available at www.sciencedirect.com

journal homepage: www.sciencedirect.com/journal/chinese-journal-of-catalysis

Article

High index surface-exposed and composition-graded PtCu₃@Pt₃Cu@Pt nanodendrites for high-performance oxygen reduction

Yuxiang Liao^a, Jun Li^a, Shiming Zhang^{a,b,#}, Shengli Chen^{a,*}^a College of Chemistry and Molecular Sciences, Wuhan University, Hubei Key Laboratory of Electrochemical Power Sources, Wuhan 430072, Hubei, China^b Institute for Sustainable Energy, College of Sciences, Shanghai University, Shanghai 200444, China

ARTICLE INFO

Article history:

Received 30 October 2020

Accepted 3 November 2020

Available online 5 March 2021

Keywords:

Oxygen reduction

Pt-Cu alloy

High-index-surfaces

Nanodendrites

Shape control

ABSTRACT

Alloying and nanostructuring are two strategies used to facilitate the efficient electrocatalysis of the oxygen reduction reaction (ORR) by Pt, where the high index surfaces (HISs) of Pt exhibit superior activity for ORR. Here, we report the fabrication of PtCu₃ nanodendrites possessing rich spiny branches exposing $n(111) \times (110)$ HISs. The dendrites were formed through an etching-modulated seeding and growing strategy. Specifically, an oxidative atmosphere was initially applied to form the concaved nanocubes of the Pt-Cu seeds, which was then switched to an inert atmosphere to promote an explosive growth of dendrites. Separately, the oxidative or inert atmosphere failed to produce this hyperbranched structure. Electrochemical dealloying of the PtCu₃ nanodendrites produced Pt₃Cu shells with Pt-rich surfaces where HIS-exposed dendrite structures were maintained. The resulting PtCu₃@Pt₃Cu@Pt nanodendrites in 0.1 M HClO₄ exhibited excellent mass and area specific activities for ORR, which were 14 and 24 times higher than that of commercial Pt/C, respectively. DFT calculations revealed that Cu alloying and HISs both contributed to the significantly enhanced activity of Pt, and that the oxygen binding energy on the step sites of HISs on the PtCu₃@Pt₃Cu@Pt nanodendrites approached the optimal value to achieve a near peak-top ORR activity.

© 2021, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

The fuel cell is a clean and efficient energy conversion technology, although its large-scale application is limited by the sluggish kinetics of the oxygen reduction reaction (ORR) and the high demand of the scarce and expensive platinum in the cathode [1–8]. While great effort has been made in the past two decades, efficient and durable ORR catalysts of low Pt-based alloys remain highly desired.

Based on the knowledge that the Pt (111) surface has the best activity among the three basic facets of Pt, considerable efforts have been made to develop Pt octahedral nanostructures [9–14]. Recent studies on a wide range of Pt single crystal surfaces have shown that some high index surfaces (HISs) of Pt, especially the $n(111) \times (110)$ and $n(111) \times (100)$ stepped Pt surfaces such as Pt (332), Pt (331), and Pt (554), exhibited enhanced ORR activity over the Pt (111) surface in acidic electrolytes [15]. Hoshi *et al.* [16] studied the ORR on a series of HISs

* Corresponding author. Tel: +86-27-68754693; E-mail: slchen@whu.edu.cn

Corresponding author. Tel: +86-21-66131689; E-mail: smzhang@shu.edu.cn

This work was supported by the National Natural Science Foundation of China (21832004, 21633008) and Shanghai Rising-Star Program (18QB1404400).

DOI: 10.1016/S1872-2067(20)63735-4 | http://www.sciencedirect.com/journal/chinese-journal-of-catalysis | Chin. J. Catal., Vol. 42, No. 7, July 2021

with the (111) terrace such as $n(111) \times (100)$ and $n(111) \times (111)$ and those with the (100) terrace such as $n(100) \times (110)$ and $n(100) \times (111)$, and found a generally increasing activity with step density on the (111) terrace, although this trend was not observed for the (100) terrace. DFT calculations suggested that the adsorption of oxygenated species on the (111) step sites is stronger than that on the pristine Pt (111) surface sites, although the sites on the neighboring (111) terrace steps bind oxygen more weakly than the pristine Pt (111) surface sites. It is well known that weakened oxygen adsorption favor the ORR on Pt [17,18].

Generally, HIS-enclosed nanocrystals with regular shapes can be synthesized only in relatively large sizes due to the high surface tension [19–21]. This is detrimental from the perspective of Pt utilization because of the low electrochemical active surface area (ECSA). Since the crystal growth in the direction perpendicular to a HIS is usually much faster than those along the normal direction of basic facets, HISs are usually eliminated during the nanocrystal growth. Therefore, the synthesis of nanocrystals with the properties of specific HISs and high surface areas remain challenging. Reassuringly, it was recently shown that this challenge may be overcome with specially designed nanostructures. For example, Huang *et al.* [22] reported a zigzagging Pt-based nanowire possessing both HISs and high ECSAs, thereby exhibiting greatly enhanced ORR activity. Moreover, nanodendrites also offer the opportunity to produce HISs with high ECSAs owing to the unique structure of plentiful slender dendrites branching out from the core [23,24].

Alloying is a general and efficient strategy to boost the catalytic activity of metallic nanocrystals. Pt alloys with various 3d transition metals, e.g., Ni, Co, Cu, etc., were shown to exhibit good ORR catalytic activity [7,25–29]. Alloying not only reduces the amount of Pt in the catalysts, but also drastically improves the activity of Pt through electronic and geometric effects. In general, electron transfer occurs between the alloying transition metal atoms and Pt, which increases the d-band filling degree of the Pt. Moreover, Pt–3d alloys generally have reduced lattice constants due to the smaller atomic radii of the 3d metals, leading to compressed Pt–Pt distances on the surface. The two effects both weaken the adsorption of oxygenated species on Pt. By combining the strategy of alloying and high index crystal planes, a PtM alloy catalyst with high ORR catalytic activity can be obtained [30–36].

