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Surface controllable anchoring of Cu onto nanostructured PtNi for efficient electrochemical hydrogen evolution from seawater

Xiong Yang^{1†}, Yu-Xuan Xiao^{2†}, Jiang-Bo Chen¹, Fei Yu¹, Ge Tian¹, Fu-Fei Pu¹, Song Zhang¹, Susana I. Córdoba de Torresi³, Mark D. Symes⁴, Christoph Janiak⁵ and Xiao-Yu Yang^{1*}

ABSTRACT Composition adjustment and establishment of multifunctional sites are promising routes to enhance the performance of Pt nanoalloys. A new strategy, involving surface controllable anchoring of Cu on nanostructured PtNi (named as Cu/PtNi), has been developed to enable precise control of stoichiometric elements. The nanostructured material contains oxophilic Ni that promotes fast water dissociation, Pt for superior H adsorption and efficient H₂ production, and Cu to give positive Gibbs free-energy of active hydrogen adsorption for H₂ desorption. The new Cu/PtNi electrocatalyst displays superior activity in the electrocatalytic hydrogen evolution reaction, associated with an overpotential of 23 mV at 10 mA cm⁻² in alkaline seawater that is five times higher than the mass activity of commercial Pt/C (at 70 mV overpotential). Results of density functional theory calculations verify that key processes including H₂O dissociation, H^{*} adsorption and H₂ desorption involved in the hydrogen evolution reaction pathway in alkaline seawater are facilitated by Pt, Ni, and Cu multifunctional metal sites.

Keywords: Cu/PtNi, seawater hydrogen evolution, surface adjustment, multifunction sites, hierarchical structure

INTRODUCTION

Platinum (Pt)-based nanometals are considered to be the most efficient catalysts for the hydrogen evolution reaction (HER) [1–5]. Nanostructure design and nanoalloy composition, which enable acceleration of the dissociation of H₂O, tuning of excessive adsorption of H^{*} and facilitation of the desorption of H₂, are very promising routes to enhance the performance of Pt [6–8]. For example, PtNi alloy is one of the most active electrocatalysts, where Ni is an oxophilic transition metal for enhancement of hydroxyl adsorption and the dissociation of H₂O [9–11], and the electronic structure of Pt is adjusted by electron migration from Ni to Pt for optimization of adsorption of H^{*} [5], although this may be detrimental for H₂ desorption. Ideally, multiple metal sites in Pt-based metals give rise to fast dissociation of H⁺ and

efficient desorption of H₂ by synergistic alloying effects. Note that the key to electrocatalysis lies in the fact that the charge carriers travel to the electrode surface during electrocatalytic reactions, and thus the surface adjustment is critical for the high performance of Pt-based alloys [12-18]. In the past few years, great efforts have been devoted to improving the catalytic efficiency through adjusting surface grain strain and the establishment of an electron-rich surface. For example, Zhou's group [19–21] reported the synthesis of heteroatom (N, P, S) doping to expand the original lattice while at the same time reduce the dband contraction and optimize the H adsorption strength on the surface. In addition, Hou's group [22-26] established the electron-rich surface active sites (Ru, Co and W, etc.) to weaken the excessive H* adsorption and improve the catalytic properties. However, there are few reports in which more than two different metals are found in reproducible ratios on the surface of nanoalloys, because different rates of crystal nuclei formation and different lattice spacings of more than two independent metal precursors would not lead to the formation of a homogeneous phase and be hard to allow precise control of stoichiometric elements [27]. It is seemingly impossible to precisely control the stoichiometry of such surface metal sites.

Metal sites in nanoalloys should perform specific functions for anticipated H₂ production. For example, in PtNiCu, oxophilic Ni shows fast water dissociation, Pt has superior H* adsorption features for efficient H₂ production, and Cu possesses positive Gibbs free-energy of hydrogen adsorption (ΔG_{H^*}) for H₂ desorption [9,28–30]. Considering the role of Cu and the amount of Cu which would cover the active sites on the surface of PtNi, an appropriate ratio of Cu in PtNiCu is required. This provides the possibility that surface adjustment of Cu enables efficient improvement of H₂ production of PtNi electrocatalysts. Due to the difficulty of surface modification, the optimization of Ptbased materials to date has mainly focused on the adjustment of lattice spacing [31].

