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Ternary Platinum-Copper-Nickel Nanoparticles Anchored to Hierarchical Carbon Supports as Free-Standing Hydrogen Evolution Electrodes

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ABSTRACT

Developing cost-effective and efficient hydrogen evolution reaction (HER) electrocatalysts for hydrogen production is of paramount importance to attain a sustainable energy future. Reported herein is a novel three-dimensional hierarchical architected electrocatalyst, consisting of platinum-copper-nickel nanoparticles decorated carbon nanofiber arrays which are conformally assembled on carbon felt fabrics (PtCuNi/CNF@CF) by an ambient-pressure chemical vapor deposition coupled with a spontaneous galvanic replacement reaction. The free-standing PtCuNi/CNF@CF monolith exhibits high porosities, a well-defined geometry shape, outstanding electron conductivity and a unique characteristic of localizing platinum-copper-nickel nanoparticles in the tips of carbon nanofibers. Such features render PtCuNi/CNF@CF as an ideal binder-free HER electrode for hydrogen production. Electrochemical measurements demonstrate that the PtCuNi/CNF@CF possesses superior intrinsic activity as well as mass specific activity in comparison with the state-of-the-art Pt/C catalysts, both in acidic and alkaline solutions. With well-tuned composition of active nanoparticles, Pt₄₂Cu₅₇Ni₁/CNF@CF showed excellent durability. The synthesis strategy reported in this work is likely to pave a new route for fabricating free-standing hierarchical electrodes for electrochemical devices.

KEYWORDS: *Hydrogen evolution reaction, ternary platinum-copper-nickel nanoparticles, carbon nanofiber arrays, free-standing electrocatalysts, chemical vapor deposition*

INTRODUCTION

Hydrogen as an efficient and environmentally-friendly energy carrier, is an ideal candidate for replacing fossil fuels.¹ Despite its great application prospect, the cost-effective and sustainable production of hydrogen proves to be a great challenge. To date, extensive efforts have been devoted to exploring advanced techniques for hydrogen production.² Of the reported techniques, the electrocatalytic hydrogen evolution reaction (HER) is considered to be one of the most promising processes.³ In a typical HER process, it requires a high-performance electrocatalyst to maximize energy efficiency. So far, Pt still remains the most active HER electrocatalyst, notwithstanding the tremendous efforts in searching for alternatives.⁴⁻⁷ Unfortunately, the scarcity and cost of Pt pose a critical obstacle for the widespread application of HER for hydrogen production.⁸ Thus, it is of great importance to increase the utilization efficiency of Pt in HER electrocatalysts. To this end, one strategy is to increase the proportion of surface atoms by downsizing Pt nanoparticles (NPs) to atomic level.^{9,10} However, the mass production and stabilization of Pt clusters with dozens of atoms are very challenging due to the extremely high surface energy. An alternative strategy is to alloy Pt with a less expensive component and further delicately engineer the surface structure to obtain the desirable exposed crystal facets.¹¹⁻¹⁵ Such well-tuned Pt electrocatalysts possess enhanced surface-to-volume ratio of Pt, resulting in more active sites per unit mass and thus allowing for decreasing Pt loadings without compromising catalyst activity. Moreover, the synergistic effects of the components as well as the optimized crystal facets could significantly improve catalytic activity.^{16,17}

Apart from the composition and morphology of catalyst NPs, the nanostructures of electrodes also play a crucial role on the efficiency of HER process.¹⁸ In general, electrocatalysts consist of active NPs dispersed in suitable supporting materials. Due to the high surface energy,

the fine NPs are apt to migration, coalescence and detachment, leading to drastic activity decay.¹⁹ Thus, stabilizing active NPs by their interactions with the supporting materials is highly desirable. In a practical HER process, catalysts are always immobilized to current collectors using binders such as Nafion solution. Besides the cost of Nafion solution, the polymer binders always increase the contact resistance and may block active sites, thereby lowering the efficiency of electrocatalysts.²⁰ In addition, the tedious catalyst loading procedure makes the HER process complicated. In view of these constraints, hierarchical free-standing electrodes with integration of electrocatalysts and current collectors are greatly beneficial to the HER process.²¹⁻²³ Herein, a novel three-dimensional (3D) hierarchical architected electrocatalyst was synthesized, which consisted of PtCuNi NPs decorated carbon nanofiber arrays which were conformally assembled on carbon felt fabrics (denoted as PtCuNi/CNF@CF for convenience) by an ambient-pressure chemical vapor deposition coupled with a spontaneous galvanic displacement process. In this reported synthesis protocol, NiCu decorated carbon nanofiber arrays were used as templates to synthesize ternary PtCuNi NPs by galvanic replacement reactions. The prominent features of as-prepared PtCuNi/CNF@CF monoliths including high porosities, a well-defined geometry shape, outstanding electron conductivity and a unique characteristic of localizing platinum-copper-nickel nanoparticles in the tips of carbon nanofibers render them as an ideal binder-free HER electrode for hydrogen production both in acidic and alkaline solutions.

