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Facile Synthesis of PdCuRu Porous Nanoplates as Highly Efficient Electrocatalysts for Hydrogen Evolution Reaction in Alkaline Medium

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Abstract: Ru is a key component of electrocatalysts for hydrogen evolution reaction (HER), especially in alkaline media. However, the catalytic activity and durability of Ru-based HER electrocatalysts are still far from satisfactory. Here we report a solvothermal approach for the synthesis of PdCuRu porous nanoplates with different Ru compositions by using Pd nanoplates as the seeds. The PdCuRu porous nanoplates were formed through underpotential deposition (UPD) of Cu on Pd, followed by alloying Cu with Pd through interdiffusion and galvanic replacement between Cu atoms and Ru precursor simultaneously. When evaluated as HER electrocatalysts, the PdCuRu porous nanoplates exhibited excellent catalytic activity and durability. Of them, the $Pd_{24}Cu_{29}Ru_{47}/C$ achieved the lowest overpotential (40.7 mV) and smallest Tafel slope (37.5 mV dec⁻¹) in an alkaline solution (much better than commercial Pt/C). In addition, the $Pd_{24}Cu_{29}Ru_{47}/C$ only lost 17% of its current density during a stability test for 10 h, while commercial Pt/C had a 59.5% drop under the same conditions. We believe that the electron coupling between three metals, unique porous structure, and strong capability of Ru for water dissociation are responsible for such an enhancement in HER performance.

Keywords: Ru-based catalysts; hydrogen evolution reaction; porous structures; nanoplates; multimetallic alloys

1. Introduction

Ongoing global warming and energy crisis issues arising from the overuse of fossil fuels have prompted scientists to urgently search for clean and sustainable alternative energy sources [1–3]. In this regard, molecular hydrogen (H₂) is considered to be the most promising candidate due to its high-energy density without pollutant emission [4,5]. However, the production of H₂ in the industry today still comes from the steam methane reforming process and requires high-energy input and a large amount of CO₂ emission [6,7]. On the contrary, hydrogen evolution reaction (HER) is a half-cell reaction of electrochemical water splitting, which offers a green and sustainable approach for large-scale production of hydrogen with high-purity [8]. Until now, platinum (Pt) is still the critical component of electrocatalysts for HER, especially in acid media. However, the exorbitant cost and insufficient stockpile severely limit the widespread application of Pt-based electrocatalysts with remarkable HER performance, especially in alkaline solution, since Pt exhibits about two or three orders of magnitude lower activity in alkaline environments than acidic media [10].

Recently, ruthenium (Ru) has received great attention as the key component of HER electrocatalysts, especially in alkaline media, due to its similar bond strength with hydrogen and relatively lower cost compared to Pt [11,12]. For instance, Liu and co-workers reported the synthesis of Ru nanoparticles@C quantum dots (Ru@CQDs) hybrid materials, showing



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). excellent catalytic properties for HER under alkaline condition [13]. In addition, much attention have been paid to Ru-based binary alloys since the introduction of second metal can improve the HER properties by electron coupling between two metals and bifunctional mechanisms [14–17]. Certainly, the cost of electrocatalysts can be reduce to one tenth by diluting noble metals with non-precious metals [18,19]. Despite the huge success in Ru-based nanocrystals, the exploration for Ru-based nanocrystals with unique structure and fantastic properties still continues, in particular for multimetallic alloys.

Over the last decade, two-dimensional (2D) nanomaterials with large lateral sizes and ultrathin thicknesses have attracted extensive attention owing to their rich variety of unconventional properties and widespread potential applications. These special geometry features associated with ultrathin 2D nanomaterials endow them with ultrahigh specific surface area, thereby making them promising candidates as advanced catalysts with excellent properties [20–25]. Unlike the intrinsically layered materials, most metals have a highly symmetric crystal lattice, leading to difficulty in the formation of 2D nanostructures thermodynamically [26,27]. Fortunately, many synthetic methods such as the addition of a capping agent or template with 2D structure have been developed to generate 2D metal nanostructures with well-controlled sizes, shapes, and compositions [28–34]. For example, Huang and co-workers reported the synthesis of unique sandwich-like Ru-Ni heterostructures with two hexagonal Ru rings caped on the two ends of a Ni pillar in the presence of polyvinyl pyrrolidone (PVP) serving as a capping agent [29]. In another study, we have developed a general and effective approach for the synthesis of Pt-based multimetallic ultrathin nanoplates with tunable thickness through epitaxial growth by using Pd nanoplates as the seeds [31]. In order to further increase the active sites of the nanoplates, the synthesis of porous 2D nanostructures is highly desirable.