Herein, a very facile direct adsorbed-reduction method has been developed to anchor and tune Cu on the surface of PtNi with a Ni to Pt ratio of around 1 in a room-temperature, open, and aqueous alkaline system. The ratios of anchored Cu sites

¹ State Key Laboratory of Advanced Technology for Materials Synthesis and Processing & Shenzhen Research Institute & International School of Materials Science and Engineering and Processing, Wuhan University of Technology, Wuhan 430070, China

² School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, China

³ Instituto de Química, Universidade de Sao Paulo, Av. Prof. Lineu Prestes 748, 05508-080 São Paulo, SP, Brazil

⁴ WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom

⁵ Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf, Düsseldorf, 40204, Germany

[†] These authors contributed equally to this work.

^{*} Corresponding author (email: xyyang@whut.edu.cn)

were tuned from 1 to 24 at%, and the sample with 4 at% of Cu on PtNi shows the best performance. Water electrolysis using abundantly available seawater would be an ideal method for low-cost and large-scale hydrogen production [32–36]. But compared with the electrocatalytic process taking place in industrially favored alkaline media, HER in seawater with Pt-based alloys is difficult to perform owing to corrosion associated with metal chloride/hydroxide formation caused by the abundance of chloride ions in seawater [33,37–39]. Therefore, alkaline seawater was selected as a relatively harsh condition to test the activity and durability of Cu/PtNi. Such directional 4 at% Cu anchored on the PtNi surface (named as Cu/PtNi) facilitates hydrogen desorption, and shows superior activity, with an overpotential of 23 mV at 10 mA cm⁻² in alkaline seawater,

compared with PtNi (60 mV), co-reduced PtNiCu (40 mV), and commercial Pt/C (92 mV). Very interestingly, Cu/PtNi shows outstanding durability, with a very small activity loss after 20-h HERs in alkaline seawater. Density functional theory (DFT) results further verify the process (water dissociation, H^* adsorption and H_2 desorption) of the HER with the help of Pt, Ni, and Cu multifunctional metal sites in alkaline seawater.

RESULTS AND DISCUSSION

A scheme of the procedure used to prepare Cu/PtNi is displayed in Fig. 1a. First, the alloy PtNi with a hexagonal closed packed (hcp) structure was prepared by using a hydrothermal method [40]. PtNi was then mixed with copper acetate and NaOH to carry out a reaction obtaining Cu(OH)₂ which tended to be



Figure 1 (a) Schematic of the procedure for preparation of Cu/PtNi (4 at%). (b) SEM image of Cu/PtNi (4 at%). (c) Low- and (d) high-magnification TEM images, (e) FFT pattern and (f) high-magnification TEM images of Cu/PtNi (4 at%). The yellow and blue regions correspond to the Cu nanoparticle and PtNi, respectively. (g) HAADF-STEM image and (h-k) the corresponding energy dispersive X-ray spectroscopy mappings.

