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Rational synthesis of Pt spheres with hollow interior and nanosponge shell using silica particles as template[†]

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Here we report a facile and efficient method to prepare Pt spheres with hollow interior and nanosponge shell with high surface area. Such a unique Pt nanostructure can effectively improve the electrocatalytic performance of Pt catalysts by facilitating the access of electroactive species to the full-extent Pt surface.

In the last decades, a great deal of attention has been paid to nano- and/or meso-structured materials with highly porous networks and high surface area due to their impressive industrial applications involving electrochemical catalysts, inclusion vessels, and adsorbents. Up to now, a wide range of compositions such as silica, carbon, inorganic-organic hybrids, polymers, and metals, have been successfully prepared by various methods.^{1,2} Recently, a great deal of effort has been devoted to the synthesis of metal-based nanostructures with high surface areas, because of their unique electrocatalytic properties.³ In particular, Pt-based nanostructured materials have currently attracted widespread interest, because of their potential application as a catalyst in PEM fuel cells. Both soft- and hard-templates have been commonly employed for the synthesis of nanostructured Pt materials. In hard-templating method, well ordered mesoporous silica has been generally used as rigid templates.^{4–8} Alternatively, soft-templates, such as surfactants, also can be used for the forming nanopores structures.^{9,10} For instance, well-ordered mesoporous Pt can be easily prepared by chemical or electrochemical reduction of dissolved Pt salts in lyotropic liquid crystals made of highly concentrated surfactants.9-12

To realize high Pt surface areas, there have been some reports on Pt hollow nanostructures, which have superior electrochemical properties.^{13–16} So far, the Pt hollow nanostructures have been successfully synthesized by coating Pt on various spherical templates such as silica,^{13,17} Co,^{16,18} Ag^{19–21} and other materials.^{14,22} However, in all of these cases, complex procedures and the use of expensive materials as templates are employed,

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which is noneconomic for practical scale up. Furthermore, in the previous works, the Pt shell thicknesses were not precisely controlled.^{13–22} The most disadvantageous point in the previous works is that the Pt shell of the hollow structures has no well-developed nanoporosity. Therefore, guest species from outside are not allowed to get access to inner parts of the hollow structures, resulting decreasing the effective Pt surfaces. Hence, the development of a facile and economic method for synthesis of Pt spheres with hollow interior and nanosponge shell with very high surface area is a practical and challenging issue to be solved urgently.

In this communication, we newly propose a facile and efficient method to prepare Pt spheres with hollow interior and nanosponge shell with high surface. Silica particles functionalized with amino group (with around 100 nm in diameter) are used as template to form the hollow interior, while nonionic surfactant assist to create the Pt nanosponge shell.^{23,24}

To prepare the Pt spheres with hollow interior and nanosponge shell, silica nanoparticles modified with amino group were ultrasonically dispersed in K₂PtCl₄ solution containing Pluronic F127. The used amounts of 20 mM K₂PtCl₄ solution were varied from 0.0 ml to 10 ml, while the amounts of the added silica particles were fixed to 6.0 mg. Then, 0.1 M ascorbic acid (AA) was added, and the mixture was sonicated for 15 min. After washing three times with water, the product was added to 10 wt% hydrofluoric acid solution and placed for 3 days at room temperature in order to completely remove silica template. The final product was washed five times with water and dried at 45 °C.

Fig. 1 shows transmission electron microscopy (TEM) images of the hollow Pt spheres prepared under a typical solution with 7.5 ml Pt solution. The lower magnification image (Fig. 1a) revealed that the resulting Pt dendritic structure was assembled with plentiful interconnected nanowires with 2 nm in diameter. The Pt hollow particles were uniform in morphology without formation of by-products, demonstrating the high yield synthesis (Fig. S1a, b†). As shown in Fig. 1b, lattice fringes with a *d* spacing of 0.23 nm were clearly observed, which corresponded to a $\langle 111 \rangle$ plane of Pt face-centered cubic (fcc) structure.

In the present synthetic process, NH₂-modified silica particles were well dispersed in Pt precursor solution containing surfactants. Then, by addition of AA to the solution, the Pt deposition was occurred. At the early stages of the reaction, the Pt seeds were formed on the silica particle surface, because of the high surface affinity for the Pt seeds which is derived from the

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Fig. 1 (a) Low-magnification and (b) high-magnification TEM images of hollow Pt spheres under a typical solution with 7.5 ml Pt solution.

strong interaction between the amino group and the metal particles.²⁵ During the progress of the Pt deposition, the primary Pt seeds covering on the silica particles served as the nucleation sites for the further growth of Pt. At this stage, Pluronic F127 chains as a structure directing agent were absorbed on the surface of deposited Pt to facilitate the growth of the dendritic Pt shells.^{23,24} To elucidate the effect of amino modification on the silica surface, further investigation was performed in which silica particles without amino group were used as template (Fig. S1c). It was clearly revealed that the amino groups on the silica surface played an important key role for making attachment sites for initial Pt seeds and then acted as nucleation sites for the subsequent Pt growth, whereas non-functioned silica template could not act as template for the formation of hollow Pt spheres and led to the separation of silica particles and Pt dendrites (Fig. S1c[†]).

