystalline lattices marked with the yellow line segment were spaced at distances of 2.2 and 1.9 Å, corresponding to the (111) and (200) plane of Pt-Cu NPs, respectively. Thus, the results imply the formation of Pt-Cu alloy.^[23,24]

The effects of temperature and the Pt–Cu mass ratio on the surface morphology were investigated and the results are shown in **Figure 2**. Figure 2a shows sporadic Pt–Cu NPs on the



Figure 1. FE-SEM images of the a) Cu/CNFs, d) Pt/CNFs, and g) Pt-Cu/CNFs-1:2. TEM image of b) Cu/CNFs, e) Pt/CNFs, and h) Pt-Cu/CNFs-1:2. c,f,i) The corresponding HRTEM image.







Figure 2. FE-SEM images of a,c,e) the Pt–Cu/CNFs-1:2 prepared at different carbonization temperature of 600, 800, and 1000 $^{\circ}$ C, respectively. b,d,f) Catalysts prepared at different mass of Pt:Cu of 1:1, 1:2, and 1:3, respectively, with a carbonization temperature of 1000 $^{\circ}$ C.

surface of the CNFs prepared with the carbonization temperature at 600 °C. With a graphitization temperature of 800 °C, many Pt–Cu NPs appeared on the CNFs, as shown in Figure 2c. Accordingly, a uniform coverage of many more Pt–Cu NPs are seen on the CNFs graphitized at 1000 °C (in Figure 2e). Furthermore, the morphology of the samples prepared with Pt–Cu NPs mass ratios of 1:1, 1:2, and 1:3 with the carbonization temperature of 1000 °C are shown in Figure 2b,d,f, respectively. As shown in Figure 2b, the diameters of the Pt–Cu NPs-1:1 are

so small that we can hardly see them clearly. However, as shown in Figure 2d, the diameters of the Pt-Cu NPs-1:2 are much larger than that of the Pt-Cu NPs-1:1. As expected, the NPs prepared with the Pt-Cu mass ratio of 1:3 had the largest diameters of the three samples. Therefore, the number of Pt-Cu NPs increased with increasing graphitization temperature and the diameter of the Pt-Cu NPs decreased when the amount of Pt increased.

As shown in **Figure 3**a, the high-angle annular dark field STEM (HAADF-STEM) and elemental mapping images illustrate that the Pt-Cu/CNFs-1:2 catalyst contains C, O, Pt, and Cu elements. The phase purity and crystal composition of the as-prepared Pt/CNFs, Cu/CNFs, and Pt-Cu/CNFs-1:2 samples were confirmed by X-ray diffraction (XRD). In Figure 3b, it can be clearly seen that the blue diffraction pattern for the Cu/CNFs has two diffraction peak located at 43.5° and 50.6°, which corresponds to the (111) and (200) planes of metallic Cu, respectively.^[25] In the black diffraction pattern for the Pt/CNFs, the 2θ values of the two main sharp peaks are located at 39.9° and 46.4°, which are indexed to (111) and (200) planes of Pt.^[26] However, for the XRD pattern of Pt–Cu/CNFs-1:2 catalyst, there are two peaks at 42.8° and 50.0°. The XRD peaks of the Pt–Cu/CNFs-1:2 catalyst shift toward lower angles compared with the Cu/CNFs, because the lattice spacing increases with the addition of platinum, which agrees with the results of HRTEM image in Figure 1, and further verifies the formation of the Pt–Cu alloy.

To better investigate the chemical composition and valence states of the samples, we used X-ray photoelectron spectroscopy (XPS) technology to examine the Pt/CNFs, Cu/CNFs, and Pt-Cu/CNFs-1:2. The XPS spectra of all of the catalysts in Figure 4 were calibrated using the C 1s peak of carbon with a fixed value of 284.6 eV. As shown in Figure 4a, the C1s peak can be deconvoluted to three peaks at 284.6, 286.0, and 289.5 eV, which are assigned to the C-C or C-H bonds of graphitic carbons and unoxidized graphitic carbons, C-O or C=C bonds, and C=O bonds, respectively.^[27] The deconvoluted O 1s spectrum of the Pt-Cu/CNFs-1:2 is shown in Figure 4b, and two peaks can be seen at 531.9 and 532.4 eV, corresponding to C=O and C-OH bonds, respectively, which may be derived from the hydroxyl group of PVA when the intramolecular dehydration reaction was not fully completed. For Pt/CNFs, the Pt 4f spectrum is decomposed into two peaks in Figure 4c with the binding energies (BEs) of 72.0 and 75.3 eV ascribed to Pt $4f_{7/2}$ and Pt 4f5/2, respectively.^[28] In addition, for Pt-Cu/CNFs-1:2 (Figure 4d), we can see that the BEs of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ are located at 71.6 and 74.9 eV, respectively. Apparently, the BEs of the XPS peaks for Pt $4f_{7/2}$ and Pt $4f_{5/2}$ have both undergone a 0.4 eV negative shift from Pt/CNFs to Pt-Cu/CNFs-1:2. Moreover, As shown in Figure 4e, it can be seen that two sharp and strong peaks in the spectrum of the Cu/CNFs appear at 932.3 and 952.0 eV and are assigned to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively.^[29] In Figure 4f, for Pt–Cu/CNFs-1:2, the BEs of Cu 2p_{3/2}