strongly absorbed onto oxophilic Ni sites. Finally, ascorbic acid (AA) was used to reduce Cu(OH)₂ to Cu forming Cu/PtNi composite. Fig. 1b shows a scanning electron microscopy (SEM) image of the as-synthesized PtNi with 4 at% Cu nanoparticles (denoted as Cu/PtNi in the studies described below, the ratio of Cu determined by electron-coupled plasma atomic emission spectrometry (ICP-AES), see Table S1). The image demonstrates that Cu/PtNi has a homogeneous hierarchically branched morphology. The transmission electron microscopy (TEM) image shows that the average length of the branches is ~150 nm and the diameter is ~30 nm (Fig. 1c, d). The fast Fourier transform (FFT) pattern of Cu/PtNi contains a set of diffraction rings assignable to the $(01\overline{1}0)$, $(01\overline{1}1)$ and $(11\overline{2}0)$ planes of hcp-PtNi (Fig. 1e). In the high-resolution TEM image of Cu/PtNi (Fig. 1f), it can be seen that the lattice spacings are 0.223 and 0.218 nm, which are consistent with the $(01\overline{1}0)$ and (0002) planes of hcp PtNi alloy. One Cu nanoparticle with a diameter of 2 nm on the branch of PtNi, shows a lattice spacing of 0.210 nm which is consistent with the (111) plane of Cu. Fig. 1g displays a highangle annular dark-field scanning TEM (HAADF-STEM) image and the corresponding elemental mapping images are given in Fig. 1h-k. The images show that Pt, Ni, and Cu are homogeneously distributed throughout the branches, further indicating the presence of highly dispersed Cu on the PtNi surface.

The morphology and composition of PtNi evaluated using TEM show that PtNi and Cu/PtNi have comparable shapes and structures (Fig. S1), indicating that the branched structure is not affected by the deposition of Cu nanoparticles. In addition, the unique branched structure endows PtNi nanoparticles with large surface areas containing an abundance of attachment sites for Cu [40]. The HAADF-STEM image and the corresponding elemental mapping images (Fig. S1e, f) show that Pt and Ni are highly homodispersed. For comparison, PtNiCu was synthesized by adding the Cu precursors during the synthetic process of PtNi. As shown in Fig. S2, PtNiCu exhibits a similar morphology to that of PtNi and Cu/PtNi.

X-ray diffraction (XRD) was employed to investigate the crystal structure of Cu/PtNi. As shown in Fig. 2a, PtNi, PtNiCu and Cu/PtNi all display characteristic diffraction peaks at around 40°, 42°, 45°, 72°, 80°, and 87° which match well with the hcp PtNi alloy as previously reported [40-42]. The similarity of the XRD patterns of Cu/PtNi and PtNi indicates that the introduction of Cu nanoparticles does not change the crystalline structure of PtNi. Note that a diffraction peak corresponding to Cu is not present in the XRD pattern of Cu/PtNi, which is likely due to its small size, well dispersity and low content (4 at%, according to ICP-AES, see Table S1) [43]. To better characterize the incorporation of Cu, pure Cu nanoparticles were synthesized for comparison. The presence of a broad peak associated with face centered cubic (fcc)-structured Cu confirms that the Cu nanoparticles have small sizes, well dispersity and low content (Fig. S3). Moreover, the XRD pattern of PtNiCu, prepared using the conventional solvothermal process, contains obvious signals for the fcc PtCu and fcc Pt, which proves the difficulty in controllable synthesis of trimetallic alloy due to the vast difference in chemical and physical properties of mixing elements (Fig. S4).

X-ray photoelectron spectroscopy (XPS) was conducted to further explore the chemical states and structures of Cu/PtNi,



Figure 2 (a) XRD patterns of PtNi, PtNiCu and Cu/PtNi (4 at%). XPS showing binding energies of (b) Pt 4f for commercial Pt/C, PtNi, PtNiCu and Cu/PtNi (4 at%), and (c) Ni 2p for PtNi, PtNiCu and Cu/PtNi (4 at%). (d) UPS spectra and (e) bar graph showing work functions of commercial Pt/C, PtNi, PtNiCu and Cu/PtNi (4 at%). (f) ESR spectra of commercial Pt/C, PtNi, PtNiCu and Cu/PtNi (4 at%).

