Facile Synthesis of Co−Pt Hollow Sphere Electrocatalyst

Ge Chen,[†] Dingguo Xia,*[,†] Zuoren Nie,[†] Zhenyao Wang,[†] Lei Wang,[†] Lei Zhang,[‡] and Jiujun Zhang*[,‡]

College of Environmental & Energy Engineering, Beijing University of Technology (BUT-CEEE), Chaoyang district 100022, Beijing, P.R. China, and Institute for Fuel Cell Innovation, National Research Council of Canada (NRC-IFCI), Vancouver, BC, V6T 1W5 Canada

Received September 29, 2006. Revised Manuscript Received February 6, 2007

In this paper, successful one-step chemical synthesis of Co−Pt hollow spheres with adjustable composition was developed in an effort to explore new synthesis methods, simplify the synthesis procedure, and improve the synthetic efficiency. In this synthesis, a direct thermolytic reduction of platinum acetylacetonate [$Pt(CH_3COHCOCH_3)_2$] and cobalt(II) acetate [$Co(CH_3COO)_2$] in refluxing ethyl glycol was explored. In the reacting mixture, an anionic surfactant sodium dodecyl sulfate (SDS) was used as the capping and structure-directing agent. These Co−Pt hollow spheres demonstrated enhanced electrocatalytic activity toward methanol oxidation in comparison with Pt nanoparticles, which is crucial for anode electrocatalysis in DMFCs.

Introduction

In an effort to improve catalyst activity and stability, Pt-based catalysts, which are the most practical catalysts for fuel cell applications, have been synthesized for the purpose of reducing catalyst particle size (nanolevel) and optimizing the particle structure.[1] The hollow metal structure, one of the important particle structures, has attracted a great deal of attention due to their distinguished properties from their solid counterparts.[2] To obtain a catalyst with a hollow metal structure, the methodological development is fairly critical. In recent years, several methods based on a template-directed synthesis have been successfully demonstrated in generating such structures.[3] Among the methods employed, template-engaged synthesis using galvanic replacement reactions is the one more commonly used. Recently, Co−Pt hollow spheres with super-paramagnetic properties were successfully synthesized by Vasquez et al. using a galvanic replacement method.[4] In this method, a strategy to control the reduction potential differences of two or more metals was employed and hollow metal structures were obtained.[5] However, the difficulty in independently controlling the individual dimensions and wall thicknesses of the resulting hollow particles is believed to be a drawback of this method.[6] It is also recognized that a bimetallic catalyst has advantages over a single-metal catalyst in many aspects. For example, a Pt−Ru alloy used as the anode catalyst in direct methanol fuel cells (DMFCs) has a much higher catalytic activity toward methanol oxidation than pure Pt.[7] Therefore, a bimetallic Pt-based catalyst with a hollow structure is fairly attractive.

In this paper, a successful one-step chemical synthesis of Co−Pt hollow spheres with adjustable composition was developed in the effort to simplify the synthesis procedure and improve the efficiency. In this synthesis, a direct thermolytic reduction of platinum acetylacetonate and cobalt(II) acetate in refluxing ethylene glycol was explored. The anionic surfactant sodium dodecyl sulfate (SDS) was used as the capping and structure-directing agent in the reacting mixture. The prepared Co−Pt hollow spheres demonstrated enhanced electrocatalytic activity for methanol oxidation compared with Pt and CoPt nanoparticles, which is very important for the anode electrocatalysis of the direct methanol fuel cells (DMFCs).

Experimental Section

In a typical hollow CoPt nanoparticle synthesis, 0.05 g of platinum acetylacetonate [$Pt(CH_3COHCOCH_3)_2$], 0.032 g of cobalt(II) acetate [$Co(CH_3COO)_2$], and 0.25 g of sodium dodecyl sulfate (SDS) were dissolved in 50 mL of ethylene glycol solvent to form a reacting mixture. The reacting mixture was then maintained at a

---

* Authors to whom correspondence should be addressed. D. Xia: fax, 86-010-67391983; e-mail, dgxia@bjut.edu.cn. J. Zhang: tel., 604-221-3087; e-mail, jiujun.zhang@nrc.gc.ca.