Here, we report one-pot approach for synthesizing PdCuRu porous nanoplates by deposition of CuRu on Pd seeds. Such PdCuRu porous nanoplates with different compositions showed the excellent catalytic properties for HER. Of them, the Pd₂₄Cu₂₉Ru₄₇ nanoplates achieved the highest activity and stability toward HER in an alkaline solution.

2. Materials and Methods

2.1. Chemicals and Materials

Palladium(II) acetylacetonate (Pd(acac)₂, 99%), ruthenium(III) acetylacetonate (Ru(acac)₃, 99%), copper(II)acetylacetonate(Cu(acac)₂, 99%), polyvinylpyrrolidone (PVP, MW = 29000), oleylamine (OAm, 70%), n-butylamine (98%) and tungsten hexacarbonyl (W(CO)₆, 97%) were purchased from Sigma-Aldrich (Saint Louis, MO, USA). Oxalic acid (OA), cetyltrimethylammonium bromide (CTAB), *N*,*N*-dimethylformamide (DMF, AR), benzyl alcohol (BA, AR), ethanol (AR), chloroform (AR), toluene (AR), cyclohexane (AR) and acetone (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were used as received without purification.

2.2. Synthesis of Pd Nanoplates

The Pd nanoplates with an average edge length of 19.8 nm and a thickness of 1.1 nm was synthesized through our previously reported method with slight modification [35,36]. Firstly, 16 mg of Pd(acac)₂, 30 mg of PVP, 60 mg of CTAB and 30 mg of OA were dissolved in 10 mL of DMF and stirred for 1 h at room temperature. Subsequently, the obtained homogeneous solution was transferred into a 25 mL glass flask and 100 mg of W(CO)₆ was then added in an Ar atmosphere. After that, the sealed flask was heated at 70 °C under magnetic stirring for 2 h. Finally, the Pd nanoplates were collected by centrifugation, washed with ethanol for three times and re-dispersed in ethanol for further use. The formation mechanism (e.g., the role of each reactant) of the Pd nanoplates has been already discussed in our previous report [35].

2.3. Synthesis of PdCuRu Nanoplates with Different Compositions

In a standard procedure for the synthesis of the $Pd_{24}Cu_{29}Ru_{47}$ nanoplates, 120 mg of PVP, 0.015 mmol of $Cu(acac)_2$, and 0.020 mmol of $Ru(acac)_3$ were dissolved in 10 mL of BA and stirred for 8 h at room temperature. 2 mL of as-synthesized Pd nanoplates was then added into the above-mentioned reaction solution. After stirring for 1 h, the mixed homogeneous solution was transferred into a 15 mL Teflon-lined stainless-steel autoclave in an Ar atmosphere. Next, the sealed autoclave was heated at 200 °C for 12 h. Finally, the product was collected by centrifugation using acetone and ethanol. This process was repeated three times. To obtain the $Pd_{32}Cu_{33}Ru_{35}$ and $Pd_{19}Cu_{25}Ru_{56}$ nanoplates, the amount of $Ru(acac)_3$ fed in the synthesis was varied from 4 to 12 mg, respectively, with all other conditions being the same as the standard procedure.

2.4. Phase-Transfer of PdCuRu Nanoplates into Hydrophobic Solvent

For a clearer observation, the above-mentioned sample was re-dispersed in a mixture of ethanol, toluene and OAm with a volume ratio of 5:1:5. After stirring for 15 min, the uniformly mixed solution was heated at 80 °C for 12 h. The final product was collected by centrifugation with ethanol and dispersed in cyclohexane.