Figure 3. a,c) High-angle annular dark field STEM and elemental mapping images of C, O, Pt, and Cu of Pt–Cu/CNFs-1:2. b) XRD patterns of Cu/CNFs, Pt–Cu/CNFs-1:2 and Pt/CNFs.



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Figure 4. The XPS spectra of a) C 1s and b) O 1s of the Pt–Cu/CNFs-1:2. The XPS spectra of Pt 4f in c) Cu/CNFs and d) Pt–Cu/CNFs-1:2, Cu 2p in Pt/CNFs and Pt–Cu/CNFs-1:2.

and Cu $2p_{1/2}$ are shifted to 932.8 and 952.5 eV, respectively. In addition, in the Cu 2p XPS spectra, no separate satellite peaks corresponding to CuO or Cu₂O were observed. Furthermore, all of the peaks in the two spectra of Cu 2p belong to metallic Cu, confirming that the Cu²⁺ in the PVA nanofibrous mats were completely reduced to the Cu metal. Furthermore, the elemental atomic ratio of C, O, Pt, and Cu in Pt–Cu/CNFs-1:2 was 96.00%, 3.61%, 0.10%, and 0.29%, respectively. Based on the results of the XPS, we observed a shift of the Pt 4f and Cu 2p BEs from the Pt/CNFs and Cu/CNFs to the Pt–Cu/CNFs-1:2, suggesting that electron transfer occurred in the Pt–Cu/CNFs-1:2 and the successful synthesis of the Pt–Cu NPs alloy in the carbon nanofibers.

The HER activities of the Pt–Cu/CNFs-1:2, Pt/CNFs, and Cu/CNFs catalysts, which were directly used as the working electrode, were performed in an aqueous solution of 0.5 M H₂SO₄ using a typical three-electrode cell testing system at room temperature with a scan rate of 2 mV s⁻¹. For reference, the catalysts of a commercial Pt/C catalyst (Johnson, 20 wt% Pt/C) and pure CNFs were also tested. From the linear sweep voltammetric (LSV) curves in **Figure 5**a, the commercial Pt/C



catalyst shows superior catalytic activity with a lowest overpotential of 30 mV at a cathodic current density of 10 mA cm⁻². By contrast, the pure CNFs have nearly no catalytic activity with a negligible current density. Compared to the pure CNFs, the Cu/ CNFs catalyst exhibits a much higher HER activity, with an overpotential of only 200 mV at a current density of 10 mA cm^{-2} and an exchange current density of 0.692 mA cm⁻². As expected, the Pt/CNFs exhibit an excellent catalytic activity and display an overpotential of 94 mV, and an exchange current density of 0.762 mA cm⁻² (in Table 1). Interestingly, the Pt-Cu/CNFs-1:2, containing the Pt-Cu alloy NPs, possess the best activity for the HER in an acidic environment. The Pt-Cu/CNFs-1:2 electrode achieves a current density of 10 mA cm⁻² at an overpotential as low as 71 mV, and the highest exchange current density of 0.863 mA cm⁻², which is superior the most recent reported Cubased or Pt-based electrocatalysts (Table S1, Supporting Information). In addition, the cathodic current density of the Pt-Cu/CNFs-1:2, 104 mA cm⁻² at η = 300 mV, is 2.2, 5.8, and 104 times higher than the current densities of the Pt/CNFs (47 mA cm⁻²), Cu/ CNFs (18 mA cm⁻²), and CNFs (1 mA cm⁻²) catalysts, respectively, further evidence of the amazing activity of the Pt-Cu NPs toward the HER.