EXPERIMENTAL SECTIONS

Synthesis of Ni-Cu oxalate

Ni-Cu oxalate nanofibers were synthesized using the method as reported by Lua and Wang.²⁴ In a typical process, 1.7 g of nickel (II) nitrate hexahydrate and 0.7 g copper (II) nitrate trihydrate (atomic nickel/copper ratio 2:1) were dissolved in 30 mL of ethanol. A stoichiometric amount of

oxalic acid, dissolved in 30 mL of ethanol, was titrated to the precursor solution under magnetic stirring. The resulting suspension was transferred into an autoclave and kept at 120 °C for 12 h. The product was thoroughly washed with di-ionized water and dried at 80 °C.

Transfer of catalyst precursors to carbon felt

Before the deposition of catalyst precursors, the carbon felt ($1.5 \times 1.5 \times 0.5$ cm) was thermally activated by heat treatment at 420 °C for 12 h under ambient atmosphere. The catalyst precursor, *i.e.*, Ni-Cu oxalate, was transferred to the CF using an impregnation method. The details of the experimental procedures are as follows: A predetermined amount of Ni-Cu oxalate was dispersed in ethanol by alternate ultrasonication and magnetic stirring to form a suspension. The activated CF was immersed into the suspension for 15 min. Subsequently, the CF was transferred into an oven and dried at 80 °C for 15 min. This immersion-dry process was repeated for three times. The loading of catalyst precursor on the CF was about 50-60 mg.

Synthesis of NiCu/CNF@CF

The NiCu/CNF@CF composite was obtained from the process of catalytic decomposition of methane.²⁵⁻²⁷ In a typical process, the carbon felt loaded with Ni-Cu oxalate was transferred to a quartz tube reactor. The catalyst precursor was reduced in-situ by methane. After the complete reduction of the precursor, a feedstock consisting of methane and nitrogen (volume ratio of 1:1) was introduced to the reactor. The temperature of the reactor was increased to 600 °C at a rate of 5 °C min⁻¹ and held for 4 hours.

Synthesis of PtCuNi/CNF@CF

The PtCuNi/CNF@CF was synthesized by the galvanic displacement reaction. The details of the experimental procedures are as follows: 3 mL of H₂PtCl₆ aqueous solution with a concentration

of 40 mg L⁻¹ was diluted with 25 mL ethanol. Three pieces of as-prepared NiCu/CNF@CF composite were immersed in the H₂PtCl₆ solution. The galvanic displacement reaction was conducted at 40 °C with varying reaction times of 2 and 24 h. After the reaction, the initial yellowish H₂PtCl₆ solution turned to a green color. The product was thoroughly washed with deionized water, dried at 80 °C overnight and subsequently subjected to a heat-treatment at 600 °C for 4 h in a hydrogen gas flow.

Characterization methods

Field emission scanning electron microscopy (FESEM) (JSM-7600F, JEOL) and transmission electron microscopy (TEM) (JEM2010, JEOL) were used to observe the morphologies of the samples. An EDX analyzer equipped in the TEM and an axis-ultra X-ray photoelectron spectrometer (Kratos-Axis Ultra System) with monochromatized Al-K α radiation were used to analyze the elemental composition of the samples. The metal content in the catalyst and the metal ions in the tested electrolyte were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Varian 710-ES) analyses. The actual metal loading in the catalyst monolith was determined by thermogravimetric analyses (TGA). The TGA test was operated at a temperature range of 50 to 1000°C using a heating rate of 20°C min⁻¹ under air flow (flowrate 50 mL min⁻¹).

Electrochemical measurements

Electrochemical measurements were performed using an electrochemical station equipped with a three-electrode cell. Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometric tests were conducted to evaluate the activity of the samples. Fig. S1 shows the digital photographs of the experimental set-up. A piece of PtCuNi/CNF@CF or NiCu/CNF@CF monolith mounted by a home-made clamper was used as the working electrode.

A saturated calomel electrode (SCE) and graphite plate were used as reference and counter electrodes, respectively. For comparison, a commercial powdered Pt/C catalyst (60 wt.%, Johnson Matthey) was also tested. The experimental procedures of the powered Pt/C catalyst were reported in the authors' previous work.²⁸⁻³⁰ In the experiments, the electrolyte (1M KOH or 1M H₂SO₄) was bubbled with nitrogen gas (purity > 99.99%) and subjected to continuous magnetic stirring. All the potentials reported in this work were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.241 + 0.059 pH) V. To correct the effects of ohmic drop, the series resistance of the system was determined from the electrochemical Impedance spectroscopy measurements. The IR-corrected polarization data were employed to study the kinetics of HER reaction on the catalysts. All the electrochemical measurements were conducted at room temperature (298 ± 1 K).

RESULTS AND DISCUSSION

Scheme 1 Schematically illustration of synthesis procedures of PtCuNi/CNF@CF. (I) deposition nickel-copper oxalates; (II) reduction of nickel-copper oxalates; (III) growth of carbon nanofibers by catalytic decomposition of methane and (IV) spontaneous galvanic displacement process

The PtCuNi/CNF@CF was synthesized by a combination of ambient-pressure chemical vapor deposition and spontaneous galvanic displacement processes. Shown in Scheme 1, the overall experimental procedures consisted of four steps. In step (I), starting from a commercial carbon felt fabric, which was made from a number of carbon fibers with sizes of several micrometers (see Fig. S2), nickel-copper oxalates were deposited onto the surface of carbon fibers by a simple impregnation method. Carbon felt was selected as supports to fabricate the hierarchical electrocatalysts because of its well-defined geometry shape, high porosity and excellent electron conductivity.³¹ The relatively large diameters of the carbon fibers was favorable for the successful deposition of nickel-copper oxalates as verified by the FESEM micrographs (see Fig. S3).³² In step (II), the deposited nickel-copper oxalates were reduced into metallic NiCu NPs in a methane gas stream at a temperature range of 350-400 °C. The resulting NiCu NPs were intimately anchored to the carbon fibers as shown in Fig. S4. Subsequently, in step (III), with further increasing temperature to 600 °C, the NiCu catalyzed decomposition of methane occurred, producing carbon nanofibers and gaseous hydrogen.^{24,25} The chemical vapor deposition process was carried out for 4 h to ensure sufficient formation of carbon nanofiber arrays on the carbon felt supports. In step (IV), after cooling to room temperature, the resulting NiCu/CNF@CF was immersed into a chloroplatinic acid alcoholic solution to initiate the galvanic replacement process as described in reactions (1) and (2):³³

After a given period of reaction time, the obtained PtCuNi/CNF@CF monolith was thoroughly washed with deionized water and then thermally treated at 600 °C in a hydrogen gas stream for 4

h to remove impurities. As illustrated in Scheme 1, the NiCu NPs serve as catalysts for the growth of carbon nanofibers (step (III)) as well as templates to deposit Pt by the galvanic replacement process (step (IV)). In the literature, the metallic NPs were always treated as impurities and removed by tedious acid leaching when carbon nanofibers/nanotubes were utilized as catalyst supports.³⁴ On the contrary, in this work, the NiCu NPs were artfully utilized as templates to synthesize ternary PtCuNi NPs. The major advantage of this strategy lies in exclusively localizing PtCuNi NPs in the tips of carbon nanofibers, which can be beneficial to the electrochemical performance.

The morphologies and structures of the as-prepared NiCu/CNF@CF were characterized as shown in Fig. 1. FESEM micrographs shown in Fig. 1a-c depict a well-defined 3D hierarchical architected structure, in which the secondary carbon nanofibers are immobilized onto the primary carbon felt. A close view reveals that the carbon nanofibers are vertically aligned to the carbon felt support, leading to the formation of a large number of empty voids within adjacent nanofibers. To fully examine the structures of NiCu/CNF@CF, the secondary carbon nanofibers were detached from the support by intense ultrasonication in ethanol and then collected for TEM observation. Fig. 1d displays the TEM micrograph of isolated carbon nanofibers. Noticeably, many NPs (black dots in Fig. 1d) are located in the tips of the filamentous carbon nanofibers. An enlarged view of a typical NP (Fig. 1e) shows distinct lattice fringes with a space value of 2.05 Å, corresponding to the distance of (111) planes of metallic NiCu alloy.²⁴ A representative high-angle annular dark-field scanning TEM (HAADF-STEM) micrograph (Fig. 1g) reveals that the NPs are well faceted into a pear-like shape owing to the growth of carbon nanofibers.^{24,25} The composition of NPs was analyzed by energy dispersive spectroscopy (EDS). In the EDS profile (Fig. 1f), the NPs consisted of Ni and Cu elements. The HAADF-STEM micrograph and the

