Angewandte Chemie International Edition

DOI: 10.1002/anie.201004408

Nanocrystals

Shaping a Bright Future for Platinum-Based Alloy Electrocatalysts**

*Byungkwon Lim, Taekyung Yu, and Younan Xia**

alloys · electrochemistry · nanocrystals · platinum · shape control

Concerns about fossil-fuel shortages and global warming have resulted in a great demand for devices that can generate power at high efficiencies with little or no emissions. Proton-exchange membrane (PEM) fuel cells, which directly convert chemical energy into electricity, represent one example of such technology, and have received increasing attention in recent years. While PEM fuel cells hold great potential for a variety of applications, for example, powering transportation vehicles or portable electronic devices, and on-site power generation, the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode and the high cost associated with platinum-based ORR electrocatalysts have limited the widespread commercialization of such devices.[1]

Over the past decade, there has been a strong effort in developing effective strategies for improving the performance and thus reducing the cost of platinum-based ORR electrocatalysts,[2] which mainly involved alloying Pt with other transition metals. Conventional methods for preparing platinum-based alloy catalysts involve mixing a Pt/C catalyst with the oxide of a chosen transition metal, followed by treatment at high temperatures (800–1000 °C) in an inert atmosphere.[3] Although platinum-based alloy catalysts from these methods have shown improvements in activity compared to pure platinum catalysts, they often exhibit poorly defined morphology and structure. In a number of studies, it was shown that the catalytic property of a metal nanocrystal can be enhanced by controlling its shape.[4] Therefore, it is not unexpected that a combination of the effect of alloying and the benefit from nanocrystal shape control would make it possible to further improve the activity of platinum-based alloy nanocrystals. However, control over the shape of platinum-based alloy nanocrystals has not been achieved until very recently.

In a recent report,[5] Kang and Murray described a synthetic route to Pt–Mn alloy nanocrystals that have a cubic shape (Figure 1), and are reported to have an enhanced activity for the ORR in H_2SO_4 compared to commercial Pt catalysts. The first step in the synthesis involved heating a mixture containing $[Pt(acac)_2]$ (acac = acetylacetonate), oleic acid, and oleylamine in benzyl ether. A solution of $[Mn_2(CO)_{10}]$ in benzyl ether was injected into the mixture when the temperature reached 160 °C. The mixture was further heated to 200–205 °C, and then kept at this temperature for 30 minutes. The injection of $[Mn_2(CO)_{10}]$ at an elevated temperature during the heating process was found to be key to the formation of the Pt–Mn alloy nanocubes. When the synthesis was conducted by heating a solution containing both $[Pt(acac)_2]$ and $[Mn_2(CO)_{10}]$, only Pt–Mn alloy nanocrystals with a spherical profile were obtained as the final product. It was also found that both oleic acid and oleylamine play important roles in the formation of Pt–Mn alloy nanocubes with a uniform size and shape. The as-synthesized nanocubes were chemically disordered, but their structure was converted to the ordered $L1_2$ phase ($AuCu_3$ structure) after annealing at 600 °C for 30 minutes.

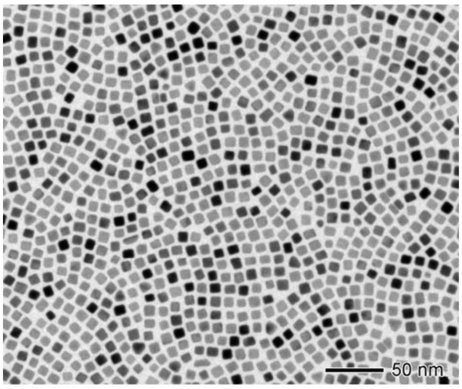

Figure 1. TEM image of the as-synthesized Pt–Mn alloy nanocubes. Modified from Ref. [5] with permission. Copyright American Chemical Society (2010).

Importantly, the ORR activity of the cubic Pt–Mn nanocrystals in H_2SO_4 was much higher than those of the commercial Pt catalysts. At 0.8 V (versus the normal hydrogen electrode), the Pt–Mn nanocubes outperformed the

---

[*] Dr. B. Lim,[+] Dr. T. Yu, Prof. Y. Xia
Department of Biomedical Engineering
Washington University
St. Louis, MO 63130 (USA)
E-mail: xia@biomed.wustl.edu

[+] Current address: School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746 (Korea)

[**] This work was supported by a grant from the NSF (DMR-0804088), startup funds from Washington University in St. Louis, and the World Class University (WCU) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R32-20031; Y.X.).

commercial Pt/C and Pt black catalysts by over a factor of three (on the basis of equivalent Pt mass). The Pt–Mn nanocubes also showed a higher ORR activity than Pt–Mn nanospheres, thus demonstrating the shape dependency of the ORR activity for Pt–Mn alloy nanocrystals. This behavior is very similar to that reported by Sun and co-workers for Pt nanocrystals,[6] and can be attributed to the structure-sensitive inhibiting effect of the sulfate ions, which can block the active site for O_2 adsorption on the nanocrystal surface and thus retard the ORR kinetics. The sulfate ions tend to bind to Pt(111) more strongly than Pt(100) for single-crystal Pt surfaces because of the symmetry matching between three oxygen atoms in the sulfate ion and Pt atoms on the (111) surface. Cubic Pt nanocrystals are enclosed by {100} facets and thus show a higher ORR activity than spherical Pt nanocrystals that are actually polyhedrons enclosed by a mix of {100} and {111} facets. The same trend may also apply to Pt–Mn surfaces and account for the higher ORR activity of the Pt–Mn nanocubes in H_2SO_4. In contrast, however, the spherical Pt–Mn nanocrystals were more active than the Pt–Mn nanocubes in $HClO_4$, thus implying that the ORR activity is higher on Pt–Mn(111) than on Pt–Mn(100) in a non-adsorbing electrolyte such as $HClO_4$.

The work by Kang and Murray clearly demonstrates the benefit from shape control of Pt–Mn alloy nanocrystals when they are used as ORR electrocatalysts in a specific electrolyte. However, it remains unclear to what extent the alloying of Pt with Mn contributes to the enhancement of the ORR activity for the Pt–Mn alloy nanocubes. A quantitative comparison between ORR activities of the spherical Pt–Mn nanocrystals and the commercial Pt catalysts was not provided, thus making it difficult to determine the actual contribution from alloying of Pt with Mn to the ORR activity of Pt–Mn nanocrystals. In other experiments, both cubic and spherical Pt–Mn alloy nanocrystals were found to be less active for the formic acid oxidation reaction than the commercial Pt/C catalyst. The Pt–Mn nanocubes showed a better activity than the Pt/C catalyst in the methanol oxidation reaction, while the Pt–Mn nanospheres were comparable in activity to the Pt/C catalyst. The effect of alloying Pt with Mn on the electrocatalytic properties deserves further investigation.

In addition to this work, breakthroughs in the synthesis of shape-controlled platinum-based alloy nanocrystals have also been achieved by several other research groups. For example, Sun and co-workers synthesized 7 nm-sized Pt–Fe nanocubes by simultaneous decomposition of $[Fe(CO)_5]$ and reduction of $[Pt(acac)_2]$ in the presence of oleic acid and oleylamine as stabilizers.[7] Fang and co-workers developed effective strategies for the preparation of Pt–M (M = Co, Fe, Ni, Cu) nanocubes.[8] In a related study,[9] the same research group also successfully synthesized Pt_3Ni nanocrystals with controlled shapes, including cubes and octahedrons, and further demonstrated that the carbon-supported Pt_3Ni octahedrons were four times more active for the ORR in $HClO_4$ than the Pt/C catalyst (on the basis of equivalent Pt mass), even though the size of the Pt_3Ni octahedrons is three times larger than that of Pt nanoparticles in the commercial Pt/C catalyst.

As can be seen in these examples, the synthesis of shape-controlled alloy nanocrystals has emerged dramatically in recent years, and is expected to become a promising strategy for the development of next-generation catalysts with superb performance for a wide variety of chemical and electrochemical reactions. Several issues regarding stability and large-scale production still need to be addressed before such shape-controlled alloy nanocrystals can be commercialized for fuel-cell applications. In particular, leaching of non-noble elements in platinum-based alloy catalysts during the fuel-cell operation has been identified as a significant problem that lowers the overall performance and accelerates the degradation of the fuel cell.[1] As Mukerjee and Srinivasan suggested,[10] one possible approach to address this issue might be to preleach platinum-based alloy nanocrystals before the preparation of an electrode to minimize the contamination of the membrane–electrode assembly during operation, even though such a treatment might produce a platinum-enriched surface or result in shape transformation. For practical applications of shape-controlled alloy nanocrystals, further reduction in size while retention of their shape might also be necessary to compete with those nanocrystals that have uncontrolled shapes but much smaller sizes.

Received: July 19, 2010

---

[1] H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, *Appl. Catal. B* **2005**, *56*, 9.

[2] a) V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas, N. M. Markovic, *Science* **2007**, *315*, 493; b) B. Lim, M. Jiang, P. H. C. Camargo, E. C. Cho, J. Tao, X. Lu, Y. Zhu, Y. Xia, *Science* **2009**, *324*, 1302; c) Z. Peng, H. Yang, *J. Am. Chem. Soc.* **2009**, *131*, 7542; d) J. Greeley, I. E. L. 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; e) J. X. Wang, H. Inada, L. Wu, Y. Zhu, Y. Choi, P. Liu, W.-P. Zhou, R. R. Adzic, *J. Am. Chem. Soc.* **2009**, *131*, 17298.

[3] a) S. Mukerjee, S. Srinivasan, *J. Electroanal. Chem.* **1993**, *357*, 201; b) S. Mukerjee, S. Srinivasan, M. P. Soriaga, J. McBreen, *J. Electrochem. Soc.* **1995**, *142*, 1409.

[4] a) Y. Xia, Y. Xiong, B. Lim, S. E. Skrabalak, *Angew. Chem.* **2009**, *121*, 62; *Angew. Chem. Int. Ed.* **2009**, *48*, 60; b) J. Chen, B. Lim, E. P. Lee, Y. Xia, *Nano Today* **2009**, *4*, 81.

[5] Y. Kang, C. B. Murray, *J. Am. Chem. Soc.* **2010**, *132*, 7568.

[6] C. Wang, H. Daimon, T. Onodera, T. Koda, S. Sun, *Angew. Chem.* **2008**, *120*, 3644; *Angew. Chem. Int. Ed.* **2008**, *47*, 3588.

[7] M. Chen, J. Kim, J. P. Liu, H. Fan, S. Sun, *J. Am. Chem. Soc.* **2006**, *128*, 7132.

[8] a) J. Zhang, J. Fang, *J. Am. Chem. Soc.* **2009**, *131*, 18543; b) D. Xu, Z. Liu, H. Yang, Q. Liu, J. Zhang, J. Fang, S. Zou, K. Sun, *Angew. Chem.* **2009**, *121*, 4281; *Angew. Chem. Int. Ed.* **2009**, *48*, 4217; c) D. Xu, S. Bliznakov, Z. Liu, J. Fang, N. Dimitrov, *Angew. Chem.* **2010**, *122*, 1304; *Angew. Chem. Int. Ed.* **2010**, *49*, 1282.

[9] J. Zhang, H. Yang, J. Fang, S. Zou, *Nano Lett.* **2010**, *10*, 638.

[10] S. Mukerjee, S. Srinivasan in *Handbook of Fuel Cells: Fundamentals, Technology, and Applications*, *Vol. 2* (Eds.: W. Vielstich, A. Lamm, H. Gasteiger), Wiley, Chichester, **2003**, p. 502.