PtNi, PtNiCu, and commercial Pt/C (Figs S5, S6). As shown in Fig. 2b, the Pt $4f_{5/2}$ binding energy of Cu/PtNi is 0.2 eV lower than that of PtNi, which indicates the electron transfer from Cu to Pt owing to the lower electronegativity of Cu (1.9) than that of Pt (2.2) [44-46]. The Pt 4f peak fitting results of commercial Pt/C, PtNi, PtNiCu, and Cu/PtNi, displayed in Table S2, clearly demonstrate that Pt⁰ is present on the surfaces of these alloys, which makes them more resistant to corrosion [46]. In addition, the Ni 2p peaks of Cu/PtNi are shifted to higher binding energies in comparison with those of PtNi (Fig. 2c and Table S2), as a result of electron migration to Pt. This electronegativity induced phenomenon leads to the electron transfer from Ni to Pt and offers a higher electron vacancy in Ni 3d orbitals, which could enhance interactions with water and create suitable hydroxyl adsorption/desorption energies needed to accelerate HER under alkaline conditions [5,47,48]. In addition, the Ni 2p fitting results (Table S2) show that significantly more Ni(OH)₂ is present in Cu/PtNi compared with that in PtNi, which could also facilitate water dissociation. This difference is likely a result of Ni oxidation by Cu(OH)2 and dissolved oxygen during the reduction reaction (Fig. 1a).

Ultraviolet photoelectron spectroscopy (UPS) was carried out to determine the change of work function associated with the introduction of Cu to PtNi giving Cu/PtNi (Fig. 2d). The work function corresponds to the energy required to move a valance electron from the material surface to infinity and is a qualitative index used to describe the activity of a material in a redox reaction [49]. The UPS derived work functions of the alloys were found to be in the following order: Cu/PtNi (4.2 eV) = PtNiCu (4.2 eV) < PtNi (4.3 eV) < commercial Pt/C (4.5 eV) (Fig. 2e). Cu/PtNi shows a lower work function than the other alloys, indicating a unique surface effect from the introduction of Cu.

To gain additional information about the influence of the introduction of Cu nanoparticles into Cu/PtNi, the localized paramagnetic species were investigated by using electron spin resonance (ESR) spectroscopy (Fig. 2f). Compared with the signals in the spectrum of the PtNi alloy, those for Cu/PtNi and PtNiCu have decreased in intensities, indicating that interactions occur between PtNi and the Cu component. Notably, the intensity of the ESR signal for Cu/PtNi is only slightly lower while that for PtNiCu is more attenuated, illustrating that only relatively weak interactions in Cu/PtNi occur due to the introduction of Cu nanoparticles, while strong interactions are created by alloying Cu into PtNiCu.

Cyclic voltammetry (CV) was carried out to examine the electrochemically active surface area (ECSA) of Cu/PtNi in contrast to those of PtNi, PtNiCu and commercial Pt/C catalysts (Fig. S7a). ECSAs were obtained by measuring the charge collected in the hydrogen adsorption/desorption region. Based on the mass of Pt, the ECSAs of commercial Pt/C, PtNi, PtNiCu, and Cu/PtNi are 59, 41, 37 and 30 m² g⁻¹, respectively (Fig. S7b, and Table S3). Note that the specific ECSA of commercial Pt/C is higher than those of other catalysts due to its small particle size [50]. As a result of introducing Cu nanoparticles onto the active sites of PtNi, Cu/PtNi shows a lower ECSA than PtNi and PtNiCu, confirming that Cu nanoparticles are well anchored onto the PtNi. Next, the catalytic activities of Cu/PtNi for HER in alkaline seawater were assessed. Polarization curves of Cu/ PtNi and the related commercial Pt/C, PtNi, and PtNiCu in N₂saturated alkaline seawater (3.5 wt% NaCl + 1 mol L^{-1} KOH) at room temperature were determined using a scan rate of 5 mV s⁻¹. As can be seen in Fig. 3a, the HER activities of the catalysts are in the following order: Cu/PtNi > PtNiCu > PtNi > commercial Pt/C. Clearly, the overpotential (at a current density of 10 mA cm⁻²) for Cu/PtNi containing 4 at% Cu (23 mV) is lower than that of PtNiCu (40 mV), PtNi (60 mV), and commercial Pt/C (92 mV) (Fig. 3b). In addition, the mass activity of Cu/PtNi is 2.32 mA μg_{Pt}^{-1} (at 70 mV overpotential) (Table S3), which is five-fold that of PtNi (0.83 mA μg_{Pt}^{-1}) and about two-fold that of PtNiCu (1.34 mA μg_{Pt}^{-1}).

