Pt$_x$Cu$_y$ nanocrystals with hexa-pod morphology and their electrocatalytic performances towards oxygen reduction reaction

Yujing Li$^{1,2}$ (✉), Fanxin Quan$^2$, Enbo Zhu$^3$, Lin Chen$^2$, Yu Huang$^{3,4}$, and Changfeng Chen$^{1,2}$

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| Pt$_x$Cu$_y$ nanocrystals with hexa-pod morphology and their electrocatalytic performances towards oxygen reduction reaction | Yujing Li$^{1,2,*}$, Fanxin Quan$^2$, Enbo Zhu$^3$, Lin Chen$^2$, Yu Huang$^{3,4}$, Changfeng Chen$^{1,2}$ | 1. State Key Laboratory of Heavy Oil, China University of Petroleum, Beijing, Changping, 102249, China.  
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Hexa-pod Pt$_x$Cu$_y$ synthesized with wet chemistry display superior electro-catalytic activity towards oxygen reduction reaction due to the existence of high-index facets.
Pt$_x$Cu$_y$ nanocrystals with hexa-pod morphology and their electrocatalytic performances towards oxygen reduction reaction

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ABSTRACT

Synthesis of bimetallic Pt$_x$Cu$_y$ nanocrystals (NCs) with well-shaped hexa-pod morphology through wet chemistry approach is reported. As-synthesized convex NCs around 20 nm in size expose by low-index (111) facets on seeds and various high-index facets on pods. The growth mechanism involves preferred growth along <100> crystallographic direction on cuboctahedral seeds. The synthetic protocol can be applied to synthesis of Pt$_x$Cu$_y$ NCs with various Cu/Pt ratios. The electro-catalytic activities of hexa-pod Pt$_x$Cu$_y$/C catalysts supported on carbon black towards oxygen reduction reaction (ORR) are studied. Hexa-pod PtCu$_2$/C catalysts exhibit the highest specific activity (3.7 mA/cm$^2$Pt) and mass activity (2.4 A/mgPt), the highest compared with data reported from literatures on Pt$_x$Cu$_y$. Comparison with Pt$_x$Cu$_y$ in other morphologies indicates that the enhanced activity originates from morphology factor. Existence of high-index facets, as well as abundant edges and steps on pods, could reasonably explain the enhanced catalytic activity. The hexa-pod Pt$_x$Cu$_y$/C catalysts also show high stability in morphology and activities after accelerated durability tests. As-synthesized hexa-pod Pt$_x$Cu$_y$ NCs are highly potential cathode electro-catalysts for proton exchange membrane fuel cells.
Carbon supported Pt nanoparticles are currently the most widely accepted cathode catalysts for proton exchange membrane fuel cells (PEMFCs), but Pt-based alloy nanocrystals (NCs), mainly Pt alloyed with transition metal M (denoted as PtM, M= Ni, Co, Fe, Mn, etc.), have gained enormous attention in the past decade due to their improved catalytic activities compared with pure Pt in oxygen reduction reaction (ORR).[1-10] The drastically improved electrocatalytic performance of PtM alloys can mainly be attributed to surface electronic effect, and geometric effect induced by the surface strain or atomic arrangement.[11-13] It has also been reported by literatures that, for PtM alloys, the formation of Pt-skin structure is crucial in achieving enhanced ORR activities.[14, 15] It is generally accepted that the formation of Pt-skin structure leads to the modified d-band electronic structure and shortened Pt-Pt distance on surface, both of which could benefit the adsorption of oxygen molecules and breakage of O-O bond.[2, 16-20] Among various PtM alloys for PEMFC cathode application, PtCu is a special alloy family that has not received much attention.[21-24] Strasser et al reported that electro-catalytic activities of PtCu towards ORR can also be drastically enhanced through voltammetric de-alloying approach, and hypothesized that lattice-contracted alloy core stabilizes the Pt-rich skin with surface strain and hence improves the surface catalytic activity.[25, 26] The same group also found that when increasing Cu/Pt ratio for PtCu alloy, the catalysts show elevated ORR activities in acidic media but declined activity in alkaline electrolyte.[27] Cu atoms on the surface remain stable in alkaline media, but tend to deplete in acid, leading to the formation of ORR-preferred Pt-rich skin in only acidic media, which explains their observed distinct behavioral differences in different electrolytes. Stephens and Chorkendorff et al engineered a Cu/Pt(111) near-surface alloy with Cu atoms in subsurface up to 1 monolayer, and demonstrated 8-fold enhancement of ORR activity over Pt(111) with appropriate amount of deposited Cu.[28] They proposed that the presence of subsurface Cu can weaken the binding of surface Pt atoms to OH* intermediates and expedite the ORR. From literatures, PtCu alloys have clearly demonstrated enhanced ORR activities via surface de-alloying.[29-31] Nonetheless, to achieve ORR activities from PtCu catalysts as high as those reported from PtNi-based alloys remains difficult. Both theoretical and experimental studies have pointed out that, for Pt-based alloy catalysts, their catalytic activities strongly depend on exposed facets.[14, 32] For instance, Stamenkovic and Markovic et al found that for single crystalline PtNi film, PtNi(111) facet shows one-order-of-magnitude enhancement in ORR activity compared with Pt(111) surface, which is attributed to modified surface d-band electronic structure induced by atomic arrangement on (111) facet and Pt-rich surface electronic compositional profiles as mentioned above.[14] For nano-sized catalysts, morphology of catalyst particle determines exposed facets, and therefore affects their activities towards ORR.[33-35] In addition, it is also known that atoms at corners and edges of catalyst particle, determined by morphology as well, situated in special strain and bonding states and thus could show distinctively high catalytic activities.[32, 36] Therefore, controlling the morphology of alloy NCs is crucial in optimizing catalytic performance and investigating catalytic mechanism.[37-39] Large amount of studies have been placed on morphology-controllable syntheses of PtNi, PtCo, and PtFe alloy families, while relative literatures are limited for PtCu alloy. Earlier literatures on PtCu nanocatalysts generally show irregular morphologies.[21, 23] Wang and Li et al reported a unique synthetic protocol of synthesizing PtCu with various Cu/Pt ratios in different shapes, including mainly spheres, truncated octahedron, flowers etc, demonstrating the possibility to control the morphology of PtCu NCs.[40] Fang et al reported the synthesis of octahedral and cubic PtCu NCs with the typical oleylamine/oleic acid protocol with the presence of tungsten hexacarbonyl.[41, 42] Saleem and Wang et al employed a two-step synthetic approach, and obtained ultrathin PtCu nanosheets, based on which PtCu nanocones could further be obtained by controllable rolling of nanosheets.[43] However, none of the above work correlates morphology of PtCu NCs with their catalytic activities towards ORR, leading to the lack of data regarding morphology-activity relation. Herein, we demonstrate a facile and robust approach for harvesting uniform monodisperse PtCu NCs with hexa-pod morphology in various Cu/Pt ratios.
As-synthesized hexa-pod PtCu\textsubscript{3} NCs are enclosed mainly by high-index crystallographic facets, hypothetically in a seeding scheme. The electrochemical activities towards ORR are determined for the PtCu\textsubscript{3} NCs with Cu/Pt ratio of 2/3, 1/1, and 2/1 supported on commercial carbon black. The highest specific activity, 3.7 mA/cm\textsuperscript{2} and mass activity, 2.4 A/mg \textit{v} \textsubscript{m} are achieved with PtCu\textsubscript{2}/C, both of which are higher than the best ever reported activities obtained from PtCu alloy nano-catalysts.

We utilized a facile solvothermal approach to synthesize the hexa-pod PtCu\textsubscript{3} NCs. [Pt(NH\textsubscript{3})\textsubscript{2}](NO\textsubscript{3})\textsubscript{2} and Cu(NO\textsubscript{3})\textsubscript{2} were used as metal precursors, and 1,2-propanediol (PDO) was used as solvent and reducing agent for the synthesis. After numerous trials, we found that a combination of polyvinylpyrrolidone (PVP) and sodium bromide (NaBr) with appropriate ratio as capping agent can be used to obtain NCs with hexa-pod and truncated octahedral (TO) morphologies. Previously reported shape-controllable syntheses of PtCu\textsubscript{3} NCs were mostly conducted in non-polar organic solvents such as oleylamine, hence the NCs commonly show hydrophobic surface and need further treatment by either ligand exchange or acid treatment for the purpose of obtaining best electrochemical activity.[33, 39] In this work, the reaction is conducted in hydrophilic solvent, and PVP/NaBr is used as capping agent combination, endowing the as-synthesized PtCu\textsubscript{3} NCs with hydrophilic surface. Besides, capping species PVP and NaBr can be easily washed off to minimize their possible hindering effects on catalytic activities. Therefore, the synthetic protocol is purely green and favored by the electrochemical application as well.