The Tafel slope is usually associated with the mechanism for the HER. The Tafel slope derived from the LSV curves are shown in Figure 5b for all of the Pt/C, Pt–Cu/CNFs-1:2, Pt/CNFs, Cu/CNFs, and CNFs catalysts, using the Tafel equation ($\eta = b\log(I) + a$,

where *b* is the Tafel slope, and *J* is the current density).^[5] As is well known, if the Tafel slope is 120 mV dec⁻¹, the rate-limiting step for the HER is the Volmer reaction; however, when the Tafel slope of the sample is 40 mV dec⁻¹ or smaller, the rate-limiting step for the HER is the Heyrovsky or Tafel reaction.^[30] In Figure 5b, there is no doubt that the commercial Pt/C catalyst has the smallest Tafel slope of 27 mV dec⁻¹. In addition, we can clearly see that the Tafel slope of the Pt–Cu/CNFs-1:2 is 68 mV dec⁻¹, which is superior to the slopes of Pt/CNFs (104 mV dec⁻¹). Cu/CNFs (234 mV dec⁻¹) as well as the CNFs (338 mV dec⁻¹). The results imply that the rate determining step for the Pt–Cu/CNFs-1:2 is the electrochemical desorption in the Volmer–Heyrovsky HER mechanism.

Furthermore, to further investigate the charge transfer mechanism of the catalysts, electrochemical impedance spectroscopy (EIS) analysis for each catalyst was performed at –0.25 V versus RHE and shown in Figure 5c. It can clearly be seen that the Nyquist plots of the Pt–Cu/CNFs-1:2, Pt/CNFs, Cu/CNFs, and CNFs are nearly semicircles. The high frequency regions are shown for clarity (inset in Figure 5c). Usually, the diameters of the semicircles are related to the charge transfer resistance ADVANCED SCIENCE NEWS _____ www.advancedsciencenews.com



Figure 5. a) Polarization curves for the HER obtained with the commercial Pt/C, Pt–Cu/CNFs-1:2, Pt/CNFs, Cu/CNFs, and CNFs in 0.5 \mbox{M} H₂SO₄. b) Tafel slopes derived from LSV curves from (a). c) Nyquist plots for the Pt–Cu/CNFs-1:2, Pt/CNFs, Cu/CNFs, and CNFs examined at -0.25 V versus RHE. In addition, the inset is the enlarged Nyquist plots of the samples. d) Chronoamperometric test of Pt–Cu/CNFs-1:2 membrane at a static potential of -0.071 V versus RHE for 10 h. The inset in (5d) is the liner fitting of the capacitive currents of Pt–Cu/ CNFs-1:2, Pt/CNFs, and Cu/CNFs versus scan rate and the photograph of H₂ bubbles on the surface of the Pt–Cu/CNFs-1:2 catalyst during the electrocatalytic process.

(R_{ct}) at the interface of the electrode and the electrolyte as well as the corresponding capacitance.^[31] It is known that a lower value of R_{ct} is produced by a greater number of exposed active sites and a higher reaction rate, in other words, a better catalytic activity for the HER.^[32] As expected, the Pt–Cu/CNFs-1:2 show a much smaller charge transfer resistance (R_{ct}) of 23.9 Ω than those of the other three catalysts: Pt/CNFs (36.8 Ω), Cu/CNFs (133 Ω), and CNFs (1412 Ω). The small R_{ct} value of the Pt–Cu/ CNFs-1:2 electrode implies that it has a higher electron transfer rates than the other catalysts. The higher HER activity of the Pt–Cu/CNFs-1:2 may be attributed to the interface effect and the highly conductive Cu of the Pt–Cu NPs in the matrix of CNFs.

The time dependence of the current density for the HER is a critical factor to evaluate the stability of the catalysts in practical