2.5. Morphological, Structural, and Compositional Characterizations

The morphology of the sample was observed through transmission electron microscopy (TEM) with a Hitachi HT-7700 microscope operated at 100 kV (Hitachi, Tokyo, Japan). High-resolution TEM (HRTEM) was performed using a FEI Tecnai F20 G2 microscope operated at 300 kV (FEI, Hillsboro, OR, USA). Energy dispersive X-ray spectroscopy (EDX) mapping analyses were achieved on a FEI Titan ChemiSTEM equipped with a probe-corrector and a Super-X EDX detector system operated at 200 kV. The X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 focus diffractometer in a scan range of 5°–80° at a scan rate of 1.0° min⁻¹. X-ray photoelectron spectrometry (XPS) was performed on a scanning X-ray microprobe (Axis Supra, Kratos Inc., Manchester, UK) with Al Ka radiation. The percentages of the elements in the samples were detected using inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP, TJA Co, Waltham, MA, USA).

2.6. Electrochemical Measurements

The electrochemical measurements were carried out at a CHI760E electrochemical analyzer (CHInstrument, Shanghai, China) based on a three-electrode cell. The working electrode was a glassy-carbon rotating disk electrode (RDE) (diameter: 5 mm and area: 0.196 cm^2) from Pine Instruments. An Ag/AgCl electrode and a graphite rod were used as the reference electrode and the counter electrode, respectively. To prepare the working electrode, 5 mg of catalyst and 25 µL of Nafion 117 (Aldrich) was dispersed into 5 mL mixed solution containing DI water (Millipore, 18.2 M Ω) and isopropanol with a volume ratio of 4:1. Then the mixture was sonicated for 30 min to form a homogeneous ink. After that, dozens of microliters of the ink were dropped onto the surface of RDE and dried at room temperature. Before electrochemical measurement, the working electrode was cleaned in the Ar-saturated 0.1 M KOH solution with a steady-state cyclic voltammetry (CV) scan for 20 cycles in the range of 0–1 V (vs. RHE) at a rate of 50 mV s⁻¹. Linear sweep voltammetry (LSV) was performed at a scan rate of 2 mV s⁻¹ in the range of 0–1 V (vs. RHE) with i-R compensation and a rotation speed of 1600 rpm was used to remove hydrogen gas bubbles formed on the catalyst surface. The chronoamperometry (I-t) curves were measured at the overpotential when the current density reached 10 mA/cm².

2.7. Measurements of Electrochemical Active Surface Area (ECSA)

The ECSA of the samples was calculated through dividing the double layer capacitance (Cd_1) by the specific capacitance (C_s) of the catalyst surface according to the equation: ECSA = Cd_1/C_s . The Cd₁ was determined by measuring CVs over a potential range of

open-circuit potential (OCP) \pm 0.1 V, at multiple scan rates of 20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 mV s⁻¹ in the non-Faradaic potential region. Then the slope derived from a plot of the measured charging current (i_c) as a function of the scan rate (v) is equal to Cd₁. In this work, C_s is taken 0.040 mF cm⁻² for ECSA calculations.

3. Results and Discussion

The Pd₂₄Cu₂₉Ru₄₇ multimetallic nanoplates were synthesized by a simple solvothermal method in benzyl alcohol (BA) using Ru(acac)₃ and Cu(acac)₂ as metal precursors under an inert atmosphere with Pd nanoplates as the seeds. From Figure S1, the hexagonal Pd nanoplates have an average edge length of ca. 19.28 nm and thickness of ca. 1.1 nm. Figure 1 shows the morphological, structural, and compositional characterizations of the Pd₂₄Cu₂₉Ru₄₇ nanoplates prepared using the standard procedure. From the TEM image in Figure 1a, the products retain the plate-like shape, whereas some porous structures with different sizes appear on the nanoplates. Such porous structures were confirmed by the HAADF-STEM image (Figure 1b). The thickness of the Pd₂₄Cu₂₉Ru₄₇ nanoplates was measured to be ca. 5.5 nm with ~25 atomic layers (Figure 1e and Figure S2). The thickness of the nanoplates were measured by mixing them with carbon nanotubes. The width of the projection for the vertically upstanding nanoplates is the corresponding thickness. As can be seen from the HRTEM image in Figure 1c, the distance of the lattice fringe in the interior of a nanoplates was measured to be 2.150 Å, which is located between Pd(111) with a lattice space of 2.246 Å and Cu (111) with a lattice space of 2.088 Å, confirming the formation of the PdCu alloy. The elemental distribution of Pd, Ru, and Cu in the flat and vertically upstanding Pd₂₄Cu₂₉Ru₄₇ nanoplates was determined by HAADF-STEM-EDX (FEI, Hillsboro, OR, USA) mapping and line-scan profile analyses, as shown in Figure 1d,e. As observed from Figure 1d, Pd and Cu are concentrated in the interior of the nanoplates, while Ru mainly exists on the surface of the nanoplates and only small amount of Ru scatters throughout the nanoplates. This demonstration was supported by the HAADF-STEM image of a vertically upstanding nanoplate (Figure 1e) and corresponding EDX line-scan analysis (FEI, Hillsboro, OR, USA) (Figure 1f). The formation of this structure was also consistent with the analysis for the formation process of the nanoplates (see next part). The atomic ratio of Pd, Cu, and Ru in the nanoplates was determined to be 24: 29: 47 through ICP-AES (Table S1), which is close to the feeding ratio of the metal precursors.



Figure 1. (a) TEM, (b) HAADF-STEM (c) HRTEM and (d) HAADF-STEM-EDX mapping images of a planar Pd₂₄Cu₂₉Ru₄₇ nanoplate. (e) HAADF-STEM-EDX images of a vertically upstanding Pd₂₄Cu₂₉Ru₄₇ nanoplate. Pd (orange), Ru (red), and Cu (green). (f) Line-scan profiles along the side of a Pd₂₄Cu₂₉Ru₄₇ nanoplate.

When the amount of the Ru precursor is varied from 4 to 12 mg, the porous nanoplates with similar shape and element distribution are also generated (Figures 2–4). The atomic ratio of Pd, Cu, and Ru in the nanoplates is varied to 32: 33: 35 and 19: 25: 56 (Table S1). We compared the size of the pores and their area percentage for above-mentioned three kinds of the nanoplates with different amounts of Ru (Figure S3). Due to the irregular shape of the pores, the data may not exactly accurate, but the trend is believable. With increasing amount of Ru, the size and area percentage of the pores both decreased due to the deposition of Ru on the surface. This result is also consistent with the EDX mapping data that Ru is rich on the surface of the nanoplates (Figure 1e).



—100 nm

Figure 2. TEM images of the (a) Pd₃₂Cu₃₃Ru₃₅ and (b) Pd₁₉Cu₂₅Ru₅₆ nanoplates.



Figure 3. (a) HAADF-STEM and (b) EDX mapping images of the Pd₃₂Cu₃₃Ru₃₅ nanoplates.



Figure 4. (a) HAADF-STEM and (b) EDX mapping images of the Pd₁₉Cu₂₅Ru₅₆ nanoplates.

The crystal structure of the nanoplates is further characterized by XRD analysis. As observed from the XRD patterns of the $Pd_{24}Cu_{29}Ru_{47}$ nanoplates (Figure 5a), there are three typical diffraction peaks located at 41.56°, 47.62°, and 70.35°, which can be assigned to (111), (200), and (220) planes of face-centered cubic (*fcc*) phases. The diffraction peaks are broadened a little due to the small and thin scale of the nanoplates. No diffraction peak associated with pure Pd, Cu or hexagonal close-packed (*hcp*) Ru was detected. According to our previous report, the formation of the *fcc*-structured Ru is attributed to the induction of the Pd *fcc* lattice during the deposition of Ru atoms on Pd nanoplates [37]. With the increasing amount of Ru, the diffraction peaks of the nanoplates are almost located at the same position due to the similar atomic size of Ru with other two atoms (Figure S4). Combined with the EDX data (Figure 1d,e), the nanoplates with an interior of PdCu alloys and a Ru richened surface were generated.



Figure 5. (a) XRD pattern, (b) high-resolution Pd 3d, (c) Ru 3p, and (d) Cu 2p XPS spectra of the Pd₂₄Cu₂₉Ru₄₇ nanoplates.