The morphology of the as-synthesized PtCu\textsubscript{3} NCs is characterized by transmission electron microscope (TEM). Fig. 1(a) represents the typical view of the sample at low magnification, indicating that NCs are distributed within a narrow size window around 20 nm and all NCs show pod-like projections. At higher magnification, NCs show well-defined morphology. The NC at lower right clearly shows the hexa-pod morphology, and other NCs in the same image also show 2D projections of hexa-pod along different zone axes. By examining 50 NCs, it is found that over 92% of the NCs show projections of hexa-pod, indicating fairly high yield of hexa-pod NCs with this synthetic protocol. A schematic of hexa-pod NC with smoothened facets is shown in the inset of Fig. 1(b). Elemental mapping images of the NCs under scanning transmission electron microscope (STEM) are shown in Fig. 1(c), indicative of uniform distribution of Pt and Cu in NCs. Atomic resolution TEM image of a NC lying along <110> zone axis is shown in Fig. 1(d-f). A close view of the pod highlighted by red rectangle can be found in Fig. 1(e). According to fast Fourier transformation (FFT) in Fig. 1(f), surface on the pod can mostly be assigned to low index facets such as (111) (yellow), (100) (orange), and (220) (light green) with abundant atomic steps and kinks. The NCs grow into well-defined morphology but most facets are smoothened out.

![Figure 1](image-url)

**Figure 1.** Typical view of as-synthesized PtCu\textsubscript{3} NCs at low magnification (a), high magnification (b) under TEM, as well as elemental mapping (c) under STEM. High resolution TEM image of one PtCu\textsubscript{3} NC aligned in <110> zone axis is shown in (d) with close view of highlighted red square region in (e) and its fast Fourier transformation (FFT) in (f). Color code in (e): Yellow for (111) facet, Orange for (100) facets, and Light green for (220) facets.

To further confirm the of hexa-pod morphology, TEM sample was tilted in \(\alpha\) direction to capture the projections of NCs along different zone axes, as shown in Fig. 2. Images were recorded at every 10-degree tilt from 10° to -30° in the direction illustrated in Fig. 2(f), by denoting horizontal position as 0°. A polygon model with similar morphology to a real NC, e.g. with simulated lengths of the six pods, was constructed as shown in Fig. 2(f). The selected model NC can be found on the left in Figs. 2(a-e). The 3D model was tilted in the same way as the real NC on the sample.
stage, and the 3D schematics were displayed as insets at corresponding angles. It can be implied through comparison that the 3D models show similar projections to the real NC viewed from different zone axes, confirming the hexa-pod morphology of the PtCu$_2$ NCs.

**Figure 2.** TEM images taken when sample holder is tilted at -30° (a), -20° (b), -10° (c), 0° (d) and 10° (e) along α direction. (f) Schematic of hexa-pod 3D model tilted in the highlighted α direction.

Understanding how the NCs grow into hexa-pod morphology is of great importance to explore the growth mechanism. To better understand the growth mechanism, a time evolution experiment was carried out to capture the morphology of NCs growing at different stages, e.g. 30min, 2h and 6h, as shown in Fig. 3. When taken at 30min, most NCs show TO and octahedral morphologies with the sizes around 9 nm. A small amount of NCs start to show pod-like structure with one or two pods as in the inset of Fig. 3(a).

**Figure 3.** TEM images of PtCu$_2$ NCs captured from reactions stopped at 30min (a), 2h (b), and 6h (c).

It is commonly known that TO NCs can easily transform into octahedron via preferable growth along <100> crystallographic direction, which makes the transition between TO and octahedron difficult to be discernible. It is a reasonable hypothesis that the NCs start from TO seeds, and evolve into octahedron through the faster growth in <100> direction. From 30min to 2h, all NCs develop into multi-pod morphology. For a TO NC, it has six (100) facets which tend to shrink and disappear by the continuing fast growth of <100> direction. Eventually, the six (100) facets can extrude and grow into pods, leading to the convex morphology shown in Fig. 3(b). At 6h, the NCs show obvious pod structure with longer pods. A close look into Fig. 3(c) indicates that NCs show uniform hexa-pod morphology, with pods varying in length on each NC.

**Figure 4.** Schematic of growth mechanism illustrating the morphology evolution of the hexa-pod PtCu$_2$ NCs.

Through the time evolution experiment, we propose that due to faster growing rate in <100> crystallographic directions, TO seeds quickly transform into octahedral NCs that sit in a meta-stable state due to the continuing fast growth in <100> directions, and eventually evolve into hexa-pod morphology. The growth trajectory can be illustrated more clearly as the schematic in Fig. 4. It can be easily deduced from the hypothesis that the surface of the hexa-pod NCs strongly depend on their growth stage, i.e. pod length. Therefore, they can hardly be assigned to a fixed crystallographic facet. Assuming that the hexa-pod NCs were perfect polygons with sharp facets, the NC should be enclosed by 32 facets, including 8 facets on the seed with and other 24 facets on the pods. It could be calculated that interfacial angle is 70.6° between two (111) facets, and 54.7° between (111) and (100) facet, both of which are higher than the maximum interfacial angle that could possibly be between the facets on the pod (highlighted with green dashed lines in Fig. 4) and (111) facets (highlighted with yellow dashed lines). It means that the surface on the pod can be neither (111) nor (100), indicating that the pod should be enclosed by facets with higher crystallographic indexes. Through tilt of TEM sample holder, two high resolution TEM images of selected PtCu$_2$ NCs viewed from <100> zone axis shown in Fig. S1 (Supporting Information). Surface highlighted by red dashed line can be designated to high index crystallographic facets such as (420), (460), (710), and (750).[44] It is noteworthy that the convex NCs in this work commonly show smoothed pods, adding that pods differ in length, meaning that pods
of NCs are enclosed by high-index facets with various indexes. Since the growth mechanism has been proposed, it is of our interest to see if the composition of the alloy NCs can be tuned. In this work, PtCu, hexa-pod NCs with three Cu/Pt ratios, determined by energy dispersive X-Ray spectroscopy (EDX) equipped in TEM and inductively coupled plasma optical emission spectrometer (ICP-OES), are shown in Fig. 5. For the alloy products with Cu/Pt ratio 2/1, 1/1 and 2/3, the starting precursors, Cu(NO$_3$)$_2$ and [Pt(NH$_3$)$_4$(NO)$_2$]$_2$, were added with the Cu/Pt ratio at 3/1, 1/1, and 1/3. The ratio difference between products and precursors comes from the reduction potential difference of Cu$^{2+}$ and Pt(NH$_3$)$_4$$^{2+}$ in PDO. In earlier work reported by Wang and Li et al, synthesis was carried out at temperatures generally above 240°C when all Cu$^{2+}$ ions can be fully reduced.[40] In this work, all syntheses were conducted at 180°C, leading to incomplete reduction of precursors. Well-shaped hexa-pod PtCu NCs can only be formed for PtCu$_2$ alloy (Fig. 5(c)), while mixed multi-pod morphologies can be formed for PtCu$_4$ and PtCu$_2$ alloys as in Fig. 5(a-b). However, it can be clearly seen for multi-pod PtCu$_2$ and PtCu$_4$ alloy NCs that, they show longer pods. EDX spectra of PtCu$_2$ and PtCu$_4$ NCs can be found in Fig. S2-S3.

![Figure 5. TEM images of PtCu$_2$ (a, d), PtCu (b, e), and PtCu$_4$ (c, f).](www.theNanoResearch.com | www.Springer.com/journal/12274 | Nano Research)

It is an obvious trend that when increasing Cu/Pt ratio, NCs tend to show more regular and uniform morphology. It is possible due to the fact that overgrowth could occur when more Pt sources exist, while slower reaction kinetics could benefit morphology evolution at the scenario with more Cu sources.[45] To avoid misunderstanding, all PtCu$_7$ alloy NCs are denoted as hexa-pod NCs because most NCs still show six pods for PtCu$_2$ and PtCu$_4$ alloys. The growth mechanism of PtCu$_2$ NCs is also explored by time evolution experiment as shown in Fig. S4. The hexa-pod PtCu$_2$ NCs also start from octahedral seeds and evolve gradually into hexa-pod alloy NCs, indicating that PtCu and PtCu$_4$ share similar growth mechanism towards hexa-pod NCs. It can be concluded that this protocol can be applied to hexa-pod PtCu$_2$ alloy NCs with various Cu/Pt ratios. X-ray diffraction (XRD) patterns of PtCu and PtCu$_2$ are shown in Fig. S5. For PtCu$_2$, the shift of (111) diffraction peak verifies that the inclusion of more Cu atoms leads to the shrink of unit cell. As comparisons, PtCu$_7$ NCs with two other morphologies were synthesized to explore the effect of morphology on ORR activities. By switching the solvent to 1, 4-butanediol (BDO), uniform and monodisperse TO and near-spherical (NS) irregular PtCu$_2$ NCs, shown in Fig. S6, can be obtained simply by manipulating the Cu/Pt feeding ratio of precursors. It has been mentioned that, at 180°C, PDO and PVP are not stong enough to reduce all Pt and Cu precursors. The reducibility is even weaker for BDO at this temperature, so the overgrowth can hardly occur when using BDO, leading to the formation of truncated octahedral NCs and NS NCs. The Cu/Pt ratio is 1/1 for both alloy samples, determined by EDX and ICP.

To maximize the active surface area and enhance the stability of hexa-pod NCs, all PtCu$_7$ NCs were loaded onto high-surface-area carbon black (Vulcan XC-72, CB), as shown in Fig. S7. The catalyst loadings are determined by total masses, with the weight percentage at 20%. According to Fig. S7, loadings of PtCu$_7$ NCs on CB are highly uniform. No aggregation can be found in TEM view. To evaluate ORR activities of the CB-supported NCs, the catalysts were loaded onto glassy carbon electrode (GCE). Masses of loaded noble metals (referred to Pt only) were the same (12 μg/cm$^2$) for all catalysts. Catalyst films on GCE were prepared by covering the pre-formed catalyst film with thin Nafion film. Electrochemical surface areas (ECSAs) were determined by integrating hydrogen adsorption/desorption peak in cyclic voltammetric (CV) curves (between −0.05 and 0.40 V vs. reversible hydrogen electrode denoted as RHE) shown in Fig. 4(a), by assuming the monolayer hydrogen adsorption.
It is worth noting that the CVs in Fig. 6(a) were recorded after the curves were stabilized. The initial de-alloying cycles, e.g., 1st, 2nd, and 10th cycles, are shown in Fig. S8. Although the characteristic desorption peak of under-potentially deposited (UPD) hydrogen is not well-shaped as on pure Pt surface, they can still be recognizable even during the 1st cycle, indicating the presence of substantial Pt atoms on NC surface for all catalysts. Surface Cu/Pt ratio determined by X-ray photoelectron spectroscopy (XPS) is 5/11 for PtCu2 sample, which deviates from bulk ratio but agrees well with the indication from hydrogen UPD in CV. Since the reaction temperature is not high enough to reduce all metallic precursors, and, Cu atoms are more reductive than Pt at such temperature, it results in the displacement reaction between Cu atoms at surface and Pt ions in solution, leading to the Pt-rich structure. The low anodic peaks between 0.5 and 0.75V on the 1st and 2nd cycle are attributed to selective Cu dissolution from NC surface. The cathodic peaks associated with the reduction of Pt oxide mixed with re-deposition peak of Cu atoms, split on 2nd cycle into distinguishable peaks. The peak around 0.75V related to reduction of Pt oxide shifts to the positive potential, while the shoulder peak at 0.6V gradually disappear on 10th cycle, implying undetectable Cu dissolution from NC surface at this stage.[25] CV curves in Fig. 6(a) are recorded once the electrochemical activation curves stabilize, which resemble that of pure Pt and indicate the formation of Pt-rich surface.

ORR activities were determined by rotating disk electrode (RDE) approach. The electrode was polarized between 0.1 and 1V in oxygen-saturated 0.1M HClO4 electrolyte via linear scanning voltammetry (LSV) at the rotating rate of 1600 rpm. Commercial Johnson Matthey (JM) Pt/C (20wt% Pt) catalyst was selected as comparison. It can be seen in Fig. 6(b) that onset potentials of PtCu/C catalysts are at least 50 mV more positive than JM Pt/C catalyst, among which PtCu2/C and PtCu/C show further 15 mV more positive onset potential than that of PtCu/C. Mass-transport-corrected specific activities between 0.88 and 0.96 V can be found through Tafel plot in the inset of Fig. 6(b). The log j-V curve of JM Pt/C catalyst shows two linear components, implying that oxygen molecules probably experience a transition between two distinct mechanism regimes when the potential is elevated from 0.88 to 0.96 V. For PtCu/C catalysts, their Tafel plots show high linearity and indicate single-reaction-mechanism and high oxygen reduction rates at the potential range.[46] It can be clearly seen that the specific activities of hexa-pod PtCu/C catalysts are higher than that of JM Pt/C by at least one order of magnitude. The calculated number of transferred electrons is 3.86 per O2 molecule, as shown in Fig. S9. For PtCu/C catalysts with TO and NS PtCu NCs, their ORR activities were also determined which can be found in Fig. S10. With almost the same composition, hexa-pod PtCu/C shows over 3-time enhancement in specific activity than those of TO and NS PtCu/C catalysts, and 4-time enhancement in mass activity. Eliminating the possible effect induced by composition, the enhancement in activity mainly originates from the morphology of NCs. It has been reported in abundant literatures that atoms located at corners and edges of catalysts are more active catalytic sites. In this work, the hexa-pod NCs obviously show higher ratio of atoms at corners and edges according to Fig. 1(d), which possibly make the surface highly active.[32] In addition, as is mentioned above, hexa-pod PtCu NCs expose partially by high-index facets, which could also endow the surface with higher activity towards ORR. Specific and mass activity values of various catalysts at 0.9V are listed in Tab. 1. The highest activities were achieved by PtCu/C catalyst, with specific activity up to 3.7 mA/cm2Pt and mass activity 2.4 A/mgPt, both of which are the highest-ever reported for PtCu/N alloys, and also higher than commercial Pt and other Pt-based alloy catalysts.[10, 35]

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<td>20</td>
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Figure 6. CV curves (a) and polarization curves (b) of PtCu2, PtCu, and PtCu/C. Inset of (b): Tafel plot of the PtCu/C electrocatalysts compared with commercial JM Pt/C.
Durability is also a crucial factor when evaluating the practical usability of catalysts. Accelerated durability tests (ADTs) were carried out for all materials. The catalysts were polarized with CV curves between 0.6 and 1.1 V at the scanning rate of 50 mV/s, in 0.1 M HClO₄ with continuous oxygen bubbling to keep electrolyte saturated. ORR activities were determined every 4000 cycles until it reaches 20000 cycles. The 50th and 20000th cycles are shown in CV and LSV in Fig. S11-S13 for PtCu/C, PtCu/C, and PtCu/C, respectively. Activities of PtCu/C catalyst shows most drop in activity, 32% in specific activity and 50% in mass activity. With the decrease of Cu/Pt ratio, the activity declines less during ADT, confirming that PtCu/C with high Cu content tend to have Cu atoms dissolved easily, thus activity tends to drop faster. For PtCu/C, it loses 11.8% in specific activity to 3.0 mA/cm² as, and 25% in mass activity to 1.2 A/mg. The amount of degradation, as well as the final activities after ADT, still meets the DOE targets on durability for fuel cell cathode catalyst. As a fair comparison, ADT was also measured for TO PtCu/C catalyst. It is interesting that PtCu/C with TO NC actually shows enhanced specific activity during ADT. We can be inferred from LSV in Fig. S14 that kinetic current at 0.9 V remains almost unchanged. As a result, the declining ECSA leads to higher specific activity, while the mass activity remains almost the same. The microstructures of catalysts after ADT were characterized with TEM, as shown in Fig. S15. The TO NCs seem to be smoothed after ADT and show near-spherical shape without distinguishable increase in size. For hexa-pod NCs, they tend to show smoothed pods after ADT without change in size, indicating the high stability of hexa-pod NCs at ADT operation condition.

**Conclusion**

To summarize, we synthesized PtCu/C NCs with hexa-pod morphology. The synthetic protocol can be employed to synthesize PtCu/C NCs with various Cu/Pt ratios. The six pods on NCs grow from (100) facets of TO seeds, along <100> crystallographic direction. The hexa-pod NCs expose by (111) and other facets with high indexes. Due to the high ratio of atoms at corners and edges, as well as the existence of high index facets, hexa-pod NCs supported on carbon black show drastically enhanced catalytic activities towards ORR, with the highest specific activity 3.7 mA/cm² as and mass activity 2.4 A/mg obtained at 0.9 V by hexa-pod PtCu/C catalysts. ADTs show high stability for alloys with lower Cu/Pt ratio. The highest durability was obtained from hexa-pod PtCu/C, with 11.8% lost in specific activity and 25% lost in mass activity after ADT. The high catalytic performance of hexa-pod PtCu/C NCs endows them with potential application as cathode catalysts in PEMFC.

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**Electronic Supplementary Material:** Supplementary material, such as Characterization, additional graphs and electrochemistry data, is available in the online version of this article at [http://dx.doi.org/10.1007/s12274-****.****.*](http://dx.doi.org/10.1007/s12274-****.****.* (automatically inserted by the publisher)).

**References**


Electronic Supplementary Material

Pt$_x$Cu$_y$ nanocrystals with hexa-pod morphology and their electrocatalytic performances towards oxygen reduction reaction

Yujing Li$^{1,2}$ (✉), Fanxin Quan$^2$, Enbo Zhu$^3$, Lin Chen$^2$, Yu Huang$^{3,4}$, Changfeng Chen$^{1,2}$

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Supporting information to DOI 10.1007/s12274-****-****-**** (automatically inserted by the publisher)

Synthesis of hexa-pod PtCu nanocrystals (NCs): For the synthesis of hexa-pod PtCu NCs, Pt[Pt(NH$_3$)$_4$](NO$_3$)$_2$ and Cu(NO$_3$)$_2$ were used as metallic precursors. Appropriate amount of precursors were dissolved in 14 mL 1, 2-propanediol (PDO) which also serves as reducing agent. Polyvinylpyrrolidone (PVP) and sodium bromide (NaBr) were also dissolved in PDO as stabilizing and capping agent. The starting solution was stirred for 10 minutes and transferred into a Teflon-lined autoclave. The solution was heated from room temperature up to 190 °C at the rate of 6 °C/min and kept at this temperature for 6 hours, and then cooled down in the air. The products were separated from the reaction solution by centrifuge. The NCs were dispersed in 2 mL of ethanol, precipitated by 15 mL of acetone, sonicated for 10 min, and then centrifuged at 8000 RPM for 10 min. The washing procedure was repeated three times. The NCs were stored in ethanol at the concentration of 1mg/mL.

The ratios of added precursors Pt[Pt(NH$_3$)$_4$](NO$_3$)$_2$/Cu(NO$_3$)$_2$ are 3/1, 1/1, and 1/3 for the synthesis of Pt$_3$Cu$_2$, PtCu, and PtCu$_2$, respectively.

For the synthesis of truncated octahedral and near-spherical PtCu NCs, all conditions were the same as above except that 1, 4-butanediol (BDO) was used as solvent and reducing agent. The ratios of added precursors Pt[Pt(NH$_3$)$_4$](NO$_3$)$_2$/Cu(NO$_3$)$_2$ are 3/1, 1/1, and 1/3 for the synthesis of Pt$_3$Cu$_2$, PtCu, and PtCu$_2$, respectively.

Preparation of carbon-supported catalysts: Carbon black (Vulcan XC-72, CB) is used as the catalyst support. For a typical catalyst preparation, CB was dissolved in ethanol at a concentration of 1 mg/mL, and sonicated for 30 min. Appropriate amount of NCs dissolved in ethanol was sonicated and mixed with the CB solution, with the NC/CB mass ratio fixed at 1/4, further sonicated for another 1 hour, and then stirred overnight. The catalysts were then collected by centrifuge at the rate of 8000 rpm, washed with ethanol, and then dried under a N$_2$ stream. As-prepared catalysts were stored in ethanol or isopropanol (IPA).

Characterization: Transmission electron microscopic (TEM) images with α angle tilt was taken on JEOL JEM 2100 at an accelerating voltage of 200 kV. High resolution transmission electron microscopy (HRTEM) and energy dispersive X-Ray spectroscopy (EDX) were taken on FEI TECNAI F-20 field emission microscope at an
accelerating voltage of 200 kV. The fast Fourier Transformations (FFTs) were obtained by high resolution image under TEM. The simulated FFT was also obtained by constructing the same crystal structure with WinX Morph, along the same zone axis with the real image. Both FFTs were aligned in the same angle (overlapped) to determine the index of the exposed facets on the pod. All TEM samples were made by casting corresponding NC solution on carbon film supported on molybdenum grid.

**Electrochemical measurement:** All electrochemical measurements were carried out in a home-made three-electrode cell. Catalyst inks were prepared by dispersing NC/CB in IPA/H₂O (volume ratio: 3/1) with the concentration of 2 mg/mL. Appropriate amounts of inks, were pipetted onto a rotating disk electrode (Pine Instrumentation) made with glassy carbon (GCE) with diameter of 5 mm. The total loading masses of Pt were controlled at the level of 12 μg/cm². In this work, the electrode was prepared by a two-step approach. The carbon-supported electro-catalysts form the first layer, followed by a Nafion® film formed by drying 10 μL of 100-time-diluted Nafion® solution on top. The catalysts were electrochemically de-alloyed by applying cyclic voltammetric (CV) scans between 0 and 1.1 V (vs. reversible hydrogen electrode, RHE) in 0.1 M HClO₄ electrolyte, at the scan rate of 50 mV/s. Electrochemical surface area (ECSA) were determined from CV curves recorded. The charges induced by the adsorption/desorption of hydrogen species were calculated by integrating the area approximately between 0.05 and 0.4 V (depending on the shape) under the CV curve. ORR was studied by recording linear scan voltammetric (LSV) curves between 0 and 1.1 V in oxygen-saturated HClO₄ electrolyte at the rotating rate of 1600 rpm. The electrolyte was bubbled with oxygen prior to, and during the measurement. The rotation rate dependent polarization curves were recorded at the rotating rates of 400, 900, 1600, and 2500 rpm. The durability tests were conducted by applying CV scans up to 4000 cycles each time at the scan rate of 50 mV/s, and recording CV curves as mentioned above, and then studying ORR afterwards. After each set of measurement, another round of ADT was applied, and a total of 20000 CV scans was applied to each catalyst for the evaluation of durability.
Figure S1. High resolution TEM images of (a) and (b) PtCu$_2$ NCs projected from $<100>$ zone axis. Inset of (a) is the 3D schematic of a hexa-pod particle with the same projection as the NC. Inset of (b) is lattice in selected region showing that the zone axis of the NC is $<100>$.

Figure S2. EDX spectrum PtCu$_2$ by focusing electron beam on one NC.
Figure S3. EDX spectrum PtCu₂ by focusing electron beam on one NC.

Figure S4. TEM images of PtCu NCs captured from reactions stopped at 30min (a), 2h (b), and 6h (c).
Figure S5. XRD patterns of PtCu2 (red) and PtCu (black), compared with pure Pt and Cu as shown in black and blue lines.

Figure S6. TEM images of truncated octahedral (TO) PtCu NCs (a, b) and near-spherical (NS) PtCu NCs (c, d).
Figure S7. TEM images of CB supported Pt$_3$Cu$_2$ (a, b), PtCu (c, d), and PtCu$_2$ (e, f) NCs.

Figure S8. Comparison of the 1st, 2nd and 10th CV curve of Pt$_3$Cu$_2$ (a), PtCu (b) and PtCu$_2$ (c).

Figure S9. Polarization curves of PtCu$_2$/C catalyst at the rotating rates of 400, 900, 1600 and 2500 rpm (a), and Levich-Koutecký plot of PtCu$_2$/C compared with JM Pt/C at 0.5 V (b).
Figure S10. Polarization curves (a) and Tafel plots (b) of hexa-pod Pt₃Cuₓ/C catalysts, truncated octahedral and near-spherical PtCu NCs.

Figure S11. CV curves (a) and polarization curves (b) of 50th and 20000th cycles during ADT for hexa-pod Pt₃Cu₂/C catalysts.
Figure S12. CV curves (a) and polarization curves (b) of 50th and 20000th cycles during ADT for hexa-pod PtCu/C catalysts.

Figure S13. CV curves (a) and polarization curves (b) of 50th and 20000th cycles during ADT for hexa-pod PtCu\textsubscript{2}/C catalysts.
Figure S14. CV curves (a) and polarization curves (b) of 50th and 20000th cycles during ADT for TO PtCu/C catalysts.

Figure S15. TEM images of TO PtCu/C (a, b) and hexa-pod Pt₃Cu₂/C (c, d) catalysts.

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