[†] Beijing University of Technology.

[‡] National Research Council of Canada.

(1) (a) Liang, H.-P.; Zhang, H.-M.; Hu, J.-S.; Guo, Y.-G.; Wan, L.-J.; Bai, C.-L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1540. (b) Guo, Y.-G., Hu, J.-S.; Zhang, H.-M.; Liang, H.-P.; Wan, L.-J.; Bai, C.-L. *Adv. Mater.* **2005**, *17*, 746. (c) Teng, X-W.; Maksimuk, S.; Frommer, S.; Yang, H. *Chem. Mater.* **2007**, *19*, 31.

(2) (a) Westcott, S. L.; Oldenburg, S. J.; Lee, T. R.; Halas, N. J. *Chem. Phys. Lett.* **1999**, *300*, 651. (b) Kim, S.-W.; Kim, M.; Lee, W. Y.; Hyeon, T. *J. Am. Chem. Soc.* **2002**, *124*, 7642. (c) *74*, 5297. (d) Liang, H.-P.; Zhang, H.-M.; Hu, J.-S.; Guo, Y.-G.; Wan, L.-J.; Bai, C.-L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1540. (e) Liang, H.-P.; Wan, L.-J.; Bai, C.-L.; Jiang, L. *J. Phys. Chem. B* **2005**, *109*, 7795.

(3) (a) Martin, C. R. *Science* **1994**, *266*, 1961. (b) Kondo, Y.; Takayanagi, K. *Science* **2000**, *289*, 606. (c) Sun, Y.; Mayers, B.; Xia, Y. *Adv. Mater.* **2003**, *15*, 641.

(4) Vasquez, Y.; Sra, A. K.; Schaak, R. E. *J. Am. Chem. Soc.* **2005**, *127*, 12504.

(5) (a) Sun, Y.; Mayers, B. T.; Xia, Y. *Nano Lett.* **2002**, *2*, 481. (b) Porter, L. A.; Choi, H. C., Jr.; Ribbe, A. E.; Buriak, J. M. *Nano Lett.* **2002**, *2*, 1067. (c) Song, J. H.; Wu, Y.; Messer, B.; Kind, H.; Yang, P. *J. Am. Chem. Soc.* **2001**, *123*, 1039.

(6) Mayers, B.; Jiang, X.; Sunderland, D.; Cattle, B.; Xia, Y. *J. Am. Chem. Soc.* **2003**, *125*, 13364.

(7) Liu, H.; Song, C.; Zhang, L.; Zhang, J.; Wang, H.; Wilkinson, D. P. *J. Power Source* **2006**, *155*, 95.

10.1021/cm062336z CCC: $37.00

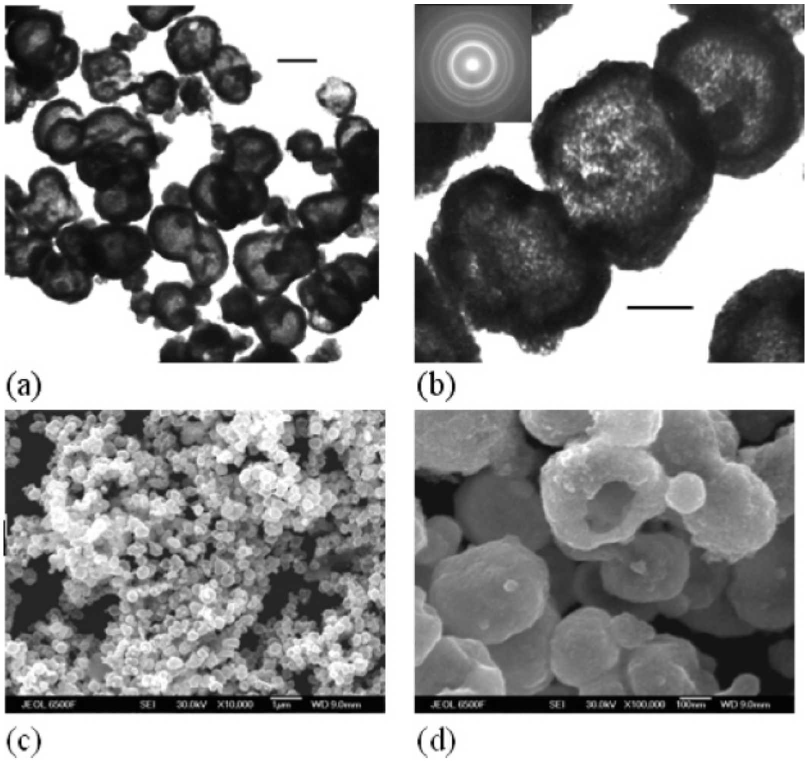

Figure 1. (a) TEM image of the Co−Pt hollow spheres with a bar scale of 200 nm; (b) HRTEM image of the Co−Pt hollow spheres with a bar scale of 100 nm; (c) SEM image of the Co−Pt hollow spheres with a bar scale of 1 μm; and (d) HRSEM image of the Co−Pt hollow spheres with a bar scale of 100 nm.

reflux temperature of 198 °C in a three-necked flask until a black precipitate was obtained on the bottom of the flask. The black precipitate was filtered out, washed with double-distilled water several times, and dried at ambient conditions. For comparison, the Pt nanoparticles were prepared in a similar manner except the cobalt acetate was absent. The CoPt nanoparticles were prepared according to the literature.[8] All experiments were performed at ambient conditions. For analysis using the transmission electron microscope (TEM), the samples were ultrasonically dispersed in water and then dropped on the carbon-coated copper grids. A JSM 6500F field emission scanning electron microscope (SEM) and a JEOL JEM 2010 transmission electron microscope operated at 200 kV were employed in the study of the morphology of Co−Pt hollow spheres. X-ray powder diffraction (XRD) was carried out on a Bruker D8 Advance X-ray diffractometer under Cu Kα radiation. For chemical composition analysis, an IRIS Intrepid ER/S ICP-AES was used. For X-ray photoelectron spectroscopy (XPS) measurements, a Physical Electronics PHI Quantera SXM (with monochromatized Al Kα radiation and an energy resolution of 0.5 eV) was used. Electrochemical measurements were conducted in an electrochemical cell with a three-electrode configuration at room temperature. An electrochemical system (Princeton Applied Research (PAR) 273) was used through all the measurements. The working electrode was a glassy carbon disk with a diameter of 4.0 mm, polished with Al_2O_3 paste, and washed ultrasonically in double-distilled water. To prepare the suspension, a 1.5 mg sample of the dried hollow CoPt spheres was weighed out. To this, 1.0 mL of ethanol and 5 μL of 2% Nafion solution were added. The resulting mixture was sonicated in a bath-type ultrasonicator for 0.5 h. Suspensions of Pt NPs and CoPt NPs were prepared using the same method. The nanoparticle suspension described above was coated onto a 4 mm diameter glassy carbon disk (GC) electrode and allowed to dry in air. A Pt wire was used as the counter electrode, and a reversible hydrogen electrode (RHE) was used as the reference electrode. Aqueous solutions of 0.5 M H_2SO_4 and 0.5 M H_2SO_4 containing 1.0 M methanol were used for the electrolytes.

Results and Discussion

Figure 1a shows bright-field (TEM) micrograph of the Co−Pt hollow sphere structures. An average diameter of the hollow spheres was determined to in the range of 100−200 nm, which was also confirmed by the scanning electron micrograph (SEM) photo shown in Figure 1c. A high-resolution TEM micrograph (Figure 1b) shows that the shell is comprised of some smaller nanoparticles, which can also be observed by a high-resolution SEM image (Figure 1d).

One important observation was that the atomic ratio of Co/Pt in the spheres can be adjusted by simply changing the amount of the SDS in the reacting mixture. For example, at SDS concentrations of 0.15 g/50 mL, 0.25 g/50 mL, 0.35 mg/50 mL, and 0.5 g/50 mL, the Co−Pt composition was changed to $Co_{40}Pt_{60}$, $Co_{32}Pt_{68}$, $Co_{21}Pt_{79}$, and $Co_{09}Pt_{91}$, respectively, with an almost constant sphere structure and wall thickness. With regards to this behavior, more work is underway to obtain a fundamental understanding. The selected area electron diffraction patterns (SAED) of the hollow sphere structures are shown as the inset in Figure 1b. The SAED indicates that the Co−Pt bimetal in the spheres has a face-centered cubic (fcc) structure. The powder XRD results also confirmed such a structure. However, compared to the pure Pt nanoparticles, the diffraction angles of these Co−Pt hollow spheres were shifted to the higher positions, reflecting the lattice contraction due to the partial

---

(8) Chinanasamy, C. N.; Jeyadevan, B.; Shinaoda, K.; Tohji, K. *J. Appl. Phys.* **2003**, *93*, 7583.

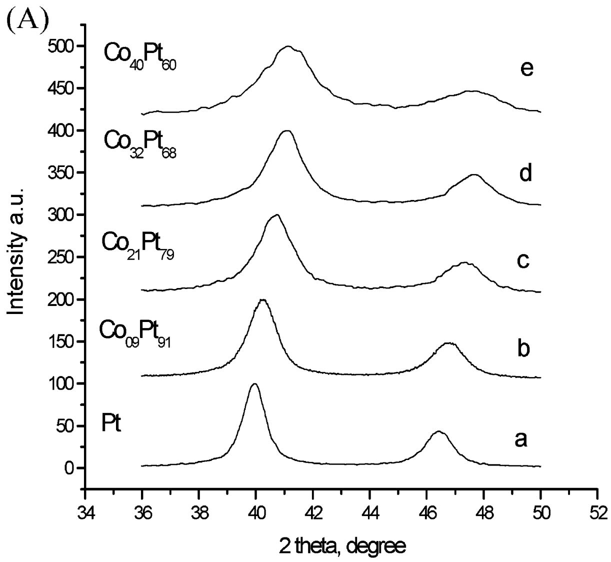

Figure 2. (A) XRD patterns for Pt nanoparticles (a) and Co−Pt hollow spheres synthesized at different concentrations of SDS: (b) 0.5 g/50 mL SDS; (c) 0.35 g/mL SDS; (d) 0.25 g/mL SDS; (e) 0.15 g/mL SDS. (B) XRD pattern of Co−Pt hollow spheres, before (lower curve) and after (upper curve) annealing treatment at 550 °C for 2 h under reducing atmosphere (5% H_2 in Ar). Diffraction patterns were collected on a Bruker D8 Advance X-ray diffractometer under Cu Kα radiation.

substitution of Pt by Co. As shown in Figure 2, the peak position of the (111) diffraction shifts toward a high angle with decreasing SDS concentration in the reaction mixture, suggesting that more Co atoms have been replaced by the Pt atoms. This result is also consistent with the ICP-AES results mentioned above. We also noticed that the widths at half-maximum of the (111) peak particle increased with the decreasing SDS concentration, which indicated the hollow CoPt particles' size decreased with the increase of Co composition. By using the Scherrer equation, we calculated the average particles size to be 9.7 nm (Pt nanoparticles), 7.3 nm ($Co_{09}Pt_{91}$), 5.9 nm ($Co_{21}Pt_{79}$), 5.8 nm ($Co_{32}Pt_{68}$), and 4.3 nm ($Co_{40}Pt_{60}$), respectively. Figure 2b shows that an annealing treatment at 550 °C (2 h) under a reducing atmosphere (5% H_2 95% Ar) can make the face-centered cubic phase transformed to a CoPt alloy with a highly ordered structure, as evidenced by the appearances of (001) and (110) superlattice peaks on the upper curve. Similar results have also been reported.[9] In addition, X-ray peak widths in Figure 2 after annealing treatment become more narrow, suggesting that heat-treatment induced particle agglomeration and decreased the microstresses. However, the hollow structure still remained after the annealing treatment. (The TEM image and SAED pattern are shown in Figure S1, Supporting Information).

Figure 3 demonstrates the XPS results showing that the Pt $4f_{7/2}$ peak of hollow $Co_{32}Pt_{68}$ spheres was at 71.56 eV, compared to 71.40 eV for Pt nanoparticles. The Pt 4f peaks are known to shift to higher energies upon forming Co alloys.[10] However, no PtO_x species were observed. The change in the electronic character of Pt will mostly affect C−H cleavage occurring at low overpotential.

The possible formation mechanism of the hollow Co−Pt spheres should involve the SDS micelle formation and the ferromagnetic Co−Pt nanoparticle aggregation. In the reacting mixture, the SDS will form micelles as reported in the literature.[11] The Co−Pt alloy nanoparticles produced by the co-reduction of $Pt(acac)_2$ and cobalt(II) acetate, which are ferromagnetic,[8] like to aggregate themselves along the SDS micelle surface under the magic dipole−dipole interaction and then form a hollow structure after the inner SDS is removed by water washing. Similar arguments can be found in the literature for the formation of Co nanorings[12] and 1D nanostructure of Co nanoparticles.[13]

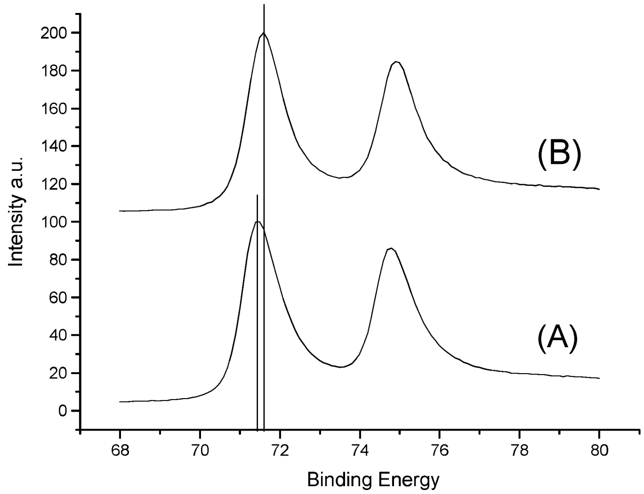

Figure 3. XPS spectrum for Pt 4f peak of Pt nanoparticles (A) and Co−Pt hollow spheres (B).

The electrocatalytic activity of the Co−Pt hollow spheres toward the oxidation of methanol was tested and the results were compared with those obtained on solid Pt nanoparticles (NPs) and CoPt nanoparticles (NPs). The measurements were

---

[9] Tzitzios, V.; Niarchos, D.; Gjoka, M.; Bookos, N.; Petridis, D. *J. Am. Chem. Soc.* **2005**, *127*, 13756.

[10] Lee, Y.-S.; Lim, K.-Y.; Chung, Y.-D.; Whang, C.-N.; Jeon, Y. *Surf. Interface Anal.* **1999**, *30,* 475.

[11] Israelachvili, J.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans.* **1976**, *72*, 1525.

[12] Tripps, S. L.; Pusztay, S. V.; Ribbe, A. E.; Wei, A. *J. Am. Chem. Soc.* **2002**, *124*, 7924.

[13] Liang, H. P.; Guo, Y. G.; Zhang, H. M.; Hu, J. S.; Wan, L. J.; Bai, C. L. *Chem. Commun.* **2004**, 1496.

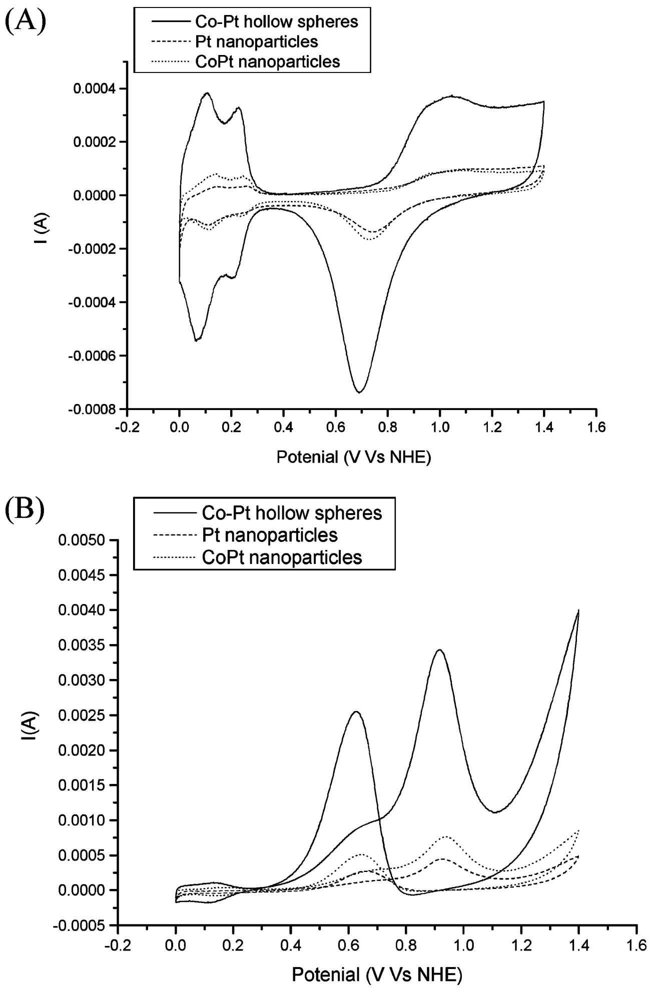

Figure 4. (A) Cyclic voltammograms of Co−Pt hollow spheres ($Co_{32}Pt_{68}$), $Co_{28}Pt_{72}$ nanoparticles, and Pt nanoparticles in 0.5 M H_2SO_4; (B) cyclic voltammograms of Co−Pt hollow spheres ($Co_{32}Pt_{68}$), $Co_{28}Pt_{72}$ nanoparticles, and Pt nanoparticles in 0.5 M H_2SO_4 containing 1 M methanol. Scan rate 200 mV/s. Pt loading 5 μg.

carried out in a 0.5 M H_2SO_4 aqueous solution and 0.5 M H_2SO_4 aqueous solution containing 1.0 M methanol. Figure 4A plots the voltammetry curves of samples in 0.5 M H_2SO_4, The current densities in the hydrogen adsorption/desorption and oxide formation/reduction regions of the hollow CoPt spheres are much larger than those of Pt NPs and CoPt NPs, indicating larger electrochemical surface areas for hollow Co−Pt spheres, which are believed to be a result of the hollow structure. Figure 4B shows the voltammetry curves of samples in 0.5 M H_2SO_4 containing 1 M MeOH. Although all samples show catalytic activities toward the methanol oxidation, the peak currents catalyzed by the Co−Pt hollow sphere are much larger than those for Pt NPs and CoPt NPs. The current density at a specified potential is a clear measure of electrocatalytic efficiency. However, in making comparisons one needs to take into account the fact that the different samples had different particle sizes and distribution. Thus, to make meaningful comparisons, the currents were normalized to the electrochemical surface area of the respective catalysts. (The specific electrochemical areas of nanoparticles that were calculated from the H_{upd}, assuming Co has no effect on hydrogen adsorption/desorption behavior, are listed in Table 1). Current density values for the different materials at various potentials are presented in Table 1. The hollow $Co_{32}Pt_{68}$ spheres showed better activity compared to Pt NPs and other Co−Pt samples at 0.5 V. The better performance of hollow $Co_{32}Pt_{68}$ spheres at 0.5 V could have been due to changes in lattice structures or the electronic properties of the Co−Pt bimetal. At 0.7 V, the current density of hollow Co−Pt spheres is a little lower than Pt NPs. However, due to their larger electrochemical surface areas, hollow Co−Pt samples still showed superior catalytic activity when compared to Pt NPs with the same Pt loading. After annealing, both the electrochemical surface areas and current densities of the hollow Co−Pt spheres decreased, the former possibly due to particle agglomeration and the latter possibly due to a change of Pt−Pt bond in the annealing process, which plays an important role in the electrocatalytic process.