The SEM images clearly confirmed the three-dimensional (3D) globular shape and also clearly verified the empty spaces of highly branched nanowires (Fig. S1a, b⁺). In the dendritic Pt shells, lots of Pt nanowires were highly branched and extended in various directions, to form an interconnected nanosponge structure. In such a nanoporous structure, accessibility to inner parts of Pt hollows will be improved by the diffusion of guest species through empty spaces among interconnected nanowires. N₂ adsorption-desorption isotherm of the obtained Pt spheres gave a BET surface area of 36.3 m² g⁻¹ (Fig. S2^{\dagger}), which is higher than the reported value (29.0 m² g⁻¹) for hollow Pt spheres prepared by photocatalytic reduction of Pt complex under light illumination.¹³ For comparison, surface areas of commercial platinum catalysts (Pt black) ranges from 20 to 25 m² g⁻¹. The improved surface area was most likely derived from the presence of nanoporous dendritic shells.

Furthermore, in our method, the Pt shell thicknesses could be precisely tuned simply by varying the amounts of Pt precursor. To investigate the effect of Pt amounts on the shell thicknesses, several hollow Pt spheres were synthesized with various amounts of Pt precursor solution in the range between 0.0 ml to 10 ml (The amounts of the added silica particles were fixed to 6.0 mg. See the details in ESI.†). TEM images of hollow Pt spheres before and after the silica removal were shown in Fig. 2 and S3,† respectively. The average shell thicknesses were measured by TEM images (Fig. 3). The average shell thicknesses were proportionally increased with increasing the Pt amounts.

It is noteworthy that in a small amount of Pt solution (2.5 ml), the hollow structures were mechanically unstable (Fig. 2a), because the spherical hollow nanostructures collapsed after the silica removal by HF treatment. When the amount of Pt solution was not enough, individual entities could not be joined well (Fig. S3b[†]) and the hollow structures were destroyed easily. As shown in TEM images (Fig. 2a and b), the hollow structures prepared from 5.0 ml Pt solution collapsed partially. In contrast, when the amounts of Pt solution were increased up to 10 ml. irregular Pt dendrites without inner hollows were formed as a by-product (Fig. 2d). The isolated Pt seeds nucleated, resulting in Pt dendrites independently grew. The optimum amount of Pt solution was found to be 7.5 ml. Under the optimized condition, after immobilization of Pt seeds on silica particles, Pt nanowires grew and branched out in various directions. Also, with the assistance of surfactants,^{23,24} nanosponge shells consisting of interconnected highly branched nanowires were uniformly coated on the silica particle surface without by-products. Even after removing silica and applying the centrifugation and sonication processes, the hollow structures did not collapse, showing very manically stable robust hollows (not shown).

As preliminary investigation on electrocatalytic activity of the obtained hollow Pt spheres with different shell thicknesses, methanol oxidation was measured by using cyclic voltammograms (CVs) method (The details of electrochemical measurements were given in ESI.†). Fig. 4 shows massnormalized activities. The Pt hollow particles with the lowest shell thicknesses (prepared with 2.5 ml Pt solution) exhibited the lowest catalytic activity. It can be supposed that access of methanol molecules to inner parts of electrode was restricted, because the inner void spaces of the original hollow structures



Fig. 2 TEM images of hollow Pt spheres after silica removal. Various hollow Pt spheres were prepared from precursor solutions containing different Pt amounts. The amounts of added Pt solution are (a) 2.5 ml, (b) 5.0 ml, (c) 7.5 ml, and (d) 10 ml, respectively. The collapse of the hollow structures is indicated by while arrows, while the isolated Pt dendrite (as by-product) is indicated by white arrows.





Fig. 3 Relationship between the average Pt shell thicknesses and the added amounts of Pt solutions. The amounts of added Pt solution in the starting solutions are noted in parentheses.

collapsed and the Pt particles were highly aggregated (Fig. 2a). With increasing the amounts of the Pt solution to 7.5 ml, electrocatalytic activity for methanol oxidation reaction was dramatically increased. The maximum electrocatalytic activity (80 mA mg^{-1}) was around 1.7 times larger than that of commercially available Pt black. By improvement of mechanical stability of hollow structures, electroactive species could easily gain access to the whole surface of Pt through the hollow spaces. However, with the further increase of Pt amounts to 10 ml, the catalytic activity was decreased. As shown in TEM results (Fig. 2d), the formation of the undesired by-products and thicker shells prevented accessibility of methanol molecules to all the exposed Pt surfaces. In other words, all of the exposed Pt surface could not effectively act as reaction media.

In conclusion, we developed a facile method to synthesize hollow Pt spheres with tunable nanosponge shell thicknesses by using silica particles as templates. The obtained hollows possessed highly nanoporous structure, providing high surface area. Such a unique Pt nanostructure effectively improved the electrocatalytic performance as Pt catalysts by facilitating the access of electroactive species to the whole Pt surface. Currently, a great deal of attention has been attracted to the



Fig. 4 Cyclic voltammograms displaying oxidation reaction of methanol, catalyzed by hollow Pt particles prepared from (a) 2.5 ml, (b) 5.0 ml, (c) 7.5 ml, (d) 10 ml Pt solution, respectively. For comparison, (e) commercially available Pt black powders are also measured.

inorganic core-shell^{26,27} and hollow materials^{28–34} in material research fields. However, their compositions have been very limited to polymers, silica, carbon, and metal oxides.^{26–34} This synthetic concept can open a new avenue to create nanostructured metals.

Notes and references

- 1 Y. Wan and D. Zhao, Chem. Rev., 2007, 107, 2821.
- 2 A. H. Lu and F. Schüth, Adv. Mater., 2006, 18, 1793.
- 3 Y. Yamauchi and K. Kuroda, *Chem.-Asian J.*, 2008, 3, 664.
- 4 Z. Liu, Y. Sakamoto, T. Ohsuna, K. Hiraga, O. Terasaki, C. H. Ko, H. J. Shin and R. Ryoo, *Angew. Chem. Int. Ed.*, 2000, **39**, 3107.
- 5 A. Takai, Y. Doi, Y. Yamauchi and K. Kuroda, J. Phys. Chem. C, 2010, 114, 7586.
- 6 H. J. Shin, C. H. Ko and R. Ryoo, J. Mater. Chem., 2001, 11, 260.
- 7 H. J. Shin, R. Ryoo, Z. Liu and O. Terasaki, J. Am. Chem. Soc., 2001, 123, 1246.
- 8 Y. Doi, A. Takai, Y. Sakamoto, O. Terasaki, Y. Yamauchi and K. Kuroda, *Chem. Commun.*, 2010, 46, 6365.
- 9 G. S. Attard, C. G. Goltner, J. M. Corker, S. Henke and R. H. Templer, *Angew. Chem.*, 1997, **109**, 1372.
- 10 G. S. Attard, P. N. Bartlett, N. R. B. Coleman, J. M. Elliott, J. R. Owen and J. H. Wang, *Science*, 1997, **278**, 838.
- 11 Y. Yamauchi, A. Sugiyama, R. Morimoto, A. Takai and K. Kuroda, Angew. Chem., Int. Ed., 2008, 47, 5371.
- 12 Y. Yamauchi, T. Yokoshima, H. Mukaibo, M. Tezuka, T. Shigeno, T. Momma, T. Osaka and K. Kuroda, *Chem. Lett.*, 2004, **33**, 542.
- 13 H. Wang, Y. Song, Z. Wang, C. J. Medforth, J. E. Miller, L. Evans, P. Li and J. A. Shelnutt, *Chem. Mater.*, 2008, **20**, 7434.
- 14 Y. Song, R. M. Garcia, R. M. Dorin, H. Wang, Y. Qiu and J. A. Shelnutt, *Angew. Chem., Int. Ed.*, 2006, **45**, 8126.
- 15 G. Lee, S. I. Choi, Y. H. Lee and J. T. Park, Bull. Korean Chem. Soc., 2009, 30, 1135.
- 16 H. P. Liang, H. M. Zhang, J. S. Hu, Y. G. Guo, L. J. Wan and C. L. Bai, Angew. Chem., Int. Ed., 2004, 43, 1540.
- 17 L. Lu, R. Capek, A. Kornowski, N. Gaponik and A. Eychmuller, Angew. Chem., Int. Ed., 2005, 44, 5997.
- 18 J. Zhao, W. Chen, Y. Zheng and X. Li, J. Power Sources, 2006, 162, 168.
- 19 S. Guo, S. Dong and E. Wang, Chem.-Eur. J., 2008, 14, 4689.
- 20 J. Yang, J. Y. Lee, H. P. Too and S. Valiyaveettil, J. Phys. Chem. B, 2006, 110, 125.
- 21 H. M. Chen, R. S. Liu, M. Y. Lo, S. C. Chang, L. D. Tsai, Y. M. Peng and J. F. Lee, *J. Phys. Chem. C*, 2008, **112**, 7522.
- 22 H. Wang, Y. Song, C. J. Medforth and J. A. Shelnutt, J. Am. Chem. Soc., 2006, **128**, 9284.
- 23 L. Wang and Y. Yamauchi, J. Am. Chem. Soc., 2009, 131, 9152.
- 24 (a) H. Ataee-Esfahani, L. Wang and Y. Yamauch, *Chem. Commun.*, 2010, 46, 3684; (b) H. Ataee-Esfahani, L. Wang, Y. Nemoto and Y. Yamauchi, *Chem. Mater.*, 2010, 22, 6310.
- 25 T. Pham, J. B. Jackson, N. J. Halas and T. R. Lee, *Langmuir*, 2002, 18, 4915.
- 26 Y. Deng, Y. Cai, Z. Sun, J. Liu, C. Liu, J. Wei, W. Li, C. Liu, Y. Wang and D. Zhao, J. Am. Chem. Soc., 2010, 132, 8466.
- 27 Y. Deng, D. Qi, C. Deng, X. Zhang and D. Zhao, J. Am. Chem. Soc., 2008, 130, 28.
- 28 J. Fu, Q. Xu, J. Chen, