Facile air oxidative induced dealloying of hierarchical branched PtCu nanodendrites with enhanced activity for hydrogen evolution

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In this work, we utilized a facile air oxidative dealloying approach to synthesize PtCu hierarchical branched nanodendrites (HBNDs). The systematical investigation on the morphology, composition, and structure of PtCu HBNDs by various techniques demonstrates they are three-dimensional open porous nanostructures. The PtCu HBNDs show composition-dependent catalysis in hydrogen evolution reaction (HER). The Pt\textsubscript{1}Cu\textsubscript{1.03}-D with average size about 40 nm composed of integrated ultrathin branches, presents the highest HER activity with only 20 mV overpotential to achieve 10 mA/cm\textsuperscript{2}, 19.34 A/mg\textsubscript{Pt} and 9.64 mA/cm\textsuperscript{2} in mass and specific activity at −0.2 V, and excellent durability. The superior HER activity is attributed to the unique porous dendritic structure and electronic synergistic interactions between Pt and Cu as indicated by X-ray photoelectron spectroscopy and density functional theory calculation. This work opens up a new facile route to design large accessible surface and high-performance electrocatalysts with low utilization of Pt for electrochemical energy conversion.

1. Introduction

With the exhaustion of traditional fossil energy, the growing global warming problems and clean energy requirements, hydrogen has been considered as a promising alternative owing to its efficient, environmentally friendly, and renewable [1–4]. For now, electrocatalytic hydrogen evolution reaction (HER) is one of the most effective and sustainable techniques to produce high-purity and large-scale hydrogen [5,6]. To expedite the HER process, a highly active and long-term stability electrocatalyst should be needed. Up to now, Platinum (Pt) is still regarded as a state-of-the-art HER electrocatalyst [7,8]. However, the low abundance and high cost of Pt seriously impede its widespread application. Consequently, developing Pt similar or higher performance catalysts with low content of Pt still remains a crucial challenge.

Recently, considerable efforts have been devoted to explore approach for improving the activity of Pt based catalysts. One of the most widely used and effective methods to minimize the usage of Pt and maximize the catalytic activity simultaneously is incorporating non-noble transition metals (e.g. Fe, Co, Cu, and Ni) into Pt nanostructures to build Pt-based alloyed nanocatalysts [9–11]. The enhancement of catalytic activity benefits from the synergetic effects between Pt and other metal atoms, including geometric effects and electronic effects, which attribute to the rearrangement of platinum atoms and the shift of the d-band center of Pt with respect to the Fermi level in the alloys, respectively [12,13]. Moreover, on account of previous reports in which the size, exposed facets, and the proportions of active sites of the catalysts could effectively tune the catalytic properties, the controlled morphology synthesis of Pt-based alloys with higher surface area and more accessible active sites is another available approach to obtain highly catalytic activity [14–16]. Among these fantastic nanostructures, much more attentions of researches have been attracted to nanodendrites (NDs) with hierarchical branches because of their arresting structural characteristics such as porosity, rich edges and corners, high surface area, interconnected nanostructure, and excellent electrical connectivity [17,18]. Based on above, Pt-based alloyed NDs can make inner catalytic sites accessible and thus provide more active sites for catalytic reaction and take full advantage of Pt at the same time.

To date, various effective methods have been developed to synthesize Pt-based NDs including chemical coreduction, thermal decomposition, seed growth, sacrificial templating, galvanic replacement,
underpotential deposition and so on, but most of these methods are subjected to relatively high cost, high reaction temperature, long reaction time, and complicated tedious reaction process [19–24]. Dealloying is a promising approach to fabricate bimetallic nanocatalysts with a continuous open porous structure and large effective surface area [25–28]. Li et al. has fabricated Au–Cu spongy nanoframes by chemically dealloying in nitric acid solution [29]. Chen et al. has fabricated nanoporous Pd–Au bimetallic catalysts by electrochemically dealloying [30]. All these dealloying methods based on electrochemical or chemical etching are usually complex, in which expensive or toxic reagents, extra expense (e.g. electric energy) are commonly required [28–32]. Therefore, developing a facile and cost effective strategy to obtain Pt-based Nd with excellent catalytic performance is of great significance.