In this work, we report a Pt–Cu alloy electrocatalyst with a graded composition of $\text{PtCu}_3@\text{Pt}_3\text{Cu}@\text{Pt}$ and nanodendrite morphologies possessing rich spiny branches exposing $n(111) \times (110)$ HISs. The nanodendrite electrocatalyst was obtained through an atmosphere-modulated solution-phase synthesis (Scheme 1) followed by electrochemical dealloying. The graded composition with a Cu-rich core and Pt-rich shell simultaneously allows significant reduction of Pt and ensures catalyst stability. DFT calculation results suggest that both the alloying Cu and the HISs enhance the ORR activity of the surface. In practice, the $\text{PtCu}_3@\text{Pt}_3\text{Cu}@\text{Pt}$ nanodendrites exhibit superior ORR activity when compared with the state-of-the-art commercial Pt catalysts, and the catalysts derived through dealloying the multipods and concave nanocubes formed without at-

Scheme 1. Schematic of the formation of Pt–Cu nanocrystals.

mospheric modulation.

2. Experimental

2.1. Reagents and chemicals

Copper(ii) nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, >99%) was supplied by Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China). Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, >98%) was supplied by Kunming Sino-Platinum Co. Ltd. (Kunming, China). Oleyl amine (OAm, >80%) was supplied by Aladdin Industrial Corporation (Shanghai, China). Commercial Pt/C catalyst (20 wt%) was purchased from Johnson Matthey. All chemicals of analytical grade were used without further purification. Milli-Q ultrapure water (Millipore, >18.25 MΩ cm) was used throughout the experiments.

2.2. Preparation of Pt–Cu nanocrystals (NCs)

A two-step atmosphere-modulation procedure was used to synthesize the various platinum-copper nanocrystals, which entailed seed formation for 5 min followed by crystal growth for 25 min (Scheme 1). The hyperbranched nanodendrites (NDs) were formed under an atmosphere of air (5 min) and Ar (25 min). In a typical synthesis process, 10 mL of OAm in a three-neck flask was initially heated to 270 °C under air. Then, 0.4 mL of an aqueous solution containing 20 mg of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.038 mmol) and 27.5 mg of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.114 mmol) was injected with vigorous magnetic stirring. Upon reacting for 5 min under air, the atmosphere was switched to argon and the reaction was allowed to proceed for another 25 min. When the reaction system was cooled to room temperature, the product was collected by centrifuging the black dispersion at 11000 rpm for 10 min, which was washed 5 times with hexane to remove the OAm. For comparison, the preparation experiments were also conducted with the same procedure but with the single gas atmosphere of argon or air, which led to irregularly shaped multipods (MPs) and concave nanocubes (CBs), respectively.

2.3. Physical characterizations

Transmission electron microscopy (TEM) images were collected with a JEM-2100 (HR) operating at 200 kV. Energy-dispersive X-ray spectroscopy (EDX) experiments were conducted in the high-angle annular dark field (HAADF) mode on an FEI TECNAIF-30 microscope with an acceleration voltage

of 300 kV. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8-Advance X-ray diffractometer used the Cu $K\alpha$ radiation source ($\lambda = 0.154178$ nm) with a velocity of 4° min^{-1} . X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Fisher ESCALAB 250Xi spectrophotometer that used Al $K\alpha$ as the excitation light source, and the spectra were calibrated with the C 1s peak (284.6 eV) and the data were fitted with the XPS PEAK41 software. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) experiments were performed on an IRIS Intrepid II XSP spectrometer (Thermo Fisher Scientific, USA).

2.4. Electrochemical measurements

Prior to the electrode preparation, the Pt-Cu nanocrystals were loaded on carbon black (Vulcan XC-72R) to form the carbon supported Pt-Cu nanocrystals samples. Typically, approximately 5 mg of the nanocrystal sample was mixed with approximately 70 mg of Vulcan XC-72R in hexane under sonication for 30 min, followed by centrifugation and drying at room temperature. The Pt loading of the carbon supported catalyst was 3.6%, which was confirmed by AES-ICP results.

All electrochemical experiments were carried out on a CHI660A electrochemical workstation using a three-electrode cell at 25°C . A Pt sheet was used as the counter electrode. A saturated calomel electrode (SCE) and an Hg/HgO electrode were used as the reference electrodes in acid and alkaline solutions, respectively. The reference electrode was separated from the working electrode by a Luggin capillary during the measurements. The reference electrodes were calibrated to the RHE scale by measuring the equilibrium electrode potential of hydrogen evolution and oxidation reactions in the same solution.

To prepare the working electrode (WE), 5 mg of the carbon-supported nanocrystals was fully dispersed in 2 mL of an iso-propanol solution containing 0.5 wt% Nafion. Certain amounts of the prepared ink were casted on a 5 mm diameter glass carbon electrode (GCE), with a Pt loading on the electrode of $7.5 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ for Pt-Cu NDs/C and $15 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ for the commercial Pt/C. Before the ORR performance tests, the Pt-Cu nanocrystals were subject to an electrochemical dealloying program, namely, 100 cycles of potential cycling between 0.06 to 1.3 V (vs. RHE) in O_2 -saturated 0.1 M HClO_4 with a scan rate of 500 mV s^{-1} .

CO stripping curves were measured with a potential scanning rate of 50 mV s^{-1} in a 0.1 M HClO_4 solution. First, CO was flushed into the solution for 30 min to allow the adsorption of CO monolayers onto the catalyst when the working electrode was kept at 0.1 V (vs. RHE), and excess CO in the electrolyte was then purged out with Ar for 30 min. The ECSA of the catalysts were calculated according to:

$$\text{ECSA} = Q/(q_0 m_{\text{Pt}}) \quad (1)$$

where Q is the CO stripping charge, q_0 ($420 \mu\text{C cm}^{-2}$) is the theoretical charge for oxidizing a CO monolayer, and m_{Pt} is the Pt loading on the WE.

The steady-state polarization curves for ORR were measured with a scanning rate of 5 mV s^{-1} at an electrode rotating speed of 1600 rpm in O_2 -saturated solutions and the kinetic

currents (j_k) at 0.90 V (vs. RHE) were calculated by applying the Koutecky-Levich equation:

$$j_k = (j \times j_L)/(j - j_L) \quad (2)$$

where j and j_L are the measured current density and diffusion-limiting current density on the polarization curve, respectively. The kinetic current was normalized to the Pt loading amount and the ECSA to generate the mass-specific activity (MA) and area-specific activity (SA), respectively.

The electrochemical stability measurements were carried out with a scanning rate of 50 mV s^{-1} by cycling the potential between 0.7–1.1 V (vs. RHE) in an O_2 -saturated 0.1 M HClO_4 solution.

2.5. DFT calculation

We performed all the spin-polarized simulations by using Quantum ESPRESSO [37]. The exchange-correlation was treated by employing the Perdew-Burke-Ernzerhof (PBE) functional under the generalized gradient approximation (GGA) and the ultrasoft pseudopotentials for core electrons. The cutoff energy of the Kohn-Sham orbits was set to be 30 Ry and the charge density cutoff energy was 300 Ry. The Fermi-surface effects were dealt with the smearing method of Methfessel and Paxton with a smearing parameter of 0.01 Ry. Periodically repeated (111) and (332) slabs of five layers were used to model the catalyst surfaces and a 20 Å vacuum layer was added in each simulation. The $4 \times 2 \times 1$ Monkhorst-Pack k -points were adopted as the slab lattice parameters ($5.327 \times 12.493 \times 31.644$ Å). The upper 2 layers and the adsorbed atoms were allowed to relax, and the bottom layers were fixed at the bulk position with the optimized lattice constants from the DFT calculations. The convergence standards of energy and force were 10^{-5} Ry and 10^{-3} Ry/bohr, respectively. Similar to the (332) surface, the (111) slab alloys were modeled with a five-layer slab with 2×2 supercells and a 20 Å vacuum layer, but $6 \times 6 \times 1$ Monkhorst-Pack k -points were adopted.

3. Results and discussion

3.1. Formation of hyperbranched PtCu_3 nanodendrites through etching-regulated seeding and growth

The major strategy used to regulate the morphology of the Pt-Cu nanocrystals in this work was to control the seed formation and nanocrystal growth processes using different reaction atmospheres in an OAm solution containing H_2PtCl_6 and $\text{Cu}(\text{NO}_3)_2$, namely, an oxidative etching atmosphere of air and an inert atmosphere of Ar. When an Ar atmosphere was applied during the initial seeding stage (5 min), nanocrystal seeds with diameters of approximately 10 nm were formed (Fig. 1(a)). Although these nanocrystal seeds were irregularly shaped, by careful inspection, they mostly contained five-fold twins consisting of five octahedrons. The inset of Fig. 1(b) shows the structure of the five-fold twinned decahedron. The five-fold twinned decahedron can be regarded as an assembly of five single crystal tetrahedral units sharing a common edge. Both sides of each tetrahedron are in contact with neighbors through

Fig. 1. TEM characterization results: (a,b) five-fold twinned nanocrystals formed under an Ar atmosphere in the initial 5 min of the seeding stage and (c) multipods grown under an Ar atmosphere for another 25 min; (d,e) concave nanocubes formed under air in the initial 5 min of the seeding stage and (f) large concave nanocubes grown under air for another 25 min; (g–i) hyperbranched nanodendrites (inset of g shows the corresponding SAED pattern) grown from the concave nanocubes by switching to the Ar atmosphere for 25 min after the seeding stage (i) and its inset show the magnified images of a typical spiny branch and the exposed HSSs in the square-marked region which are detailed in text; (j,k) HAADF-STEM, EDX mapping images and EDX line scanning profiles of an individual hyperbranched nanodendrite.

the {111} planes. Since the theoretical angle of the two {111} planes of the tetrahedron is 70.53° , the five tetrahedrons connected on both sides of {111} will leave a gap of 7.35° , resulting in internal lattice strain and disorder at the boundary area. By growing under the same inert atmosphere, the twinned nanocrystals evolved into multipods with a broad size and shape distribution (Fig. 1(c)).

As the initial seeding process took place under air containing the oxidizing gas of O_2 , concave nanocubes of approximately 7 nm in size were obtained (Figs. 1(d,e)). The presence of O_2 restrained the etching reaction during the seed formation and growth phases, which inhibited the formation of stable decahedrons. The EDX analysis revealed that the Pt/Cu ratio was approximately 32:68 (Fig. S1(a)), which was significantly higher than that of 1:3 in the initial precursor solution. This was likely because oxidative etching was mainly applied to Cu due to the more negative redox potential of Cu^{2+}/Cu (0.34 V vs. RHE) when compared with $PtCl_6^{2-}/Pt$ (0.74 V vs. RHE). It should be noted that the Cl^- introduced by $H_2PtCl_6 \cdot 6H_2O$ combined with O_2 to create a well-known Cl^-/O_2 oxidative etchant [38,39]. Thus, it was reasonable that some Cu atoms on the surface of Pt-Cu alloy seeds were selectively oxidized to the Cu^{2+} species. When the oxidative atmosphere was maintained, the concave nanocubes continuously grew to larger sizes (Fig. 1(f)).

Switching the atmosphere from air to Ar allowed the con-

cave nanocubes to grow in a non-oxidative environment, resulting in well-dispersed and uniformly sized nanodendrites with rich spiny branches (Fig. 1(g)). The electron diffraction (SAED) pattern of the selected area exhibited 5 bright rings (inset of Fig. 1(g)), which were identified as the diffraction of the {111}, {200}, {220}, {311}, and {331} planes of face-centered cubic (fcc) crystals respectively from the inner to the outer rings. The diameter of the {111} diffraction ring was 9.329 nm^{-1} , which corresponded to a d -spacing of 0.214 nm.

The high-resolution TEM image showed a zigzag edge and a lattice fringe spacing of approximately 0.214 nm for the hyperbranched Pt-Cu nanodendrites (Fig. 1(i) and the inset), which was a contraction of approximately 5.3% when compared with the d -spacing of 0.226 nm for the {111} plane of pure Pt crystal (PDF #04-0802). The angle of the zigzag was approximately 145° , indicating that the surface was bounded by high index {hhl} facets with the {111} platform and {110} edge, such as {331}, {332}, and {221}. The radial pattern structure of the nanodendrites were clearly visualized with the high-angle annular dark-field scanning TEM (HAADF-STEM) image (Fig. 1(j)). The EDX mapping patterns (Fig. 1(j)) and EDX line scanning profiles (Fig. 1(k)) showed a relatively homogeneous distribution of Pt and Cu in the dendritic branches. The Pt/Cu atomic ratio determined by using EDX was 24:76 (Fig. S1(b)), which was consistent with the value obtained with ICP-AES (23:77, Table S1) and the Pt/Cu ratio of the precursors in the initial solution. This composition was also confirmed by the XRD patterns shown in Fig. S2, which matched well with that of the standard $PtCu_3$ alloy (JCPDS 35-1358, $a = 0.370 \text{ nm}$). The lattice parameter calculated from XRD diffraction peak positions was 0.372 nm, which corresponded to a lattice compression of approximately 5.3% when compared with pure Pt (0.393 nm), which was consistent with the lattice fringe data determined from the TEM images.

In summary, rich spiny branches grew on the concave nanocubes seeds but not on the five-fold twins under the same non-oxidative Ar atmosphere, which was an intriguing result. Moreover, the multipods that evolved from the five-fold twins also contained a small number of thick conic branches on their distorted twin bodies (Fig. 1(c)). This seemed to imply that in the present system, branched growth was preferred by the Pt-Cu alloy in the absence of oxidative etching. The addition of metal precursors under non-oxidative conditions promoted the formation of large amounts of nuclei in the solution with concentration depletion occurring around the nuclei; therefore, the growth of the nuclei was slow and the deposition of Pt/Cu atoms on the {111} facets of the twin seeds was determined by thermodynamics, resulting in epitaxial growth of these facets. However, conic branches could form at the edges of the twin seeds due to the relatively high reactivity. On the other hand, the gradually intensified concentration depletion promoted growth that was controlled by kinetics, resulting in only a few relatively thick branches. For the concave nanocube seeds, the corners, edges, and facets were all active to allow fast atom deposition. Moreover, the concentration of the metal precursors were relatively high after the initial seeding process under an oxidative atmosphere. Thus, explosively rapid deposition of

the metal atoms occurred upon switching to the non-etching condition, forming large amounts of relatively thin branches. We also conducted the atmosphere-switching synthesis (used to produce the hyperbranched nanodendrites) with a low precursor concentration. The density of the branches was significantly reduced in the resulting sample (Fig. S3), which verified the effect of precursor concentration on the formation and growth of branches.

The surface composition of the PtCu₃ nanodendrites was characterized by XPS (Fig. S4). The Pt 4f_{7/2} spectrum showed that Pt⁰ (75%) was the dominant species (Fig. S4(a)), while the Cu 2p_{3/2} spectrum (Fig. S4(a)) suggested that the majority of Cu was in the form of Cu^{II} (55.7%). This suggested that the Pt element was mainly in the metallic state and that electronic coupling existed between the two atoms. Based on the integrated area and sensitivity factors of Pt 4f_{7/2} and Cu 2p_{3/2}, the surface atomic ratio of Pt to Cu atoms was calculated to be 37:63, which was different from the bulk composition determined by EDX (Fig. S1(b)). The relatively Pt-rich surface may be due to the instability of Cu atoms on the surface.

3.2. Formation of composition-graded PtCu₃@Pt₃Cu@Pt core-shell Pt-Cu nanodendrites through electrochemical dealloying

The electrochemical dealloying approach was used to make electrocatalysts from the as-prepared Pt-Cu nanocrystals. First, the nanocrystals were supported on the Vulcan XC-72R carbon black to form Pt-Cu NCs/C, with a Pt content of ~3.6 wt% as determined by ICP-AES. Electrochemical dealloying was performed with 100 cycles of cyclic voltammetry (CV) and a scan rate of 500 mV s⁻¹ between 0.06–1.3 V (vs. RHE) in O₂-saturated 0.1 M HClO₄ solution. Fig. S5 shows the CV curves at the different cycles for the hyperbranched nanodendrites. In the first two cycles, there were no hydrogen adsorption/desorption peaks, suggesting that the surface was mainly covered by Cu. The anodic scans gave an oxidation peak at approximately +0.3 V that indicated the dissolution of pure unalloyed Cu and a broad peak between +0.6 and +0.9 V that was associated with the oxidation of Cu in the Pt-Cu alloy [40].

As electrochemical dealloying proceeded, the hydrogen adsorption/desorption peaks gradually developed, suggesting a transformation from a Cu-rich to a Pt-rich surface. After approximately 50 cycles, both the peaks of Cu oxidation and deposition nearly disappeared, indicating the formation of a Pt-skin surface. Additionally, both the onset potential of Pt oxidation and the peak potential of the Pt oxide reduction gradually shifted to more positive potentials, indicating that the adsorption strength of the oxygenated species on the dealloyed Pt surface gradually decreased, which is beneficial for the ORR.

The TEM and HRTEM images (Figs. 2(a,b)) indicated that the HIS-exposed dendrite structures were maintained after electrochemical dealloying. Meanwhile, the EDX mapping results (Figs. 2 (c–f)) confirmed the formation of the typical core-shell structure with a Pt-rich surface. The XPS spectra (Fig. S6) demonstrated that the near-surface Pt/Cu ratio changed from 37:63 to 73:27. In addition, there was an obvious red shift

Fig. 2. (a,b) TEM and HRTEM image of the dealloyed PtCu₃ NDs; (c–f) EDX mapping results of the dealloyed PtCu₃ NDs.

(0.4 eV) in the binding energy of the Pt 4f peak for the dealloyed Pt-Cu/C nanodendrites when compared with that for Pt/C, suggesting a partial charge transfer from Cu to Pt, which lowers the d-band center and therefore the surface oxygen affinity [41,42]. To this end, we can conclude that electrochemical dealloying produced a catalyst with the graded composition of PtCu₃@Pt₃Cu@Pt.

3.3. Electrocatalytic properties of the dealloyed Pt-Cu NCs/C

The ORR polarization curves were recorded in O₂-saturated 0.1 M HClO₄ with a scan rate of 5 mV s⁻¹. As shown in Fig. 3(a), all the dealloyed Pt-Cu NCs/C catalysts showed better ORR activity than the commercial pure Pt/C catalyst. In particular, the hyperbranched NDs exhibited the best ORR activity, where the half-wave potential ($E_{1/2}$ = 0.930 V) was approximately 85 mV more positive than that of Pt/C. As shown in Fig. 3(b), the blank CV curves of the different sample catalysts in Ar-saturated 0.1 M HClO₄ solution at a sweep rate of 50 mV s⁻¹ were compared. Additionally, the CO-stripping curves of the catalysts are shown in Fig. S7. Clearly, the oxidation peak potentials of adsorbed CO for all the three dealloyed Pt-Cu NCs/C were negative when compared with that of Pt/C, indicating that the integration of Cu with Pt decreased the adsorption of CO on Pt. Although the multipods showed the lowest onset and oxidation peak potentials, the hyperbranched nanodendrites exhibited the highest peak intensity. Based on the voltammetric charges associated with the CO stripping charges, the ECSA values were estimated (Table S2). As expected, the hyperbranched nanodendrites provided the highest ECSA, which was comparable to that of Pt/C (80.1 m² g_{Pt}⁻¹). There were two

Fig. 3. Electrochemical properties of the three dealloyed Pt-Cu NCs/C and Pt/C in 0.1 M HClO₄ solution. (a) ORR polarization curves; (b) cyclic voltammograms; (c) mass-specific activities; (d) area-specific activities at 0.9 V (vs. RHE).

reasons for the high ECSA: the high degree of branching of the sample leading to the high specific surface area and the large amount of Cu diluting the Pt concentration in the sample.

The kinetic current density (j_k) at 0.9 V (vs. RHE) for the catalysts, normalized by the mass and ECSA of Pt on the electrode, were calculated according to the Koutecky-Levich equation. The resulting mass-specific activity (MA) and area-specific activity (SA) for the different catalysts are respectively shown in Figs. 3(c,d). The hyperbranched nanodendrites exhibited an MA of 1.55 A mg_{Pt}⁻¹ and an SA of 2.4 mA cm_{Pt}⁻², which were approximately 14 and 24 times higher than that of the commercial Pt/C (0.11 A mg_{Pt}⁻¹ and 0.1 mA cm_{Pt}⁻²), respectively. In particular, MA was approximately 3 times greater than that of the U.S. Department of Energy's 2025 target (0.44 A mg_{Pt}⁻¹).

Pt-Cu nanodendrites with different Pt/Cu ratios can also be obtained by adjusting the feed ratio. The TEM images in Fig. S8 show the morphology of the formed Pt₂Cu₂ NDs and Pt₃Cu NDs. For comparison, the systems containing the single Cu or Pt precursors produced nanoparticles rather than nanodendrites by the same synthesis method. Moreover, the electrochemical results of the two nanodendrites are shown in Fig. S9, revealing that as the proportion of Pt increased, their ECSA and MA (Table S3) declined.

Feliu *et al.* [15] studied the ORR catalytic activity of single crystal Pt electrodes in acidic and basic electrolytes. They found that the ORR activity of the HISS decreased when the solution changed from an acid to a base, while the Pt (111) facet maintained its electrocatalytic activity. In order to further confirm the electrocatalytic role of HISS in the dealloyed nanodendrites, the electrochemical properties of the hyperbranched nanodendrites were also tested in 0.1 M KOH solution (Fig. S10). The ORR activity in the acid was obviously superior to that in the base (Fig. S10(a)), and the MA in the basic solution was approximately one quarter of that in the acidic solution.

According to the CV curves shown in Fig. S10(b), the hyperbranched nanodendrites exhibited little difference in the adsorption strength of the oxygen-containing species between the acid and the base. This may suggest that the different ORR activities were ascribed to the different reaction mechanisms in the acidic and basic electrolytes [15,43,44]. To this end, the formation of HISSs should be a crucial factor for enhanced ORR activity in an acid medium.

DFT calculations were performed to further understand the origins of the enhanced ORR activity of the PtCu₃@Pt₃Cu@Pt nanodendrites (Fig. 4). In the calculations, the PtCu₃@Pt₃Cu@Pt structure was modeled with a 5-layer slab comprising 3 bottom layers of PtCu₃, a subsurface layer of Pt₃Cu, and a top surface layer of Pt. The PtCu₃@Pt₃Cu@Pt (332) stepped facet was used to simulate the HISSs (Fig. S11). The (332) single crystal surface is a typical HIS composed of (111) terraces and (110) steps. It has enough terrace width to distinguish three main types of surface sites on this class of HIS but

Fig. 4. Models and calculated values of $-AE_0$ (with respect to that on Pt(111)) for PtCu₃@Pt₃Cu@Pt(111), PtCu₃@Pt₃Cu@Pt(332), and pure Pt(111).

has a relatively small number of surface atoms, which can reduce the computation cost. The (332) surface is generally denoted as $5(111) \times 1(110)$, which means that it has a structure of 5-atom-wide (111) terraces separated by a single height (110) step. For comparison, 5-layer slabs of pure Pt (111) and $\text{PtCu}_3@Pt_3Cu@Pt$ (111) were also considered. The adsorption energy of the oxygen atom (AE_O) was used as a descriptor to compare the activity trends of these surfaces [18,41]. All the AE_O values are presented with respect to that of Pt (111). The $\text{PtCu}_3@Pt_3Cu@Pt$ (111) surface exhibited an AE_O value that was more positive than that of pure Pt (111) by 0.35 eV. There were three main types of surface sites on the $\text{PtCu}_3@Pt_3Cu$ (332) surface, namely, the sites on the (111) terrace apart from the step (sites B, C, and D in Fig. S11), the sites on the (111) terrace adjacent to the step (sites A in Fig. S11), and the sites under the steps (sites E in Fig. S11), as shown in Fig. S11. The calculated AE_O for the sites on the (111) terrace apart from the step was similar to that on the $\text{PtCu}_3@Pt_3Cu@Pt$ (111) surface, whereas that for the sites on the (111) terrace adjacent to the step was approximately 0.2 eV more negative than that on the $\text{PtCu}_3@Pt_3Cu@Pt$ (111) surface, but approximately 0.15 eV more positive than that for Pt (111). Moreover, in the DFT calculations, for the sites under the steps, O atoms were weakly adsorbed and AE_O was significantly positive-shifted compared with Pt (111). The calculated AE_O for the $\text{PtCu}_3@Pt_3Cu@Pt$ (332) surface sites are shown in Table S4. According to recent kinetic models, surface sites with AE_O values that are within 0.4 eV positive to that for Pt (111) exhibit enhanced ORR activity compared with pure Pt, and an AE_O value that is within 0.2 eV positive to that of Pt (111) gives the best ORR activity [10]. In

this respect, the two types of surface sites of $\text{PtCu}_3@Pt_3Cu@Pt$ (332) both catalyzed the ORR more efficiently than pure Pt. In particular, the activity of the near-step sites was close to those on the best ORR catalysts. The decreased affinity for oxygen (more positive AE_O) of the $\text{PtCu}_3@Pt_3Cu@Pt$ (111) surface was likely due to the strain effect caused by the alloying Cu [45]. As aforementioned, a compression of approximately 5% of the surface Pt-Pt distance occurred due to the presence of the PtCu_3 core. This compression over-weakens the O binding. The presence of the step can offset this strain effect, thus giving a near optimal AE_O for the ORR.

The electrochemical durability of catalyst is recognized as one of the most important issues for practical applications. For the $\text{PtCu}_3@Pt_3Cu@Pt$ hyperbranched nanodendrites and Pt/C catalysts, we performed stability tests with 5000 potential cycles between 0.7 and 1.1 V (vs. RHE) in O_2 -saturated 0.1 M $HClO_4$. Fig. 5(a) shows the ORR polarization curves before and after 5000 cycles. The value of $E_{1/2}$ only reduced by 2 mV for the $\text{PtCu}_3@Pt_3Cu@Pt$ catalyst but reduced by 31 mV for Pt/C. As a result, the MA of $\text{PtCu}_3@Pt_3Cu@Pt$ at 0.9 V decayed by only ~8%, in contrast to the large decrease of ~27% for Pt/C (Fig. 5(b)). Furthermore, for the CV curves before and after the stability tests, a slight change was observed for $\text{PtCu}_3@Pt_3Cu@Pt$ (Fig. 5(c)), in contrast to the sharp attenuation for Pt/C (Fig. 5(d)). The TEM images showed that the HIS structures were well maintained after the stability tests (Fig. S12). The stability of the HIS in this catalyst likely originated from the nanodendrite architecture. All the results suggested that the $\text{PtCu}_3@Pt_3Cu@Pt$ hyperbranched nanodendrite catalyst exhibited good stability.

Fig. 5. Electrochemical durability of the $\text{PtCu}_3@Pt_3Cu@Pt$ hyperbranched nanodendrites and Pt/C catalysts: ORR polarization curves (a), mass-specific activity (b), and CV curves of $\text{PtCu}_3@Pt_3Cu@Pt$ (c) and Pt/C (d) before and after 5000 cycles. The Pt loading of $\text{PtCu}_3@Pt_3Cu@Pt$ and Pt/C is $7.5\ \mu g_{Pt}\ cm^{-2}$ and $60\ \mu g_{Pt}\ cm^{-2}$, respectively.

4. Conclusions

In summary, the PtCu₃@Pt₃Cu@Pt electrocatalyst with exposed HISs on the composition-graded nanodendrites was fabricated straightforwardly by an atmosphere-modulated solution reaction followed by controlled electrochemical dealloying. Spectroscopic, electrochemical, and computational characterization results were collected to understand the oxygen reduction electrocatalysis of the PtCu₃@Pt₃Cu@Pt nanodendrites. The presence of the n(111) × (110) step sites and the graded alloy composition together promoted the oxygen binding energy on the step sites of the HISs on the PtCu₃@Pt₃Cu@Pt nanodendrites to the optimal value near the top of the ORR peak, resulting in a mass-specific activity of 1.55 A mg_{Pt}⁻¹ and area-specific activity of 2.4 mA cm_{Pt}⁻² at 0.9 V in 0.1 M HClO₄ solution, which are 14 and 24 times higher than that of commercial Pt/C, respectively.

Acknowledgment

The DFT calculations in this paper were done on the supercomputing system in the Supercomputing Center of Wuhan University.

References

- [1] F. Luo, S. Pang, Z. Yang, *Acta Phys. Chim. Sin.*, **2021**, 37, 009087.
- [2] Z. Zhang, C. Ge, Y. Chen, Q. Wu, L. Yang, X. Wang, Z. Hu, *Acta Chim. Sin.*, **2019**, 77, 60–65.
- [3] X. Lu, S. Cao, X. Wei, S. Li, S. Wei, *Acta Chim. Sin.*, **2020**, 78, 1001–1006.
- [4] S. Yu, Q. Lou, R. Liu, K. Han, Z. Wang, H. Zhu, *Acta Chim. Sin.*, **2012**, 70, 2359–2364.
- [5] A. L. Wang, Y. Sun, Z. X. Liang, S. L. Chen, *Acta Chim. Sin.*, **2009**, 67, 2554–2558.
- [6] Y. Lü, Y.-J. Song, H.-Y. Liu, H.-Q. Li, *Acta Phys.-Chim. Sin.*, **2017**, 33, 283–294.
- [7] M. C. Luo, Y. J. Sun, Y. N. Qin, Y. Yang, D. Wu, S. J. Guo, *Acta Phys.-Chim. Sin.*, **2018**, 34, 361–376.
- [8] Z. Shui, N. He, L. Chen, W. Zhao, X. Chen, *Acta Chim. Sin.*, **2020**, 78, 557–564.
- [9] J. Greeley, J. Rossmeisl, A. Hellmann, J. K. Nørskov, *Z. Phys. Chem.*, **2007**, 221, 1209–1220.
- [10] G. A. Tritsaris, J. Greeley, J. Rossmeisl, J. K. Nørskov, *Catal. Lett.*, **2011**, 141, 909–913.
- [11] I. E. L. Stephens, A. S. Bondarenko, U. Grønberg, J. Rossmeisl, I. Chorkendorff, *Energy Environ. Sci.*, **2012**, 5, 6744–6762.
- [12] V. Viswanathan, F. Y. Wang, *Nanoscale*, **2012**, 4, 5110–5117.
- [13] N. M. Marković, T. J. Schmidt, V. Stamenković, P. N. Ross, *Fuel Cells*, **2001**, 1, 105–116.
- [14] C. Wang, S. Bai, Y. Xiong, *Chin. J. Catal.*, **2015**, 36, 1476–1493.
- [15] A. M. Gomez-Marín, R. Rizo, J. M. Feliu, *Catal. Sci. Technol.*, **2014**, 4, 1685–1698.
- [16] N. Hoshi, M. Nakamura, A. Hitotsuyanagi, *Electrochim. Acta*, **2013**, 112, 899–904.
- [17] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jónsson, *J. Phys. Chem. B*, **2004**, 108, 17886–17892.
- [18] J. Greeley, I. E. Stephens, A. S. Bondarenko, T. P. Johansson, H. A. Hansen, T. F. Jaramillo, J. Rossmeisl, I. Chorkendorff, J. K. Nørskov, *Nat. Chem.*, **2009**, 1, 552–556.
- [19] N. Tian, Z. Y. Zhou, S. G. Sun, Y. Ding, Z. L. Wang, *Science*, **2007**, 316, 732–735.
- [20] F. Wang, C. Li, L. D. Sun, H. Wu, T. Ming, J. Wang, J. C. Yu, C. H. Yan, *J. Am. Chem. Soc.*, **2011**, 133, 1106–1111.
- [21] J. C. Guo, Y. F. Lin, N. Tian, S. G. Sun, *Acta Phys.-Chim. Sin.*, **2019**, 35, 749–754.
- [22] L. Bu, S. Guo, Z. Xu, S. Xuan, S. Dong, L. Gang, Z. Xing, J. Yao, J. Guo, X. Huang, *Nat. Commun.*, **2016**, 7, 11850.
- [23] F. Nosheen, Z. Zhang, G. Xiang, B. Xu, Y. Yang, F. Saleem, X. Xu, J. Zhang, X. Wang, *Nano Res.*, **2014**, 8, 832–838.
- [24] M. Gong, G. Fu, Y. Chen, Y. Tang, T. Lu, *ACS Appl. Mater. Interfaces*, **2014**, 6, 7301–7308.
- [25] F. Maillard, L. Dubau, J. Durst, M. Chatenet, J. André, E. Rossinot, *Electrochem. Commun.*, **2010**, 12, 1161–1164.
- [26] J. Wu, J. Zhang, Z. Peng, S. Yang, F. T. Wagner, H. Yang, *J. Am. Chem. Soc.*, **2010**, 132, 4984–4985.
- [27] Y. Qian, W. Wen, P. A. Adcock, Z. Jiang, N. Hakim, M. S. Saha, S. Mukerjee, *J. Phys. Chem. C*, **2008**, 112, 1146–1157.
- [28] J. Huang, C. Ding, Y. Yang, G. Liu, W. B. Cai, *Chin. J. Catal.*, **2019**, 40, 1895–1903.
- [29] M. G. Li, Z. H. Xia, Y. R. Huang, L. Tao, Y. G. Chao, K. Yin, W. X. Yang, W. W. Yang, Y. S. Yu, S. J. Guo, *Acta Phys.-Chim. Sin.*, **2020**, 36, 1912049.
- [30] Y. Zhao, L. Tao, W. Dang, L. Wang, M. Xia, B. Wang, M. Liu, F. Gao, J.

Graphical Abstract

Chin. J. Catal., 2021, 42: 1108–1116 doi: 10.1016/S1872-2067(20)63735-4

High index surface-exposed and composition-graded PtCu₃@Pt₃Cu@Pt nanodendrites for high-performance oxygen reduction

Yuxiang Liao, Jun Li, Shiming Zhang*, Shengli Chen*
Wuhan University; Shanghai University

Atmosphere-modulated synthesis followed by electrochemical dealloying produces exposed high index surfaces on the composition-graded nanodendrites of PtCu₃@Pt₃Cu@Pt to achieve mass and area activities of Pt that are respectively 14 and 24 times higher than that of pure Pt catalyst.