corresponding electron energy-loss spectroscopy (EELS) elemental mapping micrographs (Fig. 1g-j) further resolve the distributions of Ni and Cu elements. To determine the contents of Ni and Cu, at least 20 NPs were analyzed and the average atomic ratios of Ni and Cu were calculated to be 64.8 and 35.2%, respectively, which are very close to the Ni/Cu ratio of 2:1 in the oxalate feedstock.

Figure 1 (a)-(c) FESEM micrographs of NiCu/CNF@CF, (d) TEM micrograph of isolated NiCu/CNF, (e) high resolution TEM micrograph of a typical NiCu NP, (f) EDS profile of NiCu NPs, (g) HAADF-STEM micrograph of a typical NiCu NP, (h) and (i) corresponding EELS elemental mappings of Ni and Cu, respectively, and (j) atomic composition of NiCu NPs. Scale bars, 100 μm (a), 10 μm (b), 1 μm (c), 200 nm, (e) 5 nm, (g) 10 nm.

Fig. 2 shows the morphologies and structures of the as-prepared PtCuNi/CNF@CF. FESEM micrographs (Fig. 2a-c) indicate that the PtCuNi/CNF@CF maintains the well-defined hierarchical structure after the galvanic replacement process. Two types of pores, consisting of the interconnected large macropores originating from the pristine carbon felt support and the small pores arising from the assembly of carbon nanofibers, are well preserved in the PtCuNi/CNF@CF monolith. Such a bimodal pore structure is beneficial for the diffusion of electrolytes and the release of gas bubbles during the HER process. Fig. 2d presents an enlarged view of the NP which is shown in the inset. It shows clear lattice fringes, manifesting the high degree of crystallinity. HAADF-STEM micrograph (Fig. 2e) depicts the presence of NPs in the tips of carbon nanofibers. In contrast with the faceted pear-like NiCu NPs, the NPs shown in Fig. 2e exhibit a quasi-spherical morphology, indicating the occurrence of restructuring in the synthesis process. The elemental mapping micrographs shown in Fig. 2g, h and i reveal the distributions of Cu, Pt and Ni elements, respectively. The element distribution in the PtCuNi NPs was also analyzed by line scan. Shown in Fig. 2k, no significant element segregation is noted in the PtCuNi NP. Based on the EDS analyses, the atomic composition of PtCuNi NPs was calculated to be 56.8% (Cu), 42.1% (Pt) and 1.1% (Ni) as shown in Fig. 2j, which is consistent with the results of 56.1% (Cu), 42.3% (Pt) and 1.6% (Ni) as determined by ICP-AES. It is inferred from the composition of PtCuNi NPs that the occurrence of reaction (1) was dominant in the galvanic replacement process, which was related to the higher activity of Ni. The actual metal loading in the monolith was estimated by TGA as shown in Figure S5. The residue in the TGA curve is 3.4 %, which is approximatively taken as the metal content in the catalyst (without considering the oxidation of metal nanoparticles). For each catalyst monolith, the weight is averaged to be 326 ± 12.6 mg and the metal loading is estimated to be 11 mg. The surface

composition of PtCuNi/CNF@CF was studied by the X-ray photoelectron spectroscopy (XPS). As shown in Fig. S6A, the survey spectrum clearly reveals the presence of Pt 4f peak in the spectrum of PtCuNi/CNF@CF. Further analyses on the high-resolution Pt 4f spectrum (Fig. S6B) gave binding energies of 71.4 and 74.7 eV, corresponding to the metallic Pt⁰ 4f_{7/2} and 4f_{5/2} states, respectively. Such binding energies of Pt are larger than those of pure Pt nanocrystals (71.1 and 74.4 eV),³⁵ which could be attributed to the electronic interaction of Pt with Cu and Ni atoms. The presence of metallic nickel and copper elements was also confirmed by the Ni 2p and Cu 2p spectra (Fig. S6C, D). The composition of PtCuNi NPs can be facilely tuned by varying galvanic replacement reaction time. By setting the reaction time to be 2 h, PtCuNi NPs with composition of 72.8% (Cu), 12.9% (Pt) and 14.3% (Ni) were obtained. The structural and physical characteristics of the Pt₁₃Cu₇₃Ni₁₄/CNF@CF were also determined as shown in Fig. S7.