To elucidate the mechanism of HER catalyzed by Cu/PtNi, Tafel slopes were acquired by fitting experimental data using the Butler-Volmer equation (Fig. 3c). The respective Tafel slopes of commercial Pt/C, PtNi, PtNiCu, and Cu/PtNi were calculated to be 74, 42, 36, and 24 mV dec⁻¹. Compared with commercial Pt/C (74 mV dec⁻¹), the lower Tafel slope of PtNi indicates that the introduction of strongly oxophilic Ni stabilizes hydroxyl intermediates and facilitates water dissociation [10,40,51,52]. Thus, it is clear that the Heyrovsky step is rate-limiting in the processes promoted by PtNi and PtNiCu. In contrast, the Tafel slope of Cu/PtNi is 24 mV dec⁻¹, indicating that the Tafel step is rate-limiting in HER [8,53]. Moreover, a comparison of HER performance of Cu/PtNi and other catalysts in alkaline seawater shows that Cu/PtNi displays the lowest Tafel slope and potential (Fig. 3d and Table S4). To explore interface charge transfer in the newly developed catalyst, electrochemical impedance spectroscopy (EIS) was carried out. The EIS results show that the charge transfer resistance (R_{ct}) follows the sequence as PtNi $(7.6 \Omega) < Cu/PtNi (8.5 \Omega) < Pt/C (20.9 \Omega) < PtNiCu (22.4 \Omega),$ indicating a relatively small R_{ct} of Cu/PtNi (Fig. S8). The slightly increased R_{ct} of Cu/PtNi compared with PtNi may be due to the incorporation of Cu nanoparticles onto the originally ordered PtNi crystalline structure. This finding demonstrates that Cu/ PtNi has a relatively high charge transport efficiency and relatively high potential for excellent electrocatalytic performance. The turnover frequencies (TOF, Fig. 3e) of the Pt-based catalysts were determined in accordance with surface charges that are proportional to the number of electrochemically active sites [54-57], and compared at an overpotential of 70 mV (Fig. S9). The results show that the TOF of Cu/PtNi is 2.33 s⁻¹, which is fivefold that of commercial Pt/C (0.46 s^{-1}), about three-fold that of PtNi (0.85 s⁻¹) and about two-fold that of PtNiCu (1.36 s⁻¹).

The durability of the catalysts for HER was also evaluated. Chronopotentiometry measurements show that in contrast to commercial Pt/C, Cu/PtNi displays better long-term stability without suffering from such severe potential change during the HER (Fig. 3f). Chronopotentiometry (Fig. 3g) demonstrates that only a slight shift of the potential of Cu/PtNi takes place after 2000 cycles. The results suggest that the improved stability of Cu/PtNi derives from the direct anchoring of Cu. The combined results of the investigations described above definitely demonstrate that Cu/PtNi containing multifunctional sites has greatly improved HER activity and durability. In the final phase of this study, we assessed the electrocatalytic properties of Cu/PtNi containing different amounts of Cu nanoparticles. The respective ECSAs for PtNi with 1, 8 and 24 at% Cu nanoparticles were determined to be 36, 25 and 20 $m^2 g_{Pt}^{-1}$ (Fig. S10a, b and Table S4), showing that the ECSA of PtNi decreases with increasing Cu content. A comparison of polarization curves of PtNi with different contents of Cu nanoparticles (Fig. S11a and Fig. 3a) clearly shows that the 4 at% Cu/PtNi has the highest



Figure 3 (a) HER polarization curves, (b) overpotentials (at a current density of 10 mA cm⁻²), and (c) Tafel plots of commercial Pt/C, PtNi, PtNiCu, and Cu/PtNi (4 at%). (d) Performance of Cu/PtNi (4 at%) in comparison to other catalysts towards HER. (e) Calculated TOF curves of commercial Pt/C, PtNi, PtNiCu, and Cu/PtNi (4 at%). (f) Chronopotentiometry curves promoted by Cu/PtNi (4 at%) and commercial Pt/C for HER. (g) Linear sweep voltammetry (LSV) plots of Cu/PtNi (4 at%) before and after 2000 potential cycles in alkaline seawater.