applications. Thus, time dependent current density data for the Pt-Cu/CNFs-1:2 electrode were collected at a static potential of -0.071 V versus RHE for 10 h. The current density of the cell with the Pt-Cu/CNFs-1:2 electrode only degraded slightly as can be observed in Figure 5d, even after a period of 10 h in 0.5 м H₂SO₄ environment. The reasons for the slight degradation may be due to depletion of H⁺ in the electrolyte or the difficulty of the H₂ bubbles to escape from the surface of the electrode.^[33] Typically, the electrochemical active surface area is usually investigated by measured the capacitance of the double layer (Cdl).[34] Cyclic votammetry (CV) plots of the catalysts were conducted between 0.1 and 0.2 V versus RHE at various scan rate region from 0.5 to 5 mV s⁻¹ (Figure S1, Supporting Information). The Cdl of Pt/CNFs and Cu/CNFs are $0.467 \times 10^3 \text{ mF cm}^{-2}$ and 0.153×10^3 mF cm⁻², respectively. By contrast, Pt-Cu/CNFs-1:2 catalyst reveal a large Cdl value of 1.14×10^3 mF cm⁻², which is superior to that of Pt/CNFs and Cu/CNFs catalysts. No obvious change were observed after stability testing for the surface morphology and the XRD patterns of the Pt-Cu/CNFs-1:2 (in Figures S2 and S3, Supporting Information), indicating the superior stability of the catalysts.

In control experiments, we further studied the effect of the graphitization temperature on the HER activity. As observed from **Figure 6a**, the Pt–Cu/CNFs-600 °C catalyst shows the overpotential of 161 mV at a cathodic current density of 10 mA cm⁻², and the overpotential decreases with increasing graphitization temperature, with overpotential of 129 and 71 mV for the Pt–Cu/CNFs-800 °C and Pt–Cu/CNFs-1000 °C catalysts, respectively. In addition, the cathodic current density at η = 300 mV of the Pt–Cu/CNFs-1000 °C electrode is 104 mA cm⁻², which is ≈4.3 times and 2.1 times higher, respectively, than that of the Pt–Cu/CNFs-600 °C catalyst (24 mA cm⁻²) and the Pt–Cu/CNFs-800 °C catalyst (49 mA cm⁻²). In addition, increasing the graphitization temperature from 600 to 800 °C increases the exchange current density of the catalysts from 0.739 to 0.761 mA cm⁻². When the graphitization temperature

Samples	$\eta@j = 10 \text{ mA cm}^{-2}$ [mV]	Tafel slope [mV dec ⁻¹]	Current density at η = 300 mV [mA cm ⁻²]	j_0 [mA cm ⁻²]
Pt—Cu/CNFs-1:2	71	68	104	0.863
Pt/CNFs	94	104	47	0.762
Cu/CNFs	200	234	18	0.692
Pt—Cu/CNFs-600 °C	161	174	24	0.739
Pt-Cu/CNFs-800 °C	129	139	49	0.761
Pt-Cu/CNFs-1:1	79	79	71	0.795
Pt—Cu/CNFs-1:3	89	91	57	0.788

 Table 1. Electrocatalytic performance of the catalysts.







Figure 6. a,b) Polarization curves and corresponding Tafel slopes for the HER obtained with the Pt–Cu/CNFs-1:2 prepared with graphitization temperatures of 600, 800, and 1000 °C. c,d) Polarization curves and corresponding Tafel slopes for the HER obtained with the Pt–Cu/CNFs-1:3, Pt–Cu/CNFs-1:2, and Pt–Cu/CNFs-1:1 in 0.5 M H₂SO₄.

increased to 1000 °C, the exchange current density increases to 0.863 mA cm⁻². The corresponding Tafel slopes are shown in Figure 6b.The Pt–Cu/CNFs-1000 °C catalyst gives a Tafel slope of 68 mV dec⁻¹, which is much smaller than that of the Pt–Cu/CNFs-800 °C (139 mV dec⁻¹) or the Pt–Cu/CNFs-600 °C (174 mV dec⁻¹) catalysts. Obviously, among these catalysts, the Pt–Cu/CNFs-1000 °C exhibits the optimal HER activity, possibly because the higher carbonization temperature results in many more Pt–Cu NPs migrating to the surface of CNFs, as seen in the SEM results (Figure 2a,c,e).^[35]