The high-resolution XPS spectra were employed to determine the valence state of Pd 3d, Ru 3p, and Cu 2p of the $Pd_{24}Cu_{29}Ru_{47}$ nanoplates (Figure 5b–d). As observed, all three elements mainly exist in the metallic state. As shown in Figure 5b, two representative XPS peaks with the binding energies of 335.5 and 340.8 eV can be assigned to metallic Pd $3d_{5/2}$ and $3d_{3/2}$, respectively. Whereas other two weak peaks at 336.0 and 341.3 eV can be attributed to the bivalent Pd^{2+} . All these peaks are positively shifted in binding energy relative to those of the pure counterparts. Noticeably, an opposite trend associated with Ru 3p and Cu 2p was observed in the $Pd_{24}Cu_{29}Ru_{47}$ nanoplate. These results demonstrated that a strong electron coupling occurred between Pd, Ru, and Cu. Similarly, the occurrence of electron transfer has been confirmed for other two PdCuRu nanoplates (Figures S5 and S6). Such electron coupling might be expected to boost the catalytic activity of the HER electrocatalysts since Ru can weaken hydrogen adsorption and is highly efficient in water dissociation in alkaline electrolyte [38,39].

Recently, we have developed a general method for the synthesis of multimetallic Pd@PtM (M = Ni, Rh, Ru) nanoplates using Pd nanoplates as the templates [31]. For comparison, the introduction of Cu here results in the formation of the porous nanoplates, indicating the critical role of Cu. First, previous study indicated that only Cu²⁺ ions cannot be reduced by benzyl alcohol [40]. On the contrary, Ru nanoparticles are often obtained through the reduction of Ru^{3+} ions by polyol [40–42]. In this work, the presence of the Pd nanoplates facilitates the reduction of Cu²⁺ ions to Cu atoms prior to Ru precursor due to the well-known underpotential deposition (UPD) [43]. This demonstration is supported by the ICP-AES data (Figure 6d and Table S2), showing the much higher atomic ratio of Cu than Ru atoms in the product in the initial stage. According to our previous result [44], the newly formed Cu atoms could interdiffuse with Pd atoms to form alloys at 200 $^{\circ}$ C (i.e., Kirkendall effect). In addition, the strain arising from the twinned structure of the Pd nanoplates accelerated the out-diffusion of Pd atoms [44], breaking the plate-like structures. Certainly, the ultrathin Pd nanoplates (1.1 nm) is vulnerable to the variation of the strain during the interdiffusion, and may tend to be broken. The control experiment in the absence of Ru precursor (Figure 6a) shows that the Pd plate-like seeds converted into small nanoparticles, induced by the addition of Cu precursor. While, the plate-like nanostructures were maintained accompanying with some small triangular particles in the absence of Cu precursor (Figure 6b, marked by white arrows). This result further confirms that the addition of Cu is a key to induce the porous structures. Second, the newly formed Cu atoms and even the ones in alloys can reduce the Ru precursors through galvanic replacement due to the more negative reduction potential of Cu (Cu²⁺/Cu: ~0.34 V) than Ru (Ru³⁺/Ru: ~ 0.68 V) [45,46]. Such galvanic replacement also lead to the porous structures and the formation of CuRu alloys. Figure 6c shows TEM images of the product in the presence of Cu and Ru precursors without the Pd nanoplates. As can be seen, the hollow nanostructures were generated through galvanic replacement between Cu and Ru precursor (marked by white arrows). Of course, Ru precursors can be reduced by benzyl alcohol (Figure 6b). Our previous study indicated that the fcc-structured Ru was generated due to the induction of the Pd and/or Cu fcc lattice [37]. The deposition of Ru on the surface of the porous nanoplates can decrease the size of the pores. Based on these results, the formation process of the porous plates can be summarized as follows: Cu^{2+} ions are preferentially reduced through UPD and deposited on the Pd plates. The atomic ratio of Cu in PdCuRu reaches 40.1% closing to that of Pd when reacting for 5 min (Table S2). The newly formed Cu atoms not only alloy with Pd through interdiffusion, but also reduce Ru³⁺ ions through galvanic replacement, resulting in the formation of the porous structures. The time-dependent TEM images in Figure S7 show that the porous structures are formed in the initial stage (5 min). With the extension of reaction time, the porous structures are remained, but their sizes decrease slightly. Simultaneously, the atomic ratio of Cu decreases, while the atomic ratios of Ru increases (Table S1). As such, the deposition of Ru on the porous nanoplates might be responsible for the decrease in the size of the pores.

The PdCuRu nanoplates were loaded on carbon support (Vulcan XC-72R), and then evaluated as the electrocatalysts for HER with commercial Pt/C, Pd/C, and Ru/C as references. To clean the surface of these carbon-supported electrocatalysts, the cyclic voltammetry (CV) was first conducted at room temperature in Ar-purged 0.1 M KOH solutions at a scan rate of 50 mV s⁻¹ between 0 and 1.0 V versus reversible hydrogen electrode (RHE) for 50 cycles. All the HER measurements were carried out using a rotating disk electrode in 0.1 M KOH solution at a scan rate of 2 mV s⁻¹ and a rotation rate of 1600 rpm at room temperature. From polarization curves of these six samples (Figure 7a,c), their overpotentials at 10 mA cm⁻² decrease in the following order: Pd/C > Ru/C > Pd₃₂Cu₃₃Ru₃₅/C > Pd₁₉Cu₂₅Ru₅₆/C > Pt/C > Pd₂₄Cu₂₉Ru₄₇/C. As such, the Pd₂₄Cu₂₉Ru₄₇/C exhibited the best activity for HER with an overpotential of 40.7 mV, outperforming those of Pt/C (65 mV), Pd₁₉Cu₂₅Ru₅₆/C (76 mV), Pd₃₂Cu₃₃Ru₃₅/C (80 mV), Ru/C (92 mV), and Pd/C (397 mV, Figure 7d). Figure 7b shows the linear Tafel plots of three PdCuRu porous nanoplates including commercial Pt/C by fitting the Tafel

equation. As observed, the $Pd_{24}Cu_{29}Ru_{47}/C$ achieved the lowest Tafel slope with a value of 37.5 mV dec⁻¹, indicating the faster reaction kinetics of the $Pd_{24}Cu_{29}Ru_{47}/C$ than the Pt/C (42.0 mVdec⁻¹), $Pd_{19}Cu_{25}Ru_{56}/C$ (57.5 mV dec⁻¹), and $Pd_{32}Cu_{33}Ru_{35}/C$ (80.9 mV dec⁻¹). In addition, the electrochemically active surface area (ECSA) of the PdCuRu/C was determined by measuring the double-layer capacitance [47]. The capacitances of the double-layer at the solid–liquid interface were calculated from the CV curves obtained over a potential range of 0.74–0.94 V (vs. RHE) at different scan rates from 20 to 200 mV s⁻¹ in 0.1 M KOH (Figure S8). The specific capacitances for the $Pd_{32}Cu_{33}Ru_{35}/C$, $Pd_{24}Cu_{29}Ru_{47}/C$ and $Pd_{19}Cu_{25}Ru_{56}/C$ were 5.25, 8,61, and 4.71mF cm⁻², respectively (Figure 7e). As such, the corresponding ECSA of the $Pd_{24}Cu_{29}Ru_{47}/C$ (42.20 cm²) was larger than that of the $Pd_{32}Cu_{33}Ru_{35}/C$ (25.73 cm²) and $Pd_{19}Cu_{25}Ru_{56}/C$ (23.08 cm²), indicating more active sites existing in the $Pd_{24}Cu_{29}Ru_{47}/C$ due to the porous structures [48,49]. Figure S9 shows the HER polarization curves of such three PdCuRu/C catalysts normalized by ECSA, further confirming the better intrinsic activity of the $Pd_{24}Cu_{29}Ru_{47}/C$ relative to $Pd_{32}Cu_{33}Ru_{35}/C$ and $Pd_{19}Cu_{25}Ru_{56}/C$.



Figure 6. TEM images of the products prepared using the standard procedure, except for (**a**) in the absence of Ru precursor, (**b**) in the absence of Cu precursor, (**c**) in the absence of Pd seeds. (**d**) The variation in the atomic ratio of Cu and Ru to Pd for the $Pd_{24}Cu_{29}Ru_{47}$ nanoplates at different reaction time measured by ICP-AES technique.



Figure 7. (a) HER polarization curves and (b) corresponding Tafel plots. (c) HER polarization curves of the $Pd_{24}Cu_{29}Ru_{47}/C$, commercial Ru/C, Pd/C and Pt/C normalized by geometric surface area of RDE in 0.1 M KOH solutions. (d) Comparison of the overpotential values required to achieve a cathodic current density of 10 mA cm⁻² for all the catalysts. (e) Electrochemical double-layer capacitance (Cd₁) of the $Pd_{32}Cu_{33}Ru_{35}/C$, $Pd_{24}Cu_{29}Ru_{47}/C$ and $Pd_{19}Cu_{25}Ru_{56}/C$. (f) Chronoamperometry measurements of the commercial Pt/C, $Pd_{32}Cu_{33}Ru_{35}/C$, $Pd_{24}Cu_{29}Ru_{47}/C$, and $Pd_{19}Cu_{25}Ru_{56}/C$ at an overpotential with the current density being 10 mA/cm² in 0.1 M KOH for 10 h.

As is well-known, Pt is difficult to dissociate water, leading to unsatisfactory activity for HER in alkaline solution. As an oxophilic metal, Ru is active to catalyze the dissociation of water and holds great potential as highly efficient electrocatalysts for HER in an alkaline solution. The strong electron coupling between Pd, Cu and Ru could optimize the binding energy of Ru-H, which results in a weak hydrogen adsorption on the surface of the PdCuRu nanoplates [50]. On the other hand, Cu could accelerate the electron transfer between Ru and the adsorbate. At the same time, Cu near the pores will assist in the stabilization of Ru [38]. These two features endow the Pd₂₄Cu₂₉Ru₄₇/C with higher HER activity than commercial Pt/C. Besides, due to the optimized area percentage of pore structures and proportion of Ru, Pd₂₄Cu₂₉Ru₄₇/C achieved the highest HER activity among three kinds of the PdCuRu/C. Furthermore, the Pd₂₄Cu₂₉Ru₄₇/C exhibited the smallest charge transfer resistance (21.02 Ω) in the PdCuRu/C during the HER process (Figure S10), similar to that of commercial Pt/C (22.54 Ω). It is indicated that the HER kinetics at the interface of such catalysts is more efficient than other catalysts (Figure S10). Significantly, the stability of the PdCuRu/C and Pt/C was evaluated in 0.1 M KOH solution by current–time (I–t) curves with a constant current density of 10 mA cm⁻², as shown in Figure 7f. Clearly, the three PdCuRu/C show the higher steady current density relative to commercial Pt/C for HER over the entire time range, indicating their superior durability. Among them, the Pd₂₄Cu₂₉Ru₄₇/C remained the highest activity (8.30 mA cm⁻², 17% drop) after 10 h, which is much larger than that of the Pd₃₂Cu₃₃Ru₃₅/C (5.86 mA cm²), Pd₁₉Cu₂₅Ru₅₆/C (7.25 mA cm²) and commercial Pt/C (4.05 mA cm⁻², 59.5% drop). Figure S11 shows TEM images of the Pd₃₂Cu₃₃Ru₃₅/C, Pd₂₄Cu₂₉Ru₄₇/C, and Pd₁₉Cu₂₅Ru₅₆/C before and after I–t measurements. Obviously, the nanoplates are still well-dispersed on the carbon support, which is responsible for the superior stability. We have performed EDX technique to analyze the variation of element distribution of the Pd₂₄Cu₂₉Ru₄₇/C after durability test (Figure S12). From the EDX mapping image and line-scan profile, Ru is still richened on the surface, while, Pd and Cu mainly exist in the interior of the nanoplates. Clearly, some of them leached from the nanoplates, leading to the much more pores. The poor stability of commercial Pt/C can be attributed to the weak capability of water dissociation and easy aggregation of small Pt nanoparticles on carbon support.

4. Conclusions

In summary, we have successfully developed a facile one-pot solvothermal method to synthesize the PdCuRu porous nanoplates with different compositions of Ru. Secondly, the formation mechanism of the porous nanoplates were clearly revealed, and involves the deposition of Cu on Pd, alloying Cu with Pd by interdiffusion, and reduction of Ru precursor by galvanic replacement with Cu. These three PdCuRu porous nanoplates exhibited the excellent catalytic activity toward HER in alkaline solution, with the $Pd_{24}Cu_{29}Ru_{47}/C$ being the best HER electrocatalysts. Specifically, the $Pd_{24}Cu_{29}Ru_{47}/C$ achieved the lowest overpotential (40.7 mV) and smallest Tafel slope (37.5 mV dec⁻¹), which are superior to those of commercial Pt/C. In addition, these nanoplates also showed substantially enhanced stability relative to Pt/C (17% drop for the $Pd_{24}Cu_{29}Ru_{47}/C$ versus 59.5% drop for Pt/C). Fourth, such enhancement in activity and durability can be attributed to the electron coupling between three metals, unique porous structure, and strong capability of Ru for water dissociation. This work provides a simple strategy to design advanced Ru-based electrocatalysts for HER.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10 .3390/met11091451/s1. Figure S1. (a) TEM image of the Pd plate-like seeds that lay flat on the TEM grid and (b) the corresponding edge length. Figure S2. (a) TEM image of vertically upstanding of Pd₂₄Cu₂₉Ru₄₇ nanoplates and (b) the corresponding thickness. The nanoplates were firstly mixed with carbon nanotubes in an aqueous solution. After centrifugation, the product was collected and measured by TEM analysis. The width of the projection for the vertically upstanding nanoplates is the corresponding thickness. Figure S3. The size and average area percentage of the pores in three nanoplates with different amount of Ru: (a) $Pd_{32}Cu_{33}Ru_{35}$ nanoplates, (b) $Pd_{24}Cu_{29}Ru_{47}$ nanoplates, and (c) Pd₁₉Cu₂₅Ru₅₆ nanoplates. Figure S4. XRD patterns of the Pd₃₂Cu₃₃Ru₃₅, Pd₂₄Cu₂₉Ru₄₇ and Pd₁₉Cu₂₅Ru₅₆ nanoplates. Figure S5. High-resolution (a) Pd 3d, (b) Ru 3p, and (c) Cu 2p XPS spectra of the Pd₃₂Cu₃₃Ru₃₅ nanoplates. Figure S6. High-resolution (a) Pd 3d, (b) Ru 3p, and (c) Cu 2p XPS spectra of the Pd₁₉Cu₂₅Ru₅₆ nanoplates. Figure S7. TEM images of the product prepared using the standard procedure except for different reaction times: (a) 5 min, (b) 10 min, (c) 1 h, (d) 3 h, (e) 6 h, and (f) 12 h. Figure S8. Cyclic voltammograms (CV) with scan rates from 20 to 200 mV s⁻¹ of (a) Pd₃₂Cu₃₃Ru₃₅/C, (b) Pd₂₄Cu₂₉Ru₄₇/C and (c) Pd₁₉Cu₂₅Ru₅₆/C that were performed in a potential window without faradaic processes. Figure S9. HER polarization curves normalized by the ECSA for the Pd₃₂Cu₃₃Ru₃₅/C, Pd₂₄Cu₂₉Ru₄₇/C and Pd₁₉Cu₂₅Ru₅₆/C in 0.1 M KOH solution. Figure S10. Electrochemical impedance spectroscopy (EIS) curves of various electrocatalysts. Figure S11. TEM images of (a,d) Pd₃₂Cu₃₃Ru₃₅/C, (b,e) Pd₂₄Cu₂₉Ru₄₇/C and (c,f) Pd₁₉Cu₂₅Ru₅₆/C catalysts before and after the chronoamperometric measurement, correspondingly. Figure S12. (a) HAADF-STEM, (b) EDX mapping images of a planar Pd₂₄Cu₂₉Ru₄₇ nanoplate after I-t testing. (c) HAADF-STEM and EDX images of a vertically upstanding Pd₂₄Cu₂₉Ru₄₇ nanoplate after I-t testing. Pd (orange), Ru (red), Cu (green). (d) Line-scan profiles along the side of a Pd₂₄Cu₂₉Ru₄₇ nanoplate after I-t testing.

Table S1. ICP-AES data of the PdCuRu multimetallic nanoplates with different atomic ratios and the molar ratio of the Pd, Cu and Ru precursors fed in the synthesis. Table S2. The variation in the atomic percentage of Pd, Cu, and Ru for the Pd₂₄Cu₂₉Ru₄₇ nanoplates with the reaction time measured by ICP-AES technique.

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