activity, with a mass activity of 2.32 mA μg_{Pt}^{-1} , that is about two to three times higher than those containing 1, 8 and 24 at% Cu (Fig. 3b, Fig. S11b). TOF measurements show that 4 at% Cu/ PtNi has the highest HER performance (Fig. S12a and Fig. 3e), with a TOF that is almost two- to three-fold that of the respective 1, 8, and 24 at% Cu/PtNi (Fig. S12b). Finally, the 4 at% Cu/PtNi has a Tafel slope of 24 mV dec⁻¹, a value that is lower than those of the analogues containing 1 (37 mV dec⁻¹), 8 (34 mV dec⁻¹) and 24 at% Cu (43 mV dec⁻¹) (Fig. S13). This observation verifies the excellent H^{*} adsorption/desorption properties of Cu/PtNi for the establishment of multifunctional sites.

To elucidate the inherent relationship between the electronic structure and the excellent electrocatalytic HER performance of Cu/PtNi under alkaline conditions, DFT calculations were performed. Based on previous studies of hexagonal and fcc Pt [43,58], three sets of slab models of fcc (111) facets of PtNi, PtNiCu and Cu/PtNi were constructed, which correspond with hexagonal (0002) facets and are consistent with the TEM images (Figs 1d and 4a). In order to further understand the alkaline HER mechanism, we proceeded to construct models for the adsorption of intermediates on the surface (Fig. S14). As shown in Fig. 4b, c, PtNi and PtNiCu have larger water dissociation energy barriers (ΔG_{w^*}) of 1.32 and 1.21 eV and high hydrogen adsorption free energies (ΔG_{H^*}) of -0.45 and -0.30 eV, indicating that they operate through a very sluggish Volmer–Tafel

mechanism [57]. In contrast, the ΔG_{w^*} on Cu/PtNi is significantly decreased to 0.87 eV, and it has a lower $\Delta G_{\rm H^*}$ of 0.19 eV, which corresponds to a superior hydrogen desorption capability. Moreover, in order to probe the role of Cu site in Cu/ PtNi for HER, two models of hydrogen adsorbed on Cu sites of Cu/PtNi and PtNiCu respectively were constructed and compared (Fig. S15). As can be seen from Fig. S16, Cu/PtNi exhibits a much positive ΔG_{H^*} than that of PtNiCu, proving the incorporation of Cu onto PtNi will effectively accelerate H₂ desorption from Cu/PtNi catalyst. Thus, Cu/PtNi undergoes a highly active center promoted HER process, which agrees well with the experimental results. Thereby, faster H₂O dissociation and more appropriate adsorption/desorption of H render Cu/PtNi a better HER performance, indicating that the Volmer step and Tafel step work positively together. Fig. 4d shows the differential charge density diagrams calculated from the three models. It is clear the introduction of Cu nanoparticles has enhanced the asymmetric charge transfer, leading to charge polarization and electron redistribution of the surface. Fig. 4e shows the partially density of states (PDOS) diagrams for the three models of Cu/ PtNi, PtNi and PtNiCu. The overlap of the Pt 5d orbital with the Ni 3d orbital around the Fermi level indicates that orbital coupling may facilitate the HER process. According to the d-band theory [36,59-62], metal atoms with a more positive d-band center possess less occupancy of antibonding states and thus enter into stronger adsorption to the intermediates. The Cu/PtNi



Figure 4 Results of the DFT calculations and the corresponding mechanisms of the electrocatalytic HER on the surfaces of different catalysts under alkaline conditions. (a) Structural models. Calculated adsorption free energy diagrams for the (b) Volmer step and (c) Tafel step. (d) Differential charge density diagrams (the blue region represents electron depletion; the yellow region represents electron accumulation), and (e) PDOS of PtNi, PtNiCu, and Cu/PtNi.

has the more positive d-band center (-1.89 eV) than that of PtNi (-1.90 eV) and PtNiCu (-1.93 eV), which indicates the strongest adsorption to intermediates and the easiest adsorption of H₂O.