Herein, we provided a facile and convenient air oxidative induced dealloy process to fabricate PtCu hierarchical branched nanodendrites (HBNDs) with tunable branches, size, and composition. The PtCu HBNDs composed of integrated ultrathin branches present enhanced HER activity and superior durability due to the larger open porous structure, more accessible active sites and electronic synergistic effect between Pt and Cu atoms as confirmed by X-ray photoelectron spectroscopy (XPS) study and density functional theory (DFT) calculation.

2. Experimental

2.1. Reagents

Chloroplatinic (IV) acid (H2PtCl6·6H2O), oleylamine (OAm, > 80%), copper chloride (CuCl2·2H2O), dichloromethane (CH2Cl2), and ethanol (C2H6O) were purchased from Aladdin. All reagents were analytical grade and used without further purification. The deionized water was obtained from a Millipore Autopure system.

2.2. Synthesis of PtCu nanodendrites

Typically, 16 mg CuCl2·2H2O and 200 ul H2PtCl6·6H2O (0.2 g/ml) were added into 10 ml oleylamine with magnetic stirring and slowly heated to 160 °C and kept for 30 min under N2 protection to remove water and exhaust air. Then the solution were slowly heated to 240 °C and kept for 10 min and the light yellow solution turned black. The mixture was quickly cooled to room temperature under N2 protection and divided into two parts. A part of mixture was centrifuged and washed by dichloromethane and ethanol for several times and then dried under vacuum at room temperature. This part of mixture was Pt1Cu1.14 alloy nanoparticle. Another part of the mixture was transferred to 60 °C oil bath and stirred vigorously in the air for the dealloy process. After 12 h, the product was separated by centrifugation and washed with dichloromethane and ethanol for several times and then dried under vacuum at room temperature. This product was Pt1Cu1.03-D nanodendrites. Other alloys with different composition such as Pt1Cu0.3, Pt1Cu0.51, Pt1Cu1.58, and Pt1Cu1.81 were obtained by varying the dosage of Cu precursor from 4 to 8 to 24 to 32 mg, and after air oxidative dealloy process the corresponding dealloyed PtCu particles (Pt1Cu0.3-D, Pt1Cu0.51-D, Pt1Cu1.53-D, and Pt1Cu1.83-D) were achieved. (The numbers indicate the atomic ratios of Pt and Cu as measured by ICP-MS.) The pure Pt particles were prepared by the same method without Cu precursor.

2.3. Preparation of the catalysts

The synthesized particles were supported on carbon black (CB, Vulcan XC-72R, Cabot Corp.) with a loading of 10 mass % by mixing together in isopropanol and stirring overnight. Then, the above suspension was separated by centrifugation and dried under vacuum at room temperature.

2.4. Electrochemical characterization

The electrochemical measurements were performed in a three-electrode system on CHI760D electrochemical workstation (Shanghai, Chenhua Co., China). Graphite rod and Ag/AgCl (saturated KCl-filled) were used as the counter and reference electrodes, respectively. A glassy carbon electrode (GCE) with a diameter of 5 mm covered by a thin catalyst film was used as the working electrode. Typically, 2 mg catalyst was suspended in 1 ml isopropanol with 10 ul Nafion solution (5 wt%, Du pont) and sonicated for 30 min to obtain homogeneous ink. Then, 10 ul of the ink was transferred onto the GCE and dried in air under room temperature. HER tests were conducted in a N2-saturated 0.5 M H2SO4 electrolyte at room temperature [1,8,11,43,44]. The polarization curves were obtained by sweeping the potential from −0.4 to 0.1 V with a sweep rate of 5 mV/s. All the data were recorded without iR compensation after applying a number of potential sweeps until it became stable. The cyclic voltammetry (CV) was conducted between −0.4 and 0.1 V at 50 mV/s for 5000 times to investigate the cycling stability. The EIS measurements were performed with frequency range of 0.01 to 105 Hz, at a bias potential of −0.2 V. The electrochemical surface area (ECSSA) was calculated by measuring the charge associated with the H adsorption and desorption region [1,2,16]. The turnover frequency (TOF, s−1) of catalyst was calculated by the method reported previously [33,34]. All the final potentials were converted to the reversible hydrogen electrode (RHE) according to $E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.1988$ [34–36].

2.5. Characterization

Transmission electron microscopy (TEM) images were obtained by a JEM 2100 microscope (Japan). High-resolution transmission electron microscopy (HRTEM) was assessed by a JEOL-2010F instrument (Japan). X-ray diffraction (XRD) patterns were obtained by D/max4TTR 91 III with Cu Ka radiation (V = 40 kV, I = 200 mA). Inductively coupled plasma mass spectrometry (ICP-MS) was obtained by an Atomscan Advantage instrument (Thermo Jarrell Ash Corporation, USA). X-ray photoelectron spectroscopy (XPS) data were collected using a Thermo Scientific K-Alpha instrument, and all binding energies were referenced to the C1s peak, at 284.8 eV.

2.6. Calculation method

The calculation was performed by Vienna ab initio simulation package (VASP) [37]. A generalized gradient approximation (GGA) [38] with the Perdew–Burke–Ernzerhof (PBE) [39] function is used to describe exchange correlation interactions. The plane wave basis set energy cutoff is set to 370 eV. The energy convergence tolerance for self-consistent field (SCF) is 1 × 10−6 eV. Gaussian smearing with sigma value of 0.05 eV is adopted. The force convergence tolerance for geometry optimization is considered as 0.01 eV/Å. All calculations were done with spin unrestricted. The K point is sampled as $23 \times 23 \times 23$ using Monkhorst method [40] for primitive cell and $23 \times 23 \times 1$ for slab model.

3. Results and discussion

3.1. Morphology characterizations

The PtCu HBNDs were synthesized through a consecutive two-step process: firstly, PtCu alloy nanoparticles (NPs) were prepared by simply chemical coreduction using oleylamine as the stabilizing ligand and reducing reagent, then PtCu HBNDs were successfully synthesized via a facile air oxidative dealloy process. A series of different composition PtCu HBNDs and pure Pt NPs were synthesized and investigated the morphology by transmission electron microscopy (TEM). As measured by inductively coupled plasma mass spectrometry (ICP-MS) the average
molar ratio of Pt/Cu in PtCu alloy NPs were 1:0.31, 1:0.56, 1:1.14, 1:1.58, and 1:1.81 corresponding well with the initial molar ratio of the Pt and Cu precursors. After air oxidative dealloy process, the molar ratio of Pt/Cu decreased to 1:0.30, 1:0.51, 1:1.03, 1:1.43, and 1:1.63. As shown in Fig. 1, it is obviously observed that the size and branch density of the HBNDs could be tuned by the composition proportions of Pt and Cu. Without Cu, the pure Pt NPs are irregular with small size of about 10–15 nm and partial aggregated (Fig. 1A). With a very small amount of Cu, the Pt1Cu0.00-D display conspicuous dendrites. With the increase of Cu content, the distinct branched structure of PtRu alloys gradually appears, the particle size obviously increases and the entire structure becomes porous (Fig. 1B, C). When the Pt/Cu ratio increased to 1:1.03, the particles consisted of dendritic nanocrystals are most uniform and the branches are most significant and densest (Fig. 1D). When the Pt/Cu ratio further increased, the particles have fewer branches, the branched features are not obvious and the surfaces become more smooth (Fig. 1E, F). These results reveal that the presence of Cu has great effect on tailoring the product morphology and the appropriate content of Cu is beneficial to the highly branched structure.

We further compared the morphologies of the Pt1Cu1.14 and Pt1Cu1.03-D (chosen as models) to investigate the air oxidative induced dealloy process. As shown in Fig. 2A, the Pt1Cu1.14 alloy NPs were prepared by simply chemical co-reduction, they exhibit non uniform and irregular structure with an average size about 25 nm. After the facile air oxidative dealloy process, the composition of Pt/Cu proportion decreased to 1:1.03 as measured by ICP-MS. Pt1Cu1.03-D show three different crystal phases, with the absence of signals associated with pure Cu or its oxides, suggesting the formation of PtCu alloys (Fig. 3 line a). After the addition of Cu, the XRD patterns of these PtCu alloys all shift to higher diffraction angles compared to that of pure Pt NPs and the higher Cu content leads to a bigger shift. It is worth noting that after the dealloy process, the corresponding XRD patterns display a slightly downshift consistent well with the lower Cu content in dealloyed PtCu particles. The XRD peaks of these PtCu alloys are all located between pure fcc Pt (JCPDS no. 04-0802) and Cu (JCPDS no. 04-0836) crystal phases, with the absence of signals associated with pure Cu or its oxides, indicating the formation of pure high crystalline Pt NPs and these PtCu alloys with different compositions before and after dealloying. Two significant diffraction peaks for the sample pure Pt NPs at 39.76° and 46.24° (2θ) are ascribed to the (111) and (200) crystal planes of face-centered cubic (fcc) platinum (JCPDS no. 04-0802), indicating the formation of pure high crystalline Pt NPs (Fig. 3 line a). After the addition of Cu, the XRD patterns of these PtCu alloys all shift to higher diffraction angles compared to that of pure Pt NPs and the higher Cu content leads to a bigger shift. It is worth noting that after the dealloy process, the corresponding XRD patterns display a slightly downshift consistent well with the lower Cu content in dealloyed PtCu particles. The XRD peaks of these PtCu alloys are all located between pure fcc Pt (JCPDS no. 04-0802) and Cu (JCPDS no. 04-0836) crystal phases, with the absence of signals associated with pure Cu or its oxides, suggesting the formation of PtCu alloys (Fig. 3 line b-k) [13,17,18].