- Zhang, Y. Zhao, *Small*, **2019**, 15, e1900288.
- [31] Y. Li, S. Guo, *Nano Today*, **2019**, 28, 100774.
- [32] Y. Kuang, Y. Zhang, Z. Cai, G. Feng, Y. Jiang, C. Jin, J. Luo, X. Sun, *Chem. Sci.*, **2015**, 6, 7122–7129.
- [33] N. Guo, H. Xue, A. Bao, Z. Wang, J. Sun, T. Song, X. Ge, W. Zhang, K. Huang, F. He, Q. Wang, *Angew. Chem. Int. Ed.*, **2020**, 59, 13778–13784.
- [34] M. Gatalo, F. Ruiz-Zepeda, N. Hodnik, G. Dražić, M. Bele, M. Gaberšček, *Nano Energy*, **2019**, 63, 103892.
- [35] D. Fang, L. Wan, Q. Jiang, H. Zhang, X. Tang, X. Qin, Z. Shao, Z. Wei, *Nano Res.*, **2019**, 12, 2766–2773.
- [36] S. Li, Z. Q. Tian, Y. Liu, Z. Jang, P. K. Shen, *Chin. J. Catal.*, **2021**, 42, 648–657.
- [37] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougousis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, *J. Phys.-Condens. Matter.*, **2009**, 21, 395502.
- [38] M. Luo, A. Ruditskiy, H.-C. Peng, J. Tao, L. Figueroa-Cosme, Z. He, Y. Xia, *Adv. Funct. Mater.*, **2016**, 26, 1209–1216.
- [39] M. Jin, G. He, H. Zhang, J. Zeng, Z. Xie, Y. Xia, *Angew. Chem. Int. Ed.*, **2011**, 50, 10560–10564.
- [40] P. Strasser, *Rev. Chem. Eng.*, **2009**, 25, 255–295.
- [41] V. Stamenkovic, B. S. Mun, K. J. J. Mayrhofer, P. N. Ross, N. M. Markovic, J. Rossmeisl, J. Greeley, J. K. Nørskov, *Angew. Chem. Int. Ed.*, **2006**, 118, 2963–2967.
- [42] F. H. B. Lima, J. Zhang, M. H. Shao, K. Sasaki, M. B. Vukmirovic, E. A. Ticianelli, R. R. Adzic, *J. Phys. Chem. C*, **2016**, 111, 404–410.
- [43] M. Oezaslan, F. Hasché, P. Strasser, *J. Electrochem. Soc.*, **2012**, 159, B444.
- [44] F. Calle-Vallejo, J. Tymoczko, V. Colic, Q. H. Vu, M. D. Pohl, K. Morgenstern, D. Loffreda, P. Sautet, W. Schuhmann, A. S. Bandarenka, *Science*, **2015**, 350, 185–189.
- [45] M. Mavrikakis, B. Hammer, J. K. Nørskov, *Phys. Rev. Lett.*, **1998**, 81, 2819–2822.

高指数晶面和梯度组成的PtCu₃@Pt₃Cu@Pt纳米枝晶氧还原电催化剂性能

廖宇翔^a, 李俊^a, 张世明^{a,b,#}, 陈胜利^{a,*}

^a武汉大学化学与分子科学学院, 湖北省化学电源材料与技术重点实验室, 湖北武汉430072

^b上海大学理学院可持续能源研究院, 上海200244

摘要: 燃料电池作为一种清洁、高效的能量转换装置, 其大规模应用受到阴极氧还原反应(ORR)动力学缓慢以及铂资源稀缺和价格高昂等的极大制约。尽管研究人员在过去几十年中付出了巨大努力, 但研制高效、耐用的低Pt合金催化剂仍亟待突破。

近年的研究表明, Pt的一些高指数晶面能够表现出比Pt(111)晶面更高的ORR活性, 尤其是Pt(332), Pt(331)和Pt(554)等。同时, 合金化能够通过电子与几何效应减弱含氧物种在Pt表面的吸附能, 提升Pt合金催化剂的ORR活性。因此, 高指数晶面和合金化的结合将是设计开发高性能电催化剂的有效手段。

本文提出一种气氛调控的液相合成方法, 通过在油胺中加热还原Pt化合物和Cu化合物, 不添加其它保护剂, 仅通过反应气氛的调控, 成功制备了不同形貌的Pt-Cu合金纳米结构(纳米多脚、纳米凹立方体、纳米枝晶)。通过反应前期引入氧化性气氛随后切换为惰性气氛的调控策略, 合成具有高指数晶面的具有纳米枝晶结构的PtCu₃合金; 进一步对其进行电化学去合金化形成富Pt壳层, 既保持其纳米枝晶形貌和高指数晶面, 又形成具有梯度组成的PtCu₃@Pt₃Cu@Pt纳米枝晶。相比而言, 全程惰性气氛下生长得到纳米多脚结构, 全程氧化性气氛下生长则得到纳米凹立方体。电化学测试结果表明, 在0.1 M HClO₄电解液中, PtCu₃@Pt₃Cu@Pt纳米枝晶展现出较高的ORR活性, 在0.9 V (vs. RHE)处的Pt质量活性和面积活性高达1.55 A mg_{Pt}⁻¹和2.4 mA cm_{Pt}⁻², 分别为商业Pt/C催化剂的14倍和24倍; 此外, PtCu₃@Pt₃Cu@Pt纳米枝晶具有良好的电化学稳定性, 经0.7~1.1 V (vs. RHE)电势范围内循环5000圈, 其催化活性保持稳定。DFT计算表明, Cu合金效应和高指数晶面结构共同增强了Pt的ORR活性, 其中PtCu₃@Pt₃Cu@Pt纳米枝晶高指数晶面台阶位点的氧结合能接近最优值, 从而表现出火山顶点附近的ORR活性。

关键词: 氧还原; Pt-Cu合金; 高指数表面; 纳米枝晶; 形貌控制

收稿日期: 2020-10-30. 接受日期: 2020-11-03. 上网时间: 2021-03-05.

*通讯联系人. 电话: (027)68754693; 电子信箱: slchen@whu.edu.cn

#通讯联系人. 电话: (021)66131689; 电子信箱: smzhang@shu.edu.cn

基金来源: 国家自然科学基金(21832004, 21633008); 上海市青年科技启明星计划(18QB1404400).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/journal/chinese-journal-of-catalysis>).