Furthermore, the influence of the mass ratio of Pt and Cu on the HER activity was also investigated. As shown in Figure 6c, the Pt-Cu/CNFs-1:2 catalyst reveals the optimal activity for the HER compared to the two other samples. At a cathodic current density of 10 mA cm⁻², the overpotential of the Pt-Cu/ CNFs-1:2 catalyst is 71 mV, lower than those of the Pt-Cu/ CNFs-1:1 (79 mV) and the Pt-Cu/CNFs-1:3 (91 mV) catalysts (in Table 1). Moreover, the cathodic current densities at η = 300 mV of Pt–Cu/CNFs-1:1, Pt–Cu/CNFs-1:2, and Pt–Cu/ CNFs-1:3 are 71, 104, and 57 mA cm⁻², respectively. In addition, the Pt-Cu/CNFs-1:2 also exhibits the highest exchange current density (0.863 mA cm⁻²) and the smallest Tafel slope (68 mV dec⁻¹). As shown in Figure 3f, the Pt-Cu/CNFs-1:3 catalyst possesses a much larger particle size than the other catalysts and a slight aggregation tendency, which may reduce the density of active sites and thus be responsible for the deterioration of the HER activity. Although the Pt content in the highest in the Pt-Cu/CNFs-1:1 catalyst, it exhibited a lower activity compared with the Pt-Cu/CNFs-1:2 catalyst, which may be the result of the fact that most of the alloy particles were encapsulated in the CNFs, as shown in Figure 2d.

3. Conclusions

In conclusion, the present investigation demonstrates that a well-dispersed size-controlled Pt-Cu bimetallic alloy catalysts in 3D CNFs with a nanoparticle size as low as \approx 2 nm were successfully synthesized using electrospinning technology followed by a graphitization process. The HER activity of the bimetallic alloy catalyst is much superior to that of a single component catalyst. With increasing graphitization temperature, the density of the nanoparticles on the surface of the CNFs increases, improving the HER activity. Furthermore, the effect of the Pt-Cu mass ratio on the HER activity was also investigated, and the Pt-Cu/ CNFs-1:2 at 1000 °C exhibited the optimal HER activity. The extraordinarily high HER performance of the Pt-Cu/CNFs-1:2 catalysts was attributed to the synergistic interaction between Pt and Cu, the uniform distribution of the alloy NPs and the use of CNFs with 3D architectures. The present investigations may provide an efficient and green route for the design bi- or multimetal alloys with an ultrasmall size for use as the cathode electrocatalysts for the HER or other electrocatalytic devices.

4. Experimental Section

Materials: Copper chloride (CuCl₂) was purchased from Aladdin Chemical Reagent Co., Ltd. Sulfuric acid (H₂SO₄) and chloroplatinic acid (H₂PtCl₆·6H₂O, 99.9%) were supplied by Shanghai Civi Chemical Technology Co., Ltd. PVA powder ($M_w = 88\,000,\,88\,wt\%$ hydrolyzed) was manufactured by Sinopec Shanghai Petrochemical Co., Ltd. Deionized water (DIW, 18.2 MΩ) was used as the solvent in all solution preparations. All of the reagents were analytical grade and without further purification.



In the present investigations, the excellent HER performance of the Pt-Cu/CNFs-1:2 at 1000 °C catalysts is attributable to several factors: (1) A large number of Pt-Cu NPs are uniformly distributed on the outer surface of the carbon nanofibers, leading to the generation of numerous active sites. (2) The small size effect of the ultrasmall Pt-Cu NPs may increase the electrochemical activity.^[36] (3) The introduction of Pt into the Pt-Cu alloy is beneficial to prevent the oxidation of copper under atmospheric conditions, enhances the interface effect and allows the synergistic interaction between Pt and Cu. (4) The electrospun CNFs with 3D architectures not only accelerate electron transport and facilitate the contact with the electrolyte but also protect the Pt-Cu NPs from oxidation and improve their corrosion resistance.^[37] Therefore, in this paper, the synthesized Pt-Cu/CNFs catalysts exhibit amazing HER activity and stability, which may provide an efficient and green route for the design bi- or multimetal alloys with an ultrasmall size for use as cathode electrocatalysts for the HER or other electrocatalytic devices.





Synthesis of the precursor solution: In a simple process, 1.5 g PVA powder was gradually dissolved in 11 mL of DIW to form a 12 wt% homogeneous solution under magnetic stirring in a glass vial. When the solution became clear, different mass ratios of $CuCl_2$ and $H_2PtCl_6\cdot 6H_2O$ (the total amount of reagent was 0.075 g) were dropped into it with vigorous stirring for several hours until it became a homogenous solution. Subsequently, the prepared precursor solutions were stored in the refrigerator at 4 °C for further use. All experiments were performed at room temperature.

Preparation of the nanofibrous mats: The nanofibrous mats were fabricated using the as-prepared precursor solution using an electrospinning technology. First, the precursor solutions were directly transferred into a syringe with a stainless copper needle at the tip, with an inner diameter of 0.8 mm and an applied voltage of 17 kV at the needle tip. The distance between the needle tip and the collector was set at 15 cm and the flow rate of the solution was 0.5 mL h⁻¹. During the electrospinning process, the temperature of the laboratory room was 25 ± 2 °C. The electrospun nanofibrous mats were collected onto a piece of aluminum foil using a parallel plate apparatus. The electrospun nanofiber mats on the surface of the aluminum foil were dried overnight at 80 °C in a vacuum to remove the residual solvent. After that, the samples were transferred into a vacuum-dried glass dish to keep dry.

Fabrication of the carbon nanofibrous mats: The as-spun nanofibrous mats were cut into suitable rectangles, and each rectangle was placed in an alumina boat after it was peeled from the surface of the aluminum foil. Then, a boat was placed into the middle of the tube furnace and heat treated using the CVD furnace. The thermal treatment process consisted of the following steps: First, the furnace was heated to 230 °C and kept in air for 1 h to thermally equilibrate. Then, the samples were ramped at 5 °C min⁻¹ in an Ar atmosphere to 600, 800, or 1000 °C to graphitize and maintained at a constant temperature for 3 h. After the end of the program, the temperature was returned to 25 °C under an Ar atmosphere. Finally, the samples were removed from the furnace and kept in sealed polyethylene bags until needed for further characterization. The samples with the mass ratio of the $H_2PtCl_6\cdot 6H_2O$ to CuCl₂ of 0:1, 1:3, 1:2, 1:1 or 1:0 were graphitized at 1000 °C and labeled as Cu/ CNFs, Pt-Cu/CNFs-1:3, Pt-Cu/CNFs-1:2, Pt-Cu/CNFs-1:1 or Pt/CNFs, respectively. The Pt-Cu/CNFs with the mass ratio of 1:2 graphitized at 600, 800, or 1000 °C were labeled Pt-Cu/CNFs-600 °C, Pt-Cu/CNFs-800 °C, or Pt-Cu/CNFs-1000 °C, respectively.

Instrumentation: The morphology of the Cu/CNFs, Pt/CNFs, and Pt–Cu/CNFs prepared under the different reaction conditions were examined using a JEOL JSM-6700F FE-SEM (JEOL, Japan) at an acceleration voltage of 3 kV. Images of the interior structure of all samples were taken with a JSM-2100 TEM (JEOL, Japan) at an acceleration voltage of 200 kV. An X-ray photoelectron spectrometer (XPS) (Kratos Axis Ultra DLD) with an aluminum (mono) K α source (1486.6 eV) was used to measure the surface chemical composition of all samples. In addition, the XRD patterns of the products were recorded with an SIEMENS Diffractometer D5000 X-ray diffractometer using a Cu K α radiation (λ = 1.5406 A°) source at 35 kV, with a scan rate of 0.02° 2 θ s⁻¹ in the 2 θ range of 20°–60°. The STEM mapping images and HAADF-STEM images were collected by an STEM (Tecnai G2 F30 S-Twin, Philips-FEI) at an acceleration voltage of 300 kV.

Electrochemical characterizations: The HER electrochemical activity of the as-prepared catalysts was tested in an aqueous solution of 0.5 M H_2SO_4 using a typical three-electrode cell testing system. The catalysts prepared under the different conditions were directly used as the working electrode, which were cut into $1 \times 1 \text{ cm}^{-2}$ squares. In addition, a Pt wire was used as the auxiliary electrode, and a saturated calomel electrode (E(RHE) = E(SCE) + 0.244 V) was used as the reference electrode. For the HER polarization curve experiments, cyclic voltammograms (CVs), electrochemical impedance spectra (EIS), and time dependent current density curves, data were collected using an IVIUM electrochemical workstation (Ivium Technologies BV Company, Netherlands). For the HER measurements, all data were obtained after 400 cycles of CVs at a scan rate of 100 mV s⁻¹, and a continuous flow of nitrogen was supplied for at least 30 min before the CV measurements began to remove any contaminants on the electrode surface, to maintain the stability of the catalysts and to remove the dissolved oxygen in the solution. Polarization curves were measured using linear sweep voltammetry (LSV) at a scan rate of 2 mV s⁻¹. EIS was collected at a static voltage of -0.25 V versus RHE with the frequencies ranging from 100 kHz to 0.001 Hz. Time dependence of the current density curve was acquired under a constant voltage of -0.071 V versus RHE for 10 h.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Keywords

carbon nanofibers, electrocatalyst, hydrogen evolution reaction, $\mathsf{Pt}{-}\mathsf{Cu}$ alloy

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