3.3. XPS analysis

The electronic effect between Pt and Cu of PtCu HBNDs was studied by XPS. The Pt 4f spectrum of Pt1Cu1.03-D shows two strong peaks at binding energies of 70.87 and 74.23 eV corresponding to Pt 4f7/2 and Pt 4f5/2 of metallic Pt° and two weak peaks at 71.98 and 76.04 eV attributed to the Pt2+ 4f7/2 and 4f5/2 orbital, in which the percentage of Pt° species is 80% (Fig. 4A). The Cu 2p spectrum displays two significant peaks at binding energies of 932.41 (Cu 2p3/2) and 952.24 eV (Cu 2p1/2) indicating most of Cu is in the form of metallic Cu°, although two weak signals at 934.16 and 954.28 eV of Cu2+ appear due to the oxidation of surface Cu atoms in air (Fig. 4B) [17,41]. These results confirm the successfully reduction of Pt2+ and Cu2+ precursors. In addition, the binding energies of Pt in Pt1Cu1.03-D show a 0.39 eV negative shift with respect to those of the Pt/C (Fig. S1), indicating the electron transfer from Cu to Pt due to the different electronegativity [41,42]. The electron donation confirmed by XPS analysis leads to the Pt with electron-richer status in PtCu alloy than pure Pt NPs and thus improves the HER activity as indicated by DFT calculation further [36].

3.4. DFT calculation

To investigate the potential mechanism, we have used first principles calculations to test the interface between Pt and Cu. The computed work functions of Pt (111) and Cu (111) are 5.78 and 4.75 eV, respectively, driving electron transfer from Cu to Pt in order to equilibrate the electron Fermi distribution (Fig. S2). To further expound the detailed nature of electronic interactions at the Pt-Cu interfaces, the
differential charge density (see details in SI) was displayed (Fig. 5A), the charge density of Cu atoms which contact with Pt atoms distinctly decrease, while that of Pt atoms contacting with Cu atoms significantly increase. This suggests the electron transformation from Cu to Pt, resulting the substantial negative charges on Pt surface, thus, will certainly improves the HER activity [36,43]. To quantitatively analyses the amount of the transferred charge, Bader charge analysis was conducted (Fig. 5B and Table S1). The charge transformation was occurred mainly at the interface which directly connects Pt and Cu atomic layers. The atomic layers far from interface do not significantly contribute to the charge transformation. The net charge transformation per unit area at Pt-Cu interfaces is about 0.026 e/Å².

3.5. Electrocatalytic HER performance

Owing to the unique structural feature and electronic effect, we choose HER as a model reaction to evaluate the catalytic activity of PtCu HBNDs. Fig. 6A shows the polarization curves of five different compositions dealloyed PtCu HBNDs and Pt1Cu1.14 alloys supported on carbon black with the commercial Pt/C acting as the reference sample. The current density of these Pt-based catalysts follow the order Pt1Cu1.03-D > Pt1Cu1.14 > Pt1Cu0.51-D > Pt1Cu0.3-D > Pt1Cu1.43-D > Pt1Cu1.63-D > Pt/C at the same potential. To quantitatively evaluate the HER activity, Fig. 6B shows the comparison of the current density at -0.1 V and the overpotential at 10 mA/cm² of these Pt-based catalysts. Pt1Cu1.03-D exhibits prominent enhanced activity with highest current density of 63.16 mA/cm², which is 6.17 times higher than that of Pt/C (10.24 mA/cm²) and shows smallest overpotential of 20 mV for obtaining 10 mA/cm², which displays a 79 mV positive shift compared to that of Pt/C (99 mV). The samples with the presence of Cu display higher HER activity than pure Pt due to the electronic synergistic effect and the HER performance obviously enhance after dealloying process. Meanwhile, the HER activity and Cu content are neither positive nor negative correlation, the Pt1Cu1.03-D exhibits highest activity among these five dealloyed catalysts, suggesting the highly branched nanodendrite with porous structure and accessible active sites (shown in Figs. 1B–F and 2B) is the key toward the high catalytic activity.

The electrochemically active surface area (ECSA) can describe the number of available active sites more directly and it is usually calculated via hydrogen adsorption-desorption charges [1,2,16]. The ECSAs of these Pt-based catalyst are following the order Pt1Cu1.03-D (100.19 m²/g) > Pt1Cu1.14 (99.11 m²/g) > Pt1Cu0.51-D (66.95 m²/g)
Pt\textsubscript{1}Cu\textsubscript{0.3}-D (53.84 m\textsuperscript{2}/g) > Pt\textsubscript{1}Cu\textsubscript{1.43}-D (43.99 m\textsuperscript{2}/g) > Pt\textsubscript{1}Cu\textsubscript{1.63}-D (39.04 m\textsuperscript{2}/g) (normalized by the content of Pt, Fig. S3), demonstrating Pt\textsubscript{1}Cu\textsubscript{1.03}-D has the largest ECSA and most active sites resulted from the unique structure (Fig. 1B–F). We also calculated the mass activities and specific activities of all samples to compare the HER performance (Fig. 6C). Pt\textsubscript{1}Cu\textsubscript{1.03}-D shows the best mass activity (19.34 A/mg) and specific activity (9.64 mA/cm\textsuperscript{2}ECSA) at −0.2 V, which is 8.48 and 9.64 greater than those of Pt/C (mass activity: 2.28 A/mg, specific activity: 1.00 mA/cm\textsuperscript{2}ECSA), respectively. Furthermore, the electron transfer properties of these samples were also investigated by electrochemical impedance spectroscopy (EIS) tests. As shown in Fig. S4, Pt\textsubscript{1}Cu\textsubscript{1.03}-D exhibits the smallest charge transfer resistance (Rct), indicating the fastest electrocatalytic reaction rate for HER (Table S2).

The HER kinetics of these Pt-based catalysts were assessed by Tafel slope. As displayed in Fig. 6D, PtCu alloys and Pt/C have very close Tafel slopes (from 28.5 to 33 mV/dec in accordance with the order of current density), suggesting they all observe the Volmer–Tafel mechanism for HER, in which the recombination of two adsorbed H atoms is the rate-limiting step [11]. Besides, exchange current density was obtained by applying an extrapolation method to the Tafel plot. Among these Pt-based catalysts, Pt\textsubscript{1}Cu\textsubscript{1.03}-D shows the highest exchange current density of 2.43 mA/cm\textsuperscript{2} (Table S2). We also calculate the turnover frequency (TOF) of these samples, and Pt\textsubscript{1}Cu\textsubscript{1.03}-D has the largest value of 195.8 s\textsuperscript{−1} at −0.2 V (Table S2). All these results and a detailed comparison of Pt-based HER catalysts (Table S3) indicate the Pt\textsubscript{1}Cu\textsubscript{1.03}-D has the fastest HER rate and best intrinsic HER activity.

4. Conclusion

In summary, highly branched PtCu nanodendrites with tunable compositions have been successfully prepared by a facile and harmless air oxidative induced dealloy process. The catalyst have exhibited remarkable HER activity with only 20 mV overpotential to achieve 10 mA/cm\textsuperscript{2}, 19.34 A/mg, and 9.64 mA/cm\textsuperscript{2} in mass and specific activity at −0.2 V. The enhanced HER performance is attributed to the unique dendrite structural feature with large surface area and more accessible active sites and the electronic synergistic effect between Pt and Cu atoms as demonstrated by both XPS analysis and DFT calculation. This work provides a new concept to realize a win-win situation by enhancing electrocatalytic properties and reducing noble metal usage simultaneously.

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Appendix A. Supplementary data

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