Showcasing research from the Hefei National Laboratory for Physical Sciences at Microscale, University of Science & Technology of China.

Title: Activation of specific sites on cubic nanocrystals: a new pathway for controlled epitaxial growth towards catalytic applications

A method has been developed for controlled epitaxial growth on cubic nanocrystals by selectively activating their surface via etching. This method enables the growth of a noble metal with high catalytic activities on another type of cheaper metal.
Activation of specific sites on cubic nanocrystals: a new pathway for controlled epitaxial growth towards catalytic applications†

Yu Bai,†a Ran Long,a Chengming Wang,†a Ming Gong,c Yanrui Li,a Hao Huang,a Hui Xu,a Zhengquan Li,d Mingsen Dengb and Yujie Xiong*a

A method has been developed for controlled epitaxial growth on cubic nanocrystals by selectively activating their surface via etching. For example, it produces Pd concave nanocubes via seeding growth on their corners and edges, and in turn, formulates highly active sites for catalysis. This method offers a better capability of preventing atomic addition on undesired locations and maintaining particle size in the seeding process, as compared with the previous technique. With the particle size well maintained, the products fully exhibit superior electrocatalytic performance enabled by active sites and high-index facets in formic acid oxidation. Another contribution of this work is to enable the growth of a noble metal with high catalytic activities on another type of cheaper metal, which greatly reduces the usage of expensive materials while retaining high catalytic activity. In this article, we have demonstrated the deposition of a very limited amount of Pt (only 3.3 wt%) on Pd nanocrystals towards high electrocatalytic activities in an oxygen reduction reaction. Preliminary studies demonstrate that the synthetic strategy can also be applied to the controllable deposition of a different material on the faces of a nanocrystal by simply altering surface conditions.

Introduction

High-performance and low-cost catalysts are central to the development of new-generation energy and environmental technologies. Towards this goal, nanocatalysis has become an emerging and intensively studied research field in the past decade, mainly because the catalytic materials possess relatively high surface-to-volume ratios when their particle sizes enter the nanoscale regime. As the research field of nanocatalysis develops, it appears that two issues regarding materials design should be addressed to further improve the catalytic performance and reduce the materials cost of catalysts: (i) manipulation of preferential atomic addition on specific sites (e.g., corners and edges of a nanocrystal) during the synthesis of nanocatalysts, which in turn formulates active sites for catalysis, and (ii) replacement of interior materials in a catalytic nanocrystal with cheaper materials (e.g., growth of noble metals on base metals), which essentially reduces the cost of interior materials that do not participate in catalytic reactions. In terms of the first issue, the corners and edges (and/or high-index facets) of a nanocrystal are generally considered to be active sites for catalysis, according to the experimental observations and the terrace-step-kink (TSK) model. For this consideration, concave nanocubes, whose structure possesses abundant atoms on convex corners and high-index facets, have been proven to be promising candidates for catalysts in a variety of reactions.

In order to address the aforementioned two issues, one has to establish a methodology for controllable atomic addition on specific sites of nanocrystals. There is no doubt that epitaxial growth is a valid method to achieve this goal, as the well-defined shapes of seeds can help to delineate the locations for atomic addition during the nanocrystal growth. However, the key point in this synthetic protocol lies in distinguishing the preferred growth sites from other locations of a nanocrystal. In this article, we mainly use the nanocrystals with a cubic shape as an example for discussion. In the epitaxial growth into concave nanocubes, the corners and edges of seeds should be selected for preferred growth sites when cubic nanocrystals are used as seeds. Prior to our work, the synthetic processes have mainly manipulated the diffusion rate ($V_1$) of precursor from solution to the surface and the growth rate ($V_2$) at which atoms are generated and added to

† Electronic supplementary information (ESI) available: Detailed experimental procedure, calculations for atomic numbers and supplemental data. See DOI: 10.1039/c3ta00478c

‡ The first three authors contributed equally to this work.
the surface of a growing seed. In this synthetic scheme, one prerequisite to ensure preferential growth is the surface condition of seeds that can be modified by capping agents such as bromide ions for protecting Pd{100}, which makes the {100} faces passivated in the successive atomic addition. When the system maintains the situation $V_1 < V_2$ during the seeding growth, the atoms generated on the surface of a seed will be preferentially added to the sites with the highest reactivity owing to an insufficient supply of atoms. This method definitely provides the possibility of achieving preferential growth on specific sites (e.g., the corners and edges of a nanocube). On the other hand, it has been observed that the lateral size of nanocrystals significantly increases from 17 nm to 33 nm during the seeding growth of Pd concave structures. Thus in a typical assessment of catalytic properties, the resulting samples exhibit limited enhanced performance, mainly caused by their increased particle sizes. This factor causes the contribution of active sites and high-index facets to catalytic performance to be overwhelmed by the size effect. Overall, the significant increase in particle size indicates that this method cannot effectively prevent the deposition of atoms on other locations (e.g., {100} faces on a nanocube) during the seeding process.

For this reason, we attempt to develop a different approach to controllable epitaxial growth with a better capability of preventing atomic addition on undesired locations, in an effort to maintain particle size in the seeding process. In this article, we first demonstrate that the corners and edges of Pd nanocubes can be activated for atomic addition by HCl treatment, thus generating Pd and Pd–Pt concave nanocubes via Pd or Pt epitaxial growth. Pd and Pt have been widely utilized in catalysis, such as organic coupling and hydrogenation reactions, formic acid oxidation and oxygen reduction reactions in fuel cells, ammonia oxidation and nitrite reduction, and conversion of carbon monoxide. With our method established, Pd or Pt can be selectively grown at the corner and edge sites of Pd nanocubes, enabling the production of highly catalytically active nanocrystals. It is worth noting that the synthetic strategy is not limited to selectively activating the corner and edge sites. Preliminary studies demonstrate that it can be also applied to the controllable deposition of a different material on the faces of a nanocrystal by simply altering surface conditions. It is anticipated that this strategy can be further extended to the selective growth of catalytic noble metals on base metals such as copper nanocrystals.

**Experimental**

**Synthesis of Pd nanocubes**

In a typical synthesis, 8.0 mL of an aqueous solution containing 105 mg poly(vinyl pyrrolidone) (PVP, $M_w = 55000$, Sigma-Aldrich, 856568-100 g), 60 mg l-ascorbic acid (AA, Sigma-Aldrich, A0278-25 g), and 600 mg KBr in a 50 mL three-neck flask was heated for 10 min at 80 °C under magnetic stirring. Subsequently, 3.0 mL of an aqueous solution of potassium palladium(II) chloride (K$_2$PdCl$_4$, Aladdin, 1098844-1 g) (63 mg) was added with a pipette. The reaction was allowed to continue at 80 °C for 3 h. The product was collected by centrifugation and washed three times with deionized water to remove excess PVP.

**Synthesis of Pd concave nanocubes**

1.0 mL of 2 mg mL$^{-1}$ Pd nanocubes was added to 5.0 mL of an aqueous solution containing 0.3 mmol HCl and 60 mg AA in a 30 mL vial that was pre-heated for 5 min at 50 °C under magnetic stirring. Then 1.0 mL of 3 mg K$_2$PdCl$_4$ was introduced, and the solution was stirred at the same temperature for 30 min. The Pd products were collected by centrifugation and washed three times with deionized water. The as-obtained samples were then characterized by transmission electron microscopy (TEM). In comparison with the method in the literature, the current method uses a lower precursor concentration (3 mg versus 16 mg).

**Pt growth on the activated Pd nanocubes**

The procedure was similar to that used for the synthesis of Pd concave nanocubes, except that the precursor was 5 mg K$_2$PtCl$_6$ and the amount of HCl was 1.0 mol.

**Formic acid oxidation measurements**

The electrochemical measurements were performed at room temperature. A Ag/AgCl electrode and a Pt foil were used as the reference and counter electrode, respectively. The catalysts dispersed onto a glassy carbon electrode (GCE) were used as a working electrode (WE). To prepare the WE, 20 μL of an aqueous suspension of the nanoparticles (1 mg mL$^{-1}$) was transferred to the GCE with a geometric area of 0.2 cm$^2$. The nanoparticles were pre-washed with acetone once and then water three times. Upon drying under air for 3 h, the electrode was covered with 10 μL of Nafion dispersed in water (0.025%). The electrolytic solutions were deaerated by Ar bubbling for 30 min prior to each measurement, and a blanket of Ar was maintained throughout the whole experiment. Prior to electrocatalytic measurements, hundreds of potential cycles were conducted in a 0.5 M H$_2$SO$_4$ solution with saturated CO and then in another 0.5 M H$_2$SO$_4$ solution with continuous Ar gas in the potential region from −0.2 to 1.0 V until the blank CVs remained unchanged, in order to allow residue organics and ions to be released. The voltammetric behavior of Pd nanoparticles and their electrocatalytic activity were characterized at a sweep rate of 50 mV s$^{-1}$ in a 0.5 M H$_2$SO$_4$ solution and a 0.5 M H$_2$SO$_4$ + 0.25 M HCOOH mixed solution. The electrode potential was controlled by a CHI 660D electrochemical station (Shanghai Chenhua, China).

**Oxygen reduction reaction (ORR) measurements**

The electrochemical measurements were performed at room temperature. A reversible hydrogen electrode (RHE) and a platinum foil were used as the reference and counter electrode, respectively. The catalysts dispersed onto a glassy carbon (GC) rotating disk electrode (RDE) were used as a working electrode (WE). To prepare the WE, an aqueous suspension of the nanoparticles was transferred to the GC RDE with a geometric area of 0.2 cm$^2$ to make the concentrations as follows: Pd–Pt nanocubes (Pd 145 μg cm$^{-2}$, Pt 5 μg cm$^{-2}$), Pd nanocubes (145 μg cm$^{-2}$), and Pt/C (E-TEK, 3 nm Pt, Pt 5 μg cm$^{-2}$, C 20 μg cm$^{-2}$).

This journal is © The Royal Society of Chemistry 2013
respectively. The nanoparticles were pre-washed with acetone once, ethanol three times and water four times. Upon drying under air for 3 h, the electrode was covered with 8 μL of Nafion dispersed in water (0.025%). Prior to electrocatalytic measurements, hundreds of potential cycles were conducted in a 0.1 M HClO₄ solution with saturated CO and then in another 0.1 M HClO₄ solution with continuous N₂ gas in the potential region from 0.05 to 1.0 V until the blank CVs remained unchanged, in order to allow residue organics and ions to be released. The blank CVs were collected at a sweep rate of 20 mV s⁻¹ in a 0.1 M HClO₄ solution with continuous N₂ gas. For the oxygen reduction-limiting current, the Koutecky-Levich equation:

\[
\frac{1}{i} = \frac{1}{i_d} + \frac{1}{i_k}
\]

where \(i\) is the experimentally measured current, \(i_d\) is the diffusion-limiting current, and \(i_k\) is the kinetic current. For each catalyst, the kinetic current was normalized to geometric area in order to obtain specific activities.

**Results and discussion**

From the analysis in the Introduction section, one can see that the controlling methods that only rely on the capping effect of bromide ions are not versatile enough for achieving controlled epitaxial growth. It has been previously demonstrated that capping agents have selectivity to protect specific surface facets (e.g., bromide for Pd{100}). However, in the case of Pd nanocubes with sharp corners and edges, the bromide ions may have strong interactions with the locations neighboring the {100} facets, which makes the corner and edge sites not completely exposed to atomic addition during seeding growth. Given this fact, the difference between the faces and the corners/edges of a nanocrystal is not significant enough when modifying the surface condition with capping agents only. When the concentration of precursor is relatively high (i.e., the case in the literature), atomic addition can still occur on the surface of seeds (particularly at the corners and edges) even though their surface is passivated by bromide. However, the preferred growth sites cannot be precisely distinguished from other locations in this situation due to the insignificant surface difference, resulting in remarkable deposition of atoms on the {100} faces of nanocubes and thus an increase in particle size. In order to avoid the undesired atomic addition, it is very necessary to lower the concentration of metal precursor, which can substantially avoid the deposition of atoms on the {100} faces as well as the production of free nanoparticles via self-nucleation. However, this modification would make it more difficult to add atoms onto the surface of seeds entirely protected by bromide ions. In order to verify this assumption, we have performed a seeding growth on Pd nanocubes by reducing the precursor concentration from 16 mg to 2 mg. The seeds of Pd nanocubes used in our synthesis were also obtained from a reaction system involving bromide ions.² From Fig. 1a, one can see that the nanocubes have very sharp corners and edges and thus possess dominant coverage of {100} facets on the surface. It has been proven that bromide has an excellent function of capping Pd{100} facets in extensive studies.⁹⁻¹² As shown in Fig. 2a, no atomic addition occurred on the seeds of nanocubes at a low concentration of precursor, and instead, some free nanoparticles were produced via self-nucleation, as predicted by our assumption. Since the surface condition is the key to atomic addition, it is imperative to develop a method to increase the surface difference between the faces and the corners/edges, which can in turn differentiate various locations for atomic addition.

As has been analyzed above, there should be two key factors that need to be controlled for improved epitaxial growth in our work: (i) a lower concentration of metal precursor (refer to the comparison in the Experimental section) and (ii) selective activation of specific sites for atomic addition. Thus it is technically critical how to selectively activate specific sites for atomic addition. In terms of growing a concave nanocube, the specific sites should be the corners and edges of a cubic seed. One of our previous findings gives us some clues: when metal nanocubes were stored in solution, the nanocubes became truncated due to the selective oxidative etching on their corners and edges.

**Fig. 1** TEM and HRTEM images of the samples: (a and b) as-synthesized Pd nanocubes; (c and d) Pd nanocubes after HCl surface activation; and (e and f) Pd concave nanocubes obtained via surface activation and epitaxial growth. The insets of (b), (d) and (f) show magnified HRTEM images of the regions marked by red boxes.
Nevertheless, this information cannot reflect the spatial distribution of bromide on the surface.

In order to investigate the effect of HCl etching on the surface condition of nanocubes, we conducted the seeding growth of Pd on the nanocubes immediately after the HCl treatment. Fig. 1e shows a TEM image of the resulting sample (also see Fig. S3†), confirming that atomic addition preferentially occurs at the corners and edges and induces the production of Pd concave nanocrystals. The HRTEM images (Fig. 1f and S3f) reveal that the geometry of nanocrystals is identical to that of concave nanocrystals in the literature (i.e., synthesized with the conventional method) — enclosed by high-index {730} facets.10 Note that the particle size is basically maintained except for the distinct changes in the corners and edges during the seeding process. This indicates that the surface condition of the corner and edge sites is different from that of other locations after the HCl etching. Taken together with the zeta-potential information, this convinces us that HCl etching occurred on the corners/edges indeed and reduced the amount of bromide at those sites. With the corner and edge sites reactivated, atomic addition on the sites can be much faster than that on the faces, leading to the formation of concave nanocubes in the seeding growth.

The control experiment using KCl instead of HCl shows that surface activation via etching plays a vital role in epitaxial growth. In the absence of HCl, the etching is too weak to remove bromide ions from the corners and edges, as the etching power of the O2/Cl− pair can be enhanced by adding acid according to the standard electrical potentials expressed by the Nernst equation.10 As a result, atomic addition cannot occur on the surface of nanocubes (see Fig. 2b). Instead, the Pd atoms that were formed in solution from a reduction of the Pd precursor self-nucleated and produced some small nanoparticles. This experiment also informs us that the etching effect can effectively help to prevent the self-nucleation process. In comparison, when both KCl and HNO3 were added, they could play the same role as HCl in activating the corners and edges, as well as Pd nanocubes to formulate concave structures during seeding (see Fig. 2c). Thus we can conclude that the important component for surface activation is HCl rather than chloride alone. Certainly, the acid alone cannot provide the etching function so selective epitaxial growth does not occur when using HNO3 (see Fig. S4†). Furthermore, the control experiment verifies that use of most wet etchants can activate the sites for epitaxial growth: concave nanostructures were also produced when the HCl was replaced by another common etchant with relatively strong etching capability, Fe(NO3)3 (see Fig. 2d).

The etching function by HCl can also play a role in modulating the reaction kinetics, which is an important factor to ensure highly selective epitaxial growth. As demonstrated above, the slow supply of atoms is a requirement to avoid atomic addition on undesired locations. Certainly the reaction kinetics is one of the parameters to tune the rate of atomic supply. However, it is worth pointing out that the etching activation is mainly responsible for the controlled epitaxial growth, as long as the reaction kinetics is within a certain regime. In order to clarify the influence of kinetics, we have conducted the
higher than that in the literature (5.16% versus 2.66%, see the ESI†). The electrocatalytic performance of the sample prepared via the conventional method is greatly impeded by its relatively large particle size mainly due to lower portions of surface atoms and atoms at high-index facets, although its high-index facets can make the same contributions to catalytic activities as our sample.

The synthetic strategy developed in this work can be extended to controllably deposit a different metal on the nanocrystal seeds. As an example demonstration, we have attempted to grow Pt on the seeds of Pd nanocubes with an average edge length of 22 nm (Fig. S7†) by following a similar protocol. Fig. 4 shows a typical sample obtained from this synthesis. From the TEM images in Fig. 4a and b, it appears that the morphology of products where convex corners can be observed is slightly different from that of cubic seeds. The edge lengths of nanoparticles are well maintained after the seeding process.

The scanning transmission electron microscopy (STEM) image in Fig. 4c resolves better contrast on the nanocrystals, revealing that the convex region around each corner is not as large as that observed in the Pd concave nanocubes above. Nevertheless, the HRTEM characterization (see Fig. 4d) reveals that the surface facet in the convex region is also {730} although its surface coverage is relatively limited as compared to Pd concave structures. Thus the nanocrystals should be enclosed by a mix of {100} and {730} facets. It is worth pointing out that the lattice constants of Pd and Pt are very close so they cannot be distinguished on HRTEM images. In order to verify the presence of Pt in the sample, we have measured the sample composition using inductively coupled plasma mass spectrometry (ICP-MS) after dissolving the sample with a mixture of HCl and HNO3 (3 : 1, volume ratio). The results suggest that the nanocrystals are composed of Pt and Pd with a weight ratio of 1 : 29. The location of deposited Pt on the nanocrystals is further examined by energy-dispersive spectroscopy (EDS) line mapping (see Fig. 4e–h). The line mapping profiles along the diagonal and cross-section directions reveal that the addition of synthesis by altering the sequence of adding chemicals (i.e., mix HCl with the Pd precursor together, and then add them into the Pd seed suspension). In this case, there is no sufficient time for HCl to activate the surface of seeds, but HCl can still maintain the same reaction kinetics via oxidative etching. As a result, no epitaxial growth was observed in the system (see Fig. 2e), indicating that both surface activation and kinetic control are important to achieve controlled epitaxial growth. In order to assess the importance of AA, we have replaced AA with CH3CHO. Although the change of reducing agent slightly alters the reaction kinetics, concave structures can be still obtained (see Fig. 2f), indicating that the role of AA is mainly for reducing metal precursors.

Given that our concave structures can maintain the particle size comparable to that of their seeds, they are supposed to exhibit superior catalytic performance that benefits from their high-index facets. In order to evaluate their catalytic performance, we have employed electrocatalytic formic acid oxidation as a model reaction with Pd nanocubes as a reference at the same loading weight. The concave nanocubes that were prepared with the conventional method in the literature were also used for comparison. They exhibit similar structures to our samples, according to the TEM and HRTEM characterizations in Fig. S5† However, their particle size is significantly larger than that of our sample (33 nm versus 17 nm). The increase of lateral size indicates that atomic addition still occurs on the {100} facets in the conventional method, although the rate on the faces is lower than that at the corners and edges. The blank cyclic voltammograms (CVs) of all the samples are shown in Fig. S6† They clearly show the presence of adsorption and desorption states of H to various step sites. The current density of H adsorption at 0.06 V for our Pd concave nanocubes is 2.6 times that for concave structures obtained in the literature and 6.6 times that for nanocubes, implying that the electrocatalytic activities of samples are in the order of our concave nanocubes > concave nanocubes (ref) > nanocubes.

Fig. 3 shows the CVs of all the samples towards formic acid oxidation, where the current is normalized by the geometric area of glassy carbon electrodes (GCE). The maximum current densities of formic acid oxidation at our concave nanocubes, concave nanocubes in the literature and nanocubes are 10.5, 4.5 and 1.9 mA cm−2, respectively. The order of their electrocatalytic activities in formic acid oxidation is similar to that observed in the blank CVs. The comparison results of concave nanocubes prepared by the conventional method with Pd nanocubes are very consistent with those reported in the literature, verifying the validity of our measurements. It is reasonable that concave nanocubes exhibit better electrocatalytic performance than nanocubes, since the high-index {730} facets with a higher density of low-coordinate atomic steps and kinks are supposed to contribute to the enhanced activity for formic acid oxidation. Noticeably, our concave nanocubes possess much higher electrocatalytic activity, although their structure is the same as the concave structure in the literature. In the comparison of their particle sizes, one can see that the percentage of surface atoms in our sample should be much higher than that in the literature (5.16% versus 2.66%, see the
Pt atoms is mainly enriched at the corners of the nanocubes during the epitaxial growth, while a small portion of Pt atoms has been deposited on the edges. This set of data reflects that the epitaxial growth has been controlled to occur at the corners and edges of seeds by activating these sites with HCl. On the other hand, we have to address the fact that the epitaxial growth has been controlled to occur at the corners and edges of seeds by activating these sites with HCl. On the one hand, activation of these sites with HCl surface activation and Pt epitaxial growth. The inset of (d) shows a magnified HRTEM image of the region marked by the red box. (e and g) and (f and h) show EDS line mapping profiles of a Pd–Pt nanocube along diagonal and cross-section directions, respectively.

Fig. 4  (a and b) TEM, (c) STEM and (d) HRTEM images of the Pd–Pt nanocubes obtained via HCl surface activation and Pt epitaxial growth. The inset of (d) shows a magnified HRTEM image of the region marked by the red box. (e and g) and (f and h) show EDS line mapping profiles of a Pd–Pt nanocube along diagonal and cross-section directions, respectively.

from the reaction solution via direct centrifugation and then supplementing the consumed Pt precursor, for another synthesis. As shown in Fig. S8, the stock solution can be still used to grow Pd–Pt nanocrystals in another synthesis. This indicates that the material cost of our method can be kept low.

Despite the limited deposition amount of Pt (only 3.3 wt%), the controlled epitaxial growth of Pt on the Pd nanocubes enables impressive improvement in their catalytic activities in specific reactions. As Pt is a very electrocatalytically active metal in the oxygen reduction reaction (ORR), we have investigated the performance of our sample in ORR electrocatalysis. In the measurements, the electrocatalytic properties of Pd–Pt nanocubes were benchmarked against both a commercial Pt/C catalyst (E-TEK, 20 wt% of 3 nm Pt nanoparticles on a carbon support) and Pd nanocubes. The loading weights of Pd and Pt in our sample were kept the same as that of Pd in Pd nanocubes and that of Pt in Pt/C catalysts (i.e., Pd 145 μg cm\(^{-2}\) and Pt 5 μg cm\(^{-2}\)), respectively. In order to assess the ORR activities with equivalent total mass of metals, another reference sample (electrocatalysts made of 145 μg cm\(^{-2}\) Pd nanocubes plus 5 μg cm\(^{-2}\) Pt in Pt/C) has been also used for comparison. Fig. 5a shows CV curves of these four catalysts recorded at room temperature in N\(_2\)-purged 0.1 M HClO\(_4\) solutions. The maximum current densities in the curves increase in the order of Pt/C < Pd nanocubes < Pd nanocubes + Pt/C < Pd–Pt nanocubes with the loading weight above, indicating that the electrocatalytic performance of Pd–Pt nanocubes should be better than the others. Moreover, the CV curve of Pd–Pt nanocubes clearly shows the presence of adsorption states of H to Pt (110) and (100) step sites at 0.08 and 0.26 V, respectively. The (110) and (100) adsorption states can be observed in our case, because...
The ORR measurements were performed in O₂-saturated 0.1 M HClO₄ solutions by using a glassy carbon (GC) rotating disk electrode (RDE) at room temperature. Polarization curves for the ORR on the four catalysts are shown in Fig. 5b. From the curves, the diffusion-limiting currents of all the samples can be obtained at the potential between 0.3 and 0.6 V. Following the Koutecky–Levich equation, we calculated the kinetic currents from the ORR polarization curves. In principle, the kinetic currents can be obtained at any potential in the mixed kinetic-diffusion control region between 0.7 and 1.0 V. As an example, we have obtained the kinetic current densities of samples on the basis of geometric area at 0.9 V versus a reversible hydrogen electrode (RHE) in Fig. 5c. The Pd–Pt nanocubes exhibit a specific activity of 4.7 mA cm⁻², which is 2.5 times, 1.9 times and 1.5 times greater than those of Pd nanocubes, Pt/C catalysts and the mixed sample (i.e., Pd nanocubes plus Pt/C), respectively. The half-wave potential of ORR with Pd–Pt nanocubes is also significantly higher than that with Pd nanocubes, Pt/C catalysts or both (see Table 1), verifying the superior electrocatalytic performance of our Pd–Pt nanocube sample. From the measurements, one can see that our approach apparently provides a promising route to the design of catalysts with controlled catalytically active sites and with substantial reduction in Pt loading.

The success in activating the corner and edge sites of a cubic seed is followed by an attempt to the activation of other locations. In this investigation, Cu nanocubes that have been seed is followed by an attempt to the activation of other locations. In this investigation, Cu nanocubes that have been covered by a layer of oleylamine are used as seeds. Oleylamine is an effective capping agent for {111} facets, as demonstrated previously. As oleylamine does not have strong binding to the {100} faces of cubic seeds, HCl etching can effectively remove oleylamine molecules from their faces. As a result, Pd atoms are selectively deposited onto the faces of Cu nanocubes, resulting in a unique structure of Cu–Pd nanocrystals shown in Fig. S9. This preliminary study clearly demonstrates that the surface activation method can be generically employed to grow a different material on the desired locations of seeds by rationally selecting capping agents. Systematic investigations along these lines are underway.

Conclusions

In summary, we have developed a method for controlled epitaxial growth on metal nanocrystals with a better capability of preventing atomic addition on undesired locations, in order to maintain particle size in the seeding process. With the particle size well maintained, the products can fully exhibit excellent catalytic performance enabled by active sites and high-index facets in various applications. As a result, the products exhibit superior catalytic performance to their counterparts prepared with the conventional method from the literature. The central part of this technique is the use of wet etchants to selectively activate specific sites for atomic addition in epitaxial growth. With the development of this method, we can manipulate atomic addition to preferentially occur on these sites (particularly corners and edges of a nanocrystal), and in turn, we can formulate highly active sites for catalysis. Another contribution of this work is to enable the growth of a noble metal with high catalytic activities on another type of cheaper metal, which greatly reduces the use of expensive materials while retaining high catalytic activity. In this article, we have demonstrated the deposition of a very limited amount of Pt (only 3.3 wt%) on Pd nanocrystals towards high ORR activities. Successive work preliminarily demonstrates that the synthetic strategy can be also applied to the controllable deposition of a different material on the faces of a nanocrystal by simply altering surface conditions. It is anticipated that this work will open the door to controllably growing noble metals on the surface of base metal nanocrystals such as copper in an effort to fabricate low-cost and high-efficiency nanocatalysts.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (no. 21101145), the Recruitment Program of Global Experts, the CAS Hundred Talent Program, the Fundamental Research Funds for the Central Universities (no. WK2340000017), and the Construction Project for Guizhou Provincial Key Laboratories (ZJ[2011]4007). ZL acknowledges financial support from the National Natural Science Foundation of China (no. 20901068) and the Zhejiang Qianjiang Talent Project (no. 2010R10028).

Notes and references