Figure 2 (a)-(c) FESEM micrographs of $\text{Pt}_{42}\text{Cu}_{57}\text{Ni}_1/\text{CNF@CF}$ (inset in (a): an optical micrograph of a piece of $1.5 \times 1.5 \times 0.5$ cm $\text{Pt}_{42}\text{Cu}_{57}\text{Ni}_1/\text{CNF@CF}$ monolith), (d) an enlarged TEM view of a $\text{Pt}_{42}\text{Cu}_{57}\text{Ni}_1$ NP (inset in (d): a TEM micrograph of a typical $\text{Pt}_{42}\text{Cu}_{57}\text{Ni}_1$ NP located in a carbon nanofiber), (e) HAADF-STEM micrograph of isolated $\text{Pt}_{42}\text{Cu}_{57}\text{Ni}_1/\text{CNF}$, (f) high-resolution HAADF-STEM micrograph of a typical $\text{Pt}_{42}\text{Cu}_{57}\text{Ni}_1$ NP, (g)-(h) corresponding EELS elemental maps of Cu, Pt and Ni, respectively, (j) EDS profile of $\text{Pt}_{42}\text{Cu}_{57}\text{Ni}_1/\text{CNF@CF}$ NPs (inset in (j): atomic composition of $\text{Pt}_{42}\text{Cu}_{57}\text{Ni}_1$ NPs), (k) line scan and elemental distribution of a $\text{Pt}_{42}\text{Cu}_{57}\text{Ni}_1$ NP. Scale bars, 100 μm (a), 10 μm (b), 200 nm (c), 5 nm (d), 100 nm (e), 50 nm insets in (d), (f) and (k)

It was demonstrated that Pt was successfully deposited into the NiCu templates to form ternary PtCuNi NPs by the galvanic replacement process and that the hierarchical porous structure and unique location of metallic NPs in the tips of carbon nanofibers were preserved in the resulting PtCuNi/CNF@CF monoliths. Benefiting from these structural features, it is expected that the PtCuNi/CNF@CF could be ideal binder-free electrodes for the HER process.

As a proof of concept, the Pt₄₂Cu₅₇Ni₁/CNF@CF and Pt₁₃Cu₇₃Ni₁₄/CNF@CF monoliths were employed as free-standing electrodes for the HER process. The HER activity was evaluated in both 1 M H₂SO₄ and 1 M KOH at room temperature. For the purpose of comparison, a commercial powdered Pt/C catalyst was also tested. As shown in Fig. S8, the CV curves of the catalysts clearly indicate the occurrence of two typical processes, *i.e.*, hydrogen adsorption-desorption and Pt surface oxidation-reduction. No characteristic features of oxidation-reduction of Cu and Ni are noted in the CV curves of PtCuNi/CNF@CF catalysts in the scan range, indicating the formation of PtCuNi alloys.³⁶ The Pt/C catalyst shows well-resolved hydrogen adsorption-desorption on the facets of Pt crystals. In contrast, the hydrogen adsorption-desorption on the PtCuNi alloys is less defined. Careful inspection reveals that the reduction peaks of Pt alloy catalysts shifts to lower potentials when compared with those of Pt/C catalyst, indicating the changes in the electronic properties of Pt.³⁷ Based on the hydrogen adsorption (dashed area in the CV curves), the electrochemical active surface area (ECSA) of the catalyst was determined.³⁸ The Pt/C catalyst exhibits ECSAs of 64.1 and 69.8 m² g_{Pt}⁻¹ in 1 M H₂SO₄ and KOH solutions respectively, which are larger than those of Pt₄₂Cu₅₇Ni₁/CNF@CF (48.3 and 39.6 m² g⁻¹) and Pt₁₃Cu₇₃Ni₁₄/CNF@CF (39.2 and 35.8 m² g⁻¹) in 1M H₂SO₄ and 1 M KOH solution, respectively.

