Core–Shell Electrocatalysts

DOI: 10.1002/anie.201005868

Platinum-Based Electrocatalysts with Core–Shell Nanostructures**

*Hong Yang**

electrocatalysis · nanostructures · oxygen reduction reaction · platinum

The development of low-temperature hydrogen fuel cells for automotive applications has witnessed tremendous progress over the past several years,[1] and the total distance driven by fuel-cell-operated vehicles exceeded the million-mile mark in 2009. New cell modules continue to reduce the cost, volume, and weight of fuel cells at a rapid pace. One driving force for this fast development lies in the great progress made in making active cathode catalysts for proton exchange membrane fuel cells (PEMFCs). Improvement of the activity and durability of electrocatalysts for the oxygen reduction reaction (ORR) remains a key research area for the creation of future generations of PEMFCs for automotive applications. As there is still no viable alternative to the replacement of catalysts made of Pt group metals (PGMs), the need of low cost, highly active, and durable fuel-cell electrodes heightens the design criteria. In this regard, multicomponent nanostructures can play important roles in the design of ORR catalysts with high activity and durability.[1b,2]

Core–shell or core–shell-like nanostructures are a convenient way to build multifunctionality into the electrocatalysts of metallic nanoparticles, which have a typical average diameter between 2 and 5 nm. With the increasing complexity of core–shell nanoparticles, the study of structure–property relationships becomes even more important and essential than before in the design of new catalysts. Sun and co-workers recently reported a synthesis of multimetallic core–shell nanoparticles,[3] which is the latest of several recent investigations into the synthesis and electrocatalytic properties of multimetallic core–shell nanoparticles.[4] Spherical Pd/Au and Pd/Au/FePt core–shell nanoparticles were synthesized in octadecene using oleylamine and oleic acid as the capping agents. The structures were characterized by high-resolution transmission electron microscopy (TEM) and aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM). The core–shell nanoparticles were fairly monodisperse in size and had overall diameters of about 7 nm for Pd/Au bimetallic core–shell nanoparticles. Furthermore, 11 nm Pd/Au/FePt multimetallic core–shell nanoparticles were also readily produced by using a similar solution-phase synthesis. The size of these bimetallic or multimetallic core–shell nanoparticles can also be easily tuned within a certain range by changing the reaction conditions.

To date, reports on the synthesis of well-defined multimetallic core–shell nanoparticles with sizes below about 10 nm are still relatively uncommon. In principle, the synthesis of multimetallic core–shell nanoparticles or core–shell-like heterogeneous nanostructures including dendrite, particle-on-particle, raspberry, or flower, however, is usually thermodynamically favored.[2a] The synthesis is possible as the heterogeneous nucleation of second metal component on the existing nanoparticle seed or core has a lower critical energy barrier, that is, the overall excess free energy, than the homogenous nucleation. Depending on the overall excess energy, which is largely related to the surface and interfacial energy terms, and the strain energy because of lattice mismatch at the interface, three different major types of nanostructures form, namely, layer-by-layer, island-on-wetting layer, and island growth modes (Figure 1).

When the interfacial structures are not known or cannot be well defined, or the shape of the nanostructure is important, a generic description based on the morphology, such as raspberry, nanoflower, dendrite, particle-on-particle, or core–shell nanoparticle, is often used. In the solution-phase synthesis and with the use of capping ligands, metallic cores can exist in ordered or disordered forms, and can be formed from metal alloys (Figure 1). Heterogeneous deposition of a metal or metal alloy on the core occurs through one of the three growth modes to form core–shell or core–shell-like nanostructures.

So why have relatively few multimetallic core–shell nanoparticles with sizes less than 10 nm been reported? Besides the intrinsic challenges in the synthesis, one important reason perhaps lies in the difficulty of characterizing multimetallic core–shell nanoparticles in detail. Yang and co-workers have previously reported shape-controlled Pt/Pd core–shell nanoparticles. Pt/Pd core–shell nanocubes, cuboctahedra, and octahedra could be made by using Pt cube seed crystals.[5] High-resolution TEM (HRTEM) images revealed

[*] Prof. Dr. H. Yang
Department of Chemical Engineering
University of Rochester
Gavett Hall 206, Rochester, NY 14627 (USA)
Fax: (+1) 585-273-1348
E-mail: hongyang@che.rochester.edu
Homepage: http://www.che.rochester.edu/~hongyang/

[**] This work was supported in part by the U.S. National Science Foundation under grant numbers DMR-0449849 and DMR-1041811, and the New York State Energy Research and Development Agency (NYSERDA). Zhenmeng Peng and Hongjun You are thanked for help in preparing the figures.

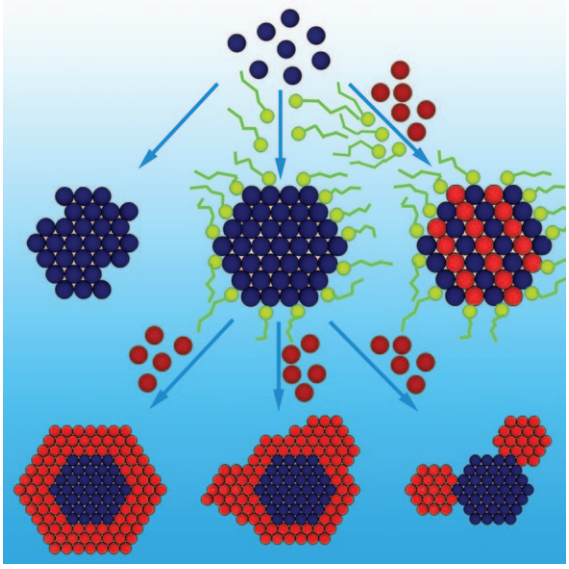

Figure 1. Synthesis of multimetallic core–shell or core–shell-like nanoparticles from metal precursors.

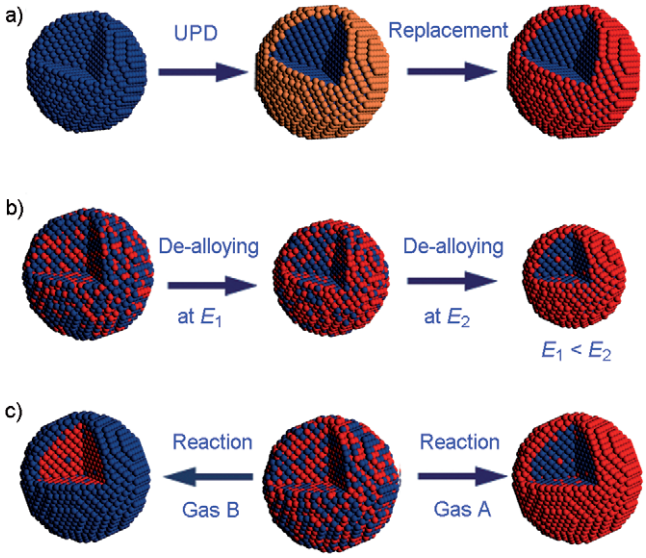

Figure 2. Methods for the synthesis and structural control of core–shell multimetallic nanoparticles. a) Underpotential deposition (UPD) replacement, b) electrochemical de-alloying, and c) reaction-driven process.

the atomic position of these metals, but the interfacial structure between Pt and Pd atoms could not be clearly resolved. The recent advance in the aberration-corrected HAADF-STEM technique allows the imaging of spatial distributions of metal elements in previously unobtainable detail. For instance, Nuzzo and co-workers were able to examine the atomic structures in 3–4 nm Pt/Pd and Pd/Pt bimetallic core–shell nanoparticles by using the aberration corrected HAADF-STEM technique.[6] The 2.4 nm core of Pt or Pd was made using polyvinylpyrrolidone (PVP) as the capping agent in ethylene glycol solution. The metal shell was subsequently deposited by using the sacrificial hydrogen layer method. The study shows finely detailed elemental distribution, which allows the accurate analysis of lattice distortion, twinning, clustering, and other structural complexities in the bimetallic nanoparticles.[6]

Besides the colloidal synthesis, electrochemical methods and chemical-reaction-driven reconstruction are some other recently developed techniques for controlling the heterogeneous structures of bi- or multimetallic core–shell nanoparticles (Figure 2). The electrochemical approach to the preparation of core–shell metallic nanoparticles include both the under potential deposition (UPD) and de-alloying methods.[7] When Cu is used as the sacrificial layer, a Pt monolayer can be deposited on different metallic nanoparticles through the electrochemical replacement reaction (Figure 2a).[7a] The electrochemical removal of more reactive metals from platinum-based alloys is another method to make the surfaces of core–shell nanoparticles Pt rich (Figure 2b).[7b] The de-alloying method should be applicable to a range of multimetallic systems to create heterogeneous nanostructures, because preferential dissolution of a particular metal is based on the difference in redox potentials of the metals. Both metal/alloy and alloy/alloy core–shell nanostructures can be made through the de-alloying method. Finally, a reaction-driven approach was used to enrich a selected metal in the surface layer of alloy nanoparticles by using reacting gases, such as CO, NO, O_2, and H_2 (Figure 2c).[8] For a Pd/Rh alloy, exposure to an oxidizing gas of NO results in the nanoparticle with Rh rich in the surface. Rh atoms can move back to the core, if the nanoparticle is exposed to a reducing gas of CO. Thus, the use of reactive gases is a rather unique way to engineer the structures of bimetallic core–shell-like nanoparticles.

A report by Adzic and co-workers describes the design of multimetallic core–shell nanoparticles as durable ORR catalysts.[9] Nanostructures of a carbon-supported Pt monolayer on Pd (Pt_{ML}/Pd/C) or Pd_9Au_1 (Pt_{ML}/Pd_9Au_1/C) were tested. These two types of core–shell nanoparticles were generated by UPD and replacement reactions, and showed a surprisingly good durability in the ORR under acidic conditions. It is known that the degradation of platinum-based catalysts in the cathode region is a major problem under harsh acidic fuel-cell operating conditions.[10] A study of durability based on highly active ORR catalysts made from Pt_3Ni and Pt/Pd core–shell nanoparticles is therefore especially meaningful.

Pt/Pd dendrites or particle-on-particle heterogeneous nanostructures have previously been shown to be very active in the ORR under acidic conditions,[11] and the durability is much better than those of the commercial Pt/C catalysts.[11b] What makes the featured work stand out is its demonstration that, even with one single layer of Pt atoms, the Pt mass activity at 0.9 V (vs. reversible hydrogen electrode, RHE) can retain 80% of its initial value, that is, a drop from 0.30 A mg^{-1} to 0.24 A mg^{-1} after 60000 potential cycles, and to 0.19 A mg^{-1} after 100000 potential cycles between 0.7 to 0.9 V.[9] The density functional theory (DFT) calculation results show the structural changes of the Pd cores affect the stability of the Pt monolayer. Partial dissolution of Pd helps to improve the interaction between the Pt shells and Pd cores, thus resulting

in better stability of the Pt surface atoms. By replacing Pd with Pd_9Au_1 alloy as the core, $Pt_{ML}/Pd_9Au_1/C$ catalysts can have Pt mass activity of 0.20 A mg^{-1} after 200000 potential cycles in an expanded testing range between 0.6 and 1.0 V. This final Pt mass activity is still higher than that of the freshly made Pt/C catalyst (ca. 0.13 A mg^{-1}).

Besides core–shell nanoparticles, other platinum-based nanostructures have been found to be useful in the design of electrocatalysts.[12] X. L. Sun and co-workers have reported the durability of multiarmed Pt nanowires.[13] Accelerated durability tests were carried out using a rotating disc electrode (RDE). After 4000 potential cycles between 0.6 and 1.2 V, the multiarmed Pt nanowires without a carbon support were shown to retain most of the electrochemical surface area (ECSA), or about 87% of the initial value. This work further demonstrates the important effect of shape and crystalline structure on the durability of ORR catalysts.

This collection of recent reports highlight the impressive progress in the design and synthesis of multimetallic core–shell and other relevant nanostructures as active and durable electrocatalysts for PEMFC applications. Core–shell nanoparticles with sizes less than 10 nm are within the range relevant to be used as catalysts in practical applications. It will be interesting to see if the overall shape of these core–shell nanoparticles can also be finely controlled at this length scale, since the morphology of nanoparticles can profoundly affect the ORR activity of metal-alloy catalysts.[14] The rapid improvement in the ORR performance of these bimetallic and multimetallic core–shell nanoparticles is equally promising. It is becoming increasingly clear that a new era for the design, synthesis, and understanding of the structure–property relationships of multimetallic core–shell nanoparticles has arrived.

Received: September 18, 2010
Published online: February 21, 2011

[1] a) J. Tollefson, *Nature* **2010**, *464*, 1262 – 1264; b) F. T. Wagner, B. Lakshmanan, M. F. Mathias, *J. Phys. Chem. Lett.* **2010**, *1*, 2204 – 2219.

[2] a) Z. M. Peng, H. Yang, *Nano Today* **2009**, *4*, 143 – 164; b) Y. Xia, Y. J. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem.* **2008**, *121*, 62 – 108; *Angew. Chem. Int. Ed.* **2008**, *48*, 60 – 103; c) J. Greeley, I. E. L. Stephens, A. S. Bondarenko, T. P. Johansson, H. A. Hansen, T. F. Jaramillo, J. Rossmeisl, I. Chorkendorff, J. K. Norskov, *Nat. Chem.* **2009**, *1*, 552 – 556; d) V. R. Stamenkovic, B. S. Mun, M. Arenz, K. J. J. Mayrhofer, C. A. Lucas, G. F. Wang, P. N. Ross, N. M. Markovic, *Nat. Mater.* **2007**, *6*, 241 – 247; e) J. L. Zhang, K. Sasaki, E. Sutter, R. R. Adzic, *Science* **2007**, *315*, 220 – 222.

[3] V. Mazumder, M. Chi, K. L. More, S. Sun, *Angew. Chem.* **2010**, *122*, 9558 – 9562; *Angew. Chem. Int. Ed.* **2010**, *49*, 9368 – 9372.

[4] a) V. Mazumder, M. F. Chi, K. L. More, S. H. Sun, *J. Am. Chem. Soc.* **2010**, *132*, 7848 – 7849; b) C. Wang, D. van der Vliet, K. L. More, N. J. Zaluzec, S. Peng, S. H. Sun, H. Daimon, G. Wang, J. Greeley, J. Pearson, A. P. Paulikas, G. Karapetrov, D. Strmcnik, N. M. Markovic, V. R. Stamenkovic, *Nano Lett.* **2010**, DOI: 10.1021/nl102369k.

[5] S. E. Habas, H. Lee, V. Radmilovic, G. A. Somorjai, P. Yang, *Nat. Mater.* **2007**, *6*, 692 – 697.

[6] S. I. Sanchez, M. W. Small, J. M. Zuo, R. G. Nuzzo, *J. Am. Chem. Soc.* **2009**, *131*, 8683 – 8689.

[7] a) R. R. Adzic, J. Zhang, K. Sasaki, M. B. Vukmirovic, M. Shao, J. X. Wang, A. U. Nilekar, M. Mavrikakis, J. A. Valerio, F. Uribe, *Top. Catal.* **2007**, *46*, 249 – 262; b) Z. M. Peng, H. J. You, H. Yang, *Adv. Funct. Mater.* **2010**, *20*, 3734 – 3741; c) P. Strasser, S. Koh, T. Anniyev, J. Greeley, K. More, C. F. Yu, Z. C Liu, S. Kaya, D. Nordlund, H. Ogasawara, M. F. Toney, A. Nilsson, *Nat. Chem.* **2010**, *2*, 454 – 460.

[8] F. Tao, M. E. Grass, Y. W. Zhang, D. R. Butcher, J. R. Renzas, Z. Liu, J. Y. Chung, B. S. Mun, M. Salmeron, G. A. Somorjai, *Science* **2008**, *322*, 932 – 934.

[9] K. Sasaki, H. Naohara, Y. Cai, Y. M. Choi, P. Liu, M. B. Vukmirovic, J. X. Wang, R. R. Adzic, *Angew. Chem.* **2010**, *122*, 8784 – 8789; *Angew. Chem. Int. Ed.* **2010**, *49*, 8602 – 8607.

[10] F. A. de Bruijn, V. A. T. Dam, G. J. M. Janssen, *Fuel Cells* **2008**, *8*, 3 – 22.

[11] a) B. Lim, M. J. Jiang, P. H. C. Camargo, E. C. Cho, J. Tao, X. M. Lu, Y. M. Zhu, Y. A. Xia, *Science* **2009**, *324*, 1302 – 1305; b) Z. M. Peng, H. Yang, *J. Am. Chem. Soc.* **2009**, *131*, 7542 – 7543.

[12] a) Z. M. Peng, J. B. Wu, H. Yang, *Chem. Mater.* **2010**, *22*, 1098 – 1106; b) X. W. Teng, S. Maksimuk, S. Frommer, H. Yang, *Chem. Mater.* **2007**, *19*, 36 – 41; c) E. P. Lee, Z. M. Peng, D. M. Cate, H. Yang, C. T. Campbell, Y. Xia, *J. Am. Chem. Soc.* **2007**, *129*, 10634 – 10635; d) X. W. Teng, X. Y. Liang, S. Maksimuk, H. Yang, *Small* **2006**, *2*, 249 – 253.

[13] S. H. Sun, G. X. Zhang, D. S. Geng, Y. G. Chen, R. Y. Li, M. Cai, X. L. Sun, *Angew. Chem.* **2010**, *123*, 442 – 446; *Angew. Chem. Int. Ed.* **2010**, *50*, 422 – 426

[14] a) V. R. Stamenkovic, B. Fowler, B. S. Mun, G. F. Wang, P. N. Ross, C. A. Lucas, N. M. Markovic, *Science* **2007**, *315*, 493 – 497; b) J. Zhang, H. Z. Yang, J. Y. Fang, S. Z. Zou, *Nano Lett.* **2010**, *10*, 638 – 644; c) J. B. Wu, J. L. Zhang, Z. M. Peng, S. C. Yang, F. T. Wagner, H. Yang, *J. Am. Chem. Soc.* **2010**, *132*, 4984 – 4985; d) J. B. Wu, A. Gross, H. Yang, *Nano Lett.* **2011**, *11*, 798-802.