CONCLUSIONS

In summary, we have developed an effective strategy for efficient and durable Cu/PtNi catalyst design by surface controllable anchoring of Cu onto nanostructured PtNi to establish multifunctional sites toward HER. The existence of multifunctional sites has been revealed by both experiments and DFT calculations. Moreover, Cu/PtNi exhibits a five-fold higher mass activity and much higher durability towards HER than that of the commercial Pt/C catalyst. The enhanced electrocatalytic performance of Cu/PtNi is ascribed to the multifunctional sites, which optimize water dissociation, adsorption of H_{ads}, and desorption of molecular hydrogen. The results of this investigation shed new light on the design of Pt-based nanomaterials that have multifunctional sites for high catalytic performance in the HER.

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Author contributions Yang X performed the experiments related to the synthesis and electrocatalytic performance. Yang X, Xiao YX, and Yang XY conceived the project, provided the ideas and designed the experiments. Tian G performed TEM and EDX characterizations. Chen JB and Yu F performed DFT calculation and analysis. Pu FF provided guidance for material synthesis. Yang X, Xiao YX, and Yang XY wrote and revised the paper. de Torresi SIC, Symes MD, Zhang S, and Janiak C revised the paper. All the authors discussed the results, analyzed the data, and gave their approval for the submission of the final version of the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.



Xiong Yang received his Bachelor degree in materials science from Wuhan University of Technology in 2019. He is currently a PhD candidate under the supervision of Prof. Xiaoyu Yang at Wuhan University of Technology. His research interest focuses on Pt-based metal compounds for applications in the electrocatalysis field.





Yu-Xuan Xiao received his PhD degree from Wuhan University of Technology in 2021. Currently, he is a postdoctoral fellow at Sun Yat-sen University. His research interest is focused on the design and synthesis of metal nanomaterials, as well as their applications in electrocatalysis.



Xiao-Yu Yang earned his BS degree from Jilin University in 2000 and his joint PhD degree from Jilin University, China and Facultes Universitaires Notre-Dame de la Paix (FUNDP), Belgium (co-education) in 2007. After a postdoctoral fellowship at FUNDP, he worked as a "Chargé de Recherches" at Le Fonds de la Recherche Scientifique (F.N. R.S.) of Belgium. He is currently working as a full professor at the State Key Laboratory of Advanced Technology for Material Synthesis and Processing and a visiting professor at Harvard University.

Cu在纳米结构PtNi上的表面可控锚定用于高效海水 产氢

杨雄^{1†}, 肖宇轩^{2†}, 陈江波¹, 余菲¹, 田歌¹, 蒲福飞¹, 章嵩¹, Susana I. Córdoba de Torresi³, Mark D. Symes⁴, Christoph Janiak⁵, 阳晓宇^{1*}

摘要 表面组分调控及建立多功能活性位点是提高Pt基催化剂性能的 有效途径.通过将Cu可控地错定在纳米结构PtNi表面(Cu/PtNi)可以精 确控制Pt基催化剂表面元素的化学计量比,其中亲氧的非贵金属Ni能 加速水的解离,Pt由于具有适中的H吸附能,可有效地将游离态的H转 换成氢气,Cu由于具有正的H吸附吉布斯自由能(ΔG_{H*}),有助于H₂的脱 附.其中具有最优组分比例的Cu/PtNi电催化剂在海水中表现出优异的 电化学析氢活性和稳定性,在碱性海水中,10 mA cm⁻²下的过电位为 23 mV (在70 mV过电位下,其质量活性是商用Pt/C的5倍).同时,密度 泛函理论结果进一步验证了在碱性海水中Pt,Ni和Cu多功能金属活性 位点可提高HER的H₂O解离、H*吸附和H₂脱附的过程.