The HER activity of the catalysts was evaluated by LSV measurements. In Fig. 3, the current density was normalized by the ECSA of Pt. It shows that the Ni₆₅Cu₃₅/CNF@CF possesses limited HER activity in the tested potential range. When compared with the Pt/C, the Pt₄₂Cu₅₇Ni₁/CNF@CF and Pt₁₃Cu₇₃Ni₁₄/CNF@CF require lower potentials to achieve identical current densities. For instance, to obtain a current density of 5 mA cm⁻² in 1 M H₂SO₄, potentials of 70, 83 and 87 mV are required for the Pt₁₃Cu₇₃Ni₁₄/CNF@CF, Pt₄₂Cu₅₇Ni₁/CNF@CF and

Pt/C catalysts, respectively (see Fig. 3a). A comparison of the LSV curves (Fig. 3a and 3b) reveals that all the catalysts shows lower HER activity in 1 M KOH than that in 1 M H₂SO₄, which is attributed to the sluggish kinetics of HER in alkaline solutions.³⁹ To fully characterize the catalyst activity, the current density was normalized by Pt mass (Fig. S9). The results verify that the Pt₄₂Cu₅₇Ni₁/CNF@CF and Pt₁₃Cu₇₃Ni₁₄/CNF@CF show better activity than that of the Pt/C and the activity of the catalysts results in the following order: Pt₁₃Cu₇₃Ni₁₄/CNF@CF > Pt₄₂Cu₅₇Ni₁/CNF@CF > Pt/C. The superior HER activity of Pt₁₃Cu₇₃Ni₁₄/CNF@CF could be attributed to three aspects. First of all, alloying of Pt with Cu and Ni atoms could significantly modify the electronic structure of Pt by the so-called electronic and ligand effects,⁴⁰ which leads to downshifts of the d-band centers of Pt with respect to the Fermi levels. Based on the d-band theory,⁴¹ the adsorption of H_{ads} in the alloyed Pt surface is weakened. It was established that the extremely strong bonding of hydrogen to Pt atoms greatly limited the HER activity of Pt.⁴¹ As a result, the reduced bonding strength of Pt-H_{ads} in the alloyed Pt surface would facilitate the HER process according to the Sabatier principle.⁴² Secondly, the synergetic effects of Cu and Ni could play an important role. Owing to the electronic structures, Pt tends to adsorb hydrogen and the adsorbed hydrogen intermediates in Pt surface are facilely converted into molecular hydrogen.¹⁵ However, Pt is not sufficiently active in water dissociation.⁴³ In contrast, Ni and Cu are capable of breaking HO-H bonds but show low efficiency in converting the resulting hydrogen intermediates to molecular hydrogen.⁴⁴ Thus, the ternary PtCuNi catalyst NPs exhibit significant synergistic effects in HER process, where Ni and Cu atoms initiate water dissociation and Pt atoms are responsible for the adsorption of resulting hydrogen intermediates and their subsequent conversion to H₂.⁴⁵ Lastly, the unique hierarchical structure of Pt₁₃Cu₇₃Ni₁₄/CNF@CF promotes HER activity. The location of binder-free PtCuNi NPs in the tips of the carbon nanofibers

facilitates their full contact with the electrolyte. The carbon nanofiber arrays not only effectively stabilize the PtCuNi NPs, but also provide fast highways for electron transport in the HER process. The porous structures of PtCuNi/CNF@CF are also highly favorable for the diffusion of electrolyte as well as the release of gas bubbles.³¹

Figure 3 (a) and (b) HER activities of catalysts in 1 M H₂SO₄ and 1 M KOH at room temperature, respectively. The polarization curves in (a, b) were recorded at a scan rate of 2 mV s⁻¹ and all the current densities were normalized by the electrochemical active surface areas of Pt.