Conclusions

In summary, a Co−Pt catalyst with a hollow sphere structure has been synthesized via a very simple thermolytic reaction. The Co−Pt composition can be easily adjusted by controlling the amount of SDS. With the increase of SDS in the reacting mixture, the ratio of Co/Pt in hollow Co−Pt spheres decreased, and particle sizes decreased with the increasing ratio of Co/Pt. Compared to the pure Pt nanoparticle catalyst and Co−Pt nanoparticles, this Co−Pt hollow sphere catalyst exhibited a superior electrocatalytic activity toward the methanol oxidation reaction at the same Pt loading.

Acknowledgment. This work is financially supported by the Funding Project for Academic Human Resources Development in Institutions of Higher Learning Under the Jurisdiction of Beijing Municipality, Beijing Natural Science Foundation (Grant

Table 1. Electrochemical Characteristics of Co−Pt Hollow Spheres, CoPt Nanoparticles, and Pt Nanoparticles

sample	electrochemical surface areas[a] $(\mathrm{cm^2\ mg_{Pt}})$	j_k at 0.50 V[b] vs RHE	j_k at 0.70 V[b] vs RHE
Pt NPs	38	2.172×10^{-4} A cm^{-2}	7.707×10^{-4} A cm^{-2}
$Co_{28}Pt_{72}$ NPs	87	1.879×10^{-4} A cm^{-2}	6.142×10^{-4} A cm^{-2}
hollow CoPt NPs ($Co_{09}Pt_{91}$)	132	1.347×10^{-4} A cm^{-2}	5.443×10^{-4} A cm^{-2}
hollow CoPt NPs ($Co_{21}Pt_{79}$)	220	1.775×10^{-4} A cm^{-2}	5.686×10^{-4} A cm^{-2}
hollow CoPt NPs ($Co_{32}Pt_{68}$)	320	3.874×10^{-4} A cm^{-2}	5.764×10^{-4} A cm^{-2}
hollow CoPt NPs ($Co_{40}Pt_{60}$)	327	2.075×10^{-4} A cm^{-2}	5.370×10^{-4} A cm^{-2}
hollow CoPt NPs ($Co_{40}Pt_{60}$) annealed	178	1.714×10^{-4} A cm^{-2}	4.511×10^{-4} A cm^{-2}

[a] Using a charge for H_{upd} of 210 μC cm^{-2}. [b] Normalized to the electrochemical surface area.

No.205001), and by the National 973 Program of China (Grant No. 2002CB211807). Dr. Dingguo Xia acknowledges financial support from the Institute for Fuel Cell Innovation, National Research Council of Canada (NRC-IFCI) for his research as a visiting professor at NRC-IFCI. We also want to thank Professor Ji Yuan and Professor Xu Xuedong (Beijing University of Technology, Institute of Solid and Microstructure) for their help in SEM and TEM analysis. Mr. Ryan Baker's editing assistance is also highly appreciated.

Supporting Information Available: TEM image and SEM pattern of annealed hollow Co−Pt spheres. This material is available free of charge via the Internet at http://pubs.acs.org.

CM062336Z