To study the kinetics of the HER process, Tafel slopes were obtained by plotting the potential versus the logarithm of current density. As shown in Fig. 4, the Ni₆₅Cu₃₅/CNF@CF manifested Tafel slopes of 123 and 210 mV dec⁻¹ in 1 M H₂SO₄ and 1 M KOH, respectively, which are much larger than those of Pt₁₃Cu₇₃Ni₁₄/CNF@CF, Pt₄₂Cu₅₇Ni₁/CNF@CF and Pt/C catalysts. The Tafel plots also reveal that the Pt/C shows slightly smaller Tafel slopes than the Pt₁₃Cu₇₃Ni₁₄/CNF@CF and Pt₄₂Cu₅₇Ni₁/CNF@CF catalysts. For instance, in 1 M H₂SO₄, the Tafel slope for Pt/C is 31 mV dec⁻¹ while the Tafel slopes for Pt₁₃Cu₇₃Ni₁₄/CNF@CF and Pt₄₂Cu₅₇Ni₁/CNF@CF are 38 mV dec⁻¹. In 1 M KOH solution, the Pt₁₃Cu₇₃Ni₁₄/CNF@CF and Pt₄₂Cu₅₇Ni₁/CNF@CF catalysts yielded slopes of 54 and 51 mV dec⁻¹, respectively, which are also slightly larger than that of Pt/C catalyst (48 mV dec⁻¹). The deviations of Tafel slopes in acidic and alkaline solutions could be related to the differences in the rate-limiting step.⁴⁶

Fig. 4 (a) and (b) Tafel plots of catalysts in 1 M H₂SO₄ and 1 M KOH, respectively.

Apart from current density, stability is also a significant criterion to evaluate electrocatalysts. To investigate the stability of the catalysts, accelerated CV tests were conducted in the potential range of -0.3 to 0.1 V with a scan rate of 50 mV s^{-1} . As shown in Fig. 5a, b, among the three catalysts, the Pt₄₂Cu₅₇Ni₁/CNF@CF catalyst exhibits smallest negative potential shifts in the LSV curves after 2000 cyclic test, manifesting the superior durability during the long-term test. It also shows that all the catalysts exhibit better stability in 1 M KOH than in 1 M H₂SO₄. The stability of the catalyst was also evaluated by chronoamperometric measurements. Fig. 5c, d shows the normalized current density as a function of time. The results verify that, amongst the three catalysts, the Pt₄₂Cu₅₇Ni₁/CNF@CF catalyst shows the slowest decay rates in both 1 M H₂SO₄ and 1 M KOH. For instance, after a test period of 1000 s in 1 M H₂SO₄, the Pt₄₂Cu₅₇Ni₁/CNF@CF catalyst maintains 82% of its initial current density, which is higher than those of 68 and 63% obtained from the Pt₁₃Cu₇₃Ni₁₄/CNF@CF and Pt/C catalysts, respectively. Notably, the Pt₄₂Cu₅₇Ni₁/CNF@CF catalyst maintains 93% of its initial current density after testing in 1 M KOH for 1000 s.

Fig. 5 (a) and (b) Cycling stability of catalysts in 1 M H₂SO₄ and 1 M KOH, respectively, (c) and (d) Normalized chronoamperometric curves of catalysts recorded at constant potentials of 50 and 100 mV in 1 M H₂SO₄ and 1 M KOH, respectively.

Pt is considered to be stable under HER conditions because its oxidation-dissolution occurs at higher potentials.⁴⁷ Nevertheless, the poor adhesion of Pt NPs on carbon supports and the corrosion of carbon supports always lead to the detachment and agglomeration of Pt NPs in the HER process, thereby resulting in activity decay of Pt/C catalyst.¹⁹ In the Pt₄₂Cu₅₇Ni₁/CNF@CF and Pt₁₃Cu₇₃Ni₁₄/CNF@CF catalysts, each catalyst NP is strongly adhered to a carbon nanofiber, which greatly suppresses the migration and detachment of catalyst NPs. Thus, the detachment and coalescence of active NPs could not be the main reason for the activity decay of Pt₄₂Cu₅₇Ni₁/CNF@CF and Pt₁₃Cu₇₃Ni₁₄/CNF@CF catalysts. Considering the alloy structure of active NPs, the decay in activity of the catalysts was possibly related to the dissolution of nickel

and/or copper. To verify this, the spent catalysts after 2000 cyclic test were examined by FESEM and TEM. Fig. 6 and Fig. S10 display the morphologies of the spent Pt₁₃Cu₇₃Ni₁₄/CNF@CF after 2000 cyclic test in 1 M H₂SO₄. The micrographs confirm that the active NPs still remain in the tips of carbon nanofibers. In contrast with the pristine catalyst NPs, the spent catalyst NPs exhibit rougher surfaces. A high resolution TEM micrograph shown in Fig. 6c reveals a nanoporous structure in the spent catalyst NPs. The formation of nanoporous structure could be attributed to the dissolution of Ni and Cu during the cyclic tests. In fact, a quantity of nickel ions and a trace of copper ions were detected in the tested electrolyte by ICP analysis and the ratio of the elements in the spent Pt₁₃Cu₇₃Ni₁₄ nanoparticles was determined to be 24Pt:70Cu:6Ni. Contrary to the Pt₁₃Cu₇₃Ni₁₄/CNF@CF, the Pt₄₂Cu₅₇Ni₁/CNF@CF did not show significant metal dissolution during the cyclic tests. Fig. S11 shows that the Pt₄₂Cu₅₇Ni₁/CNF@CF maintains the hierarchical structure with integrity of carbon nanofiber arrays. TEM micrographs confirm that the nonporous catalyst NPs are well preserved in the tip of carbon nanofibers. These findings suggest that the composition of PtCuNi NPs plays a critical role in the formation of nanoporosity and stability of the catalysts, which are consistent with the results reported by Gan *et al.*⁴⁸ It was suggested that a minimum composition in the transition metal was required for the formation of nanoporosity in PtNi alloy NPs.⁴⁸ In this study, the variation in the stability of Pt₁₃Cu₇₃Ni₁₄ and Pt₄₂Cu₅₇Ni₁ NPs could also be explained from the different compositions of the metallic NPs.

Fig. 6 (a) TEM micrographs of isolated spent $\text{Pt}_{13}\text{Cu}_{73}\text{Ni}_{14}/\text{CNF@CF}$, (b) and (c) TEM and high-resolution TEM micrographs of a typical spent $\text{Pt}_{13}\text{Cu}_{73}\text{Ni}_{14}$ NP, (e) and (i) high-resolution HAADF-STEM micrographs of spent $\text{Pt}_{13}\text{Cu}_{73}\text{Ni}_{14}$ NP, (f)-(h) and (j)-(l) corresponding EELS elemental mapping micrographs of Cu, Pt and Ni, respectively. Scale bars, 100 nm (a), 50 nm (b), 10 nm (c), 10 nm (e) and (i)

CONCLUSION

In summary, 3D hierarchical $\text{PtCuNi}/\text{CNF@CF}$ monoliths were synthesized by the combination of ambient-pressure chemical vapor deposition and galvanic replacement reaction. The NiCu NPs served as catalysts for the growth of carbon nanofibers as well as sacrificial templates to deposit Pt. The composition of PtCuNi alloy NPs could be tuned by varying the galvanic replacement reaction time. The resulting $\text{PtCuNi}/\text{CNF@CF}$ monoliths were employed as bind-free electrodes for the HER process. Due to the unique structural features including the alloying of Pt with Cu and Ni atoms, the exclusive location of PtCuNi NPs in the tips of carbon

nanofibers as well as hierarchical porous structure, the PtCuNi/CNF@CF monoliths showed superior activity than the-state-of-art Pt/C catalyst. Electrochemical measurements illustrated that the composition of PtCuNi NPs played a critical role in the stability of catalyst. With well-tuned composition, the Pt₄₂Cu₅₇Ni₁/CNF@CF showed outstanding durability in the HER process. The reported synthesis strategy can be extended to prepare other hierarchical architectures with different supports and metallic components, rendering it possible to design and prepare advanced materials with exceptional properties and functionalities. Owing to the structural merits, such novel architectures will find great applications in energy conversion and storage, water treatment and catalysis.

ASSOCIATED CONTENT

Supporting Information

Digital photos of experimental set-up, FESEM micrographs of pristine carbon felt, nickel-copper oxalates decorated carbon felt and metallic nickel-copper decorated carbon felt, XPS spectra, FESEM and TEM micrographs of Pt₁₃Cu₇₃Ni₁₄/CNF@CF, cyclic voltammetry curves, Pt-mass normalized polarization curves and FESEM micrographs of spent catalysts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

Author contributions

The synthesis of NiCu/CNF@CF was conducted by Y. Shen under the supervision of A.C. Lua at the Nanyang Technological University. The synthesis and evaluation of PtCuNi/CNF@CF were performed by Y. Shen at the Institute of Green Chemistry and Energy, Graduate School at Shenzhen, Tsinghua University. Y. Shen conceived this project, conducted the experiments and wrote the manuscript. J. Xi and X. Qiu joined the discussion of data and revision of this manuscript and gave valuable suggestions. A.C. Lua and Y. Shen revised the manuscript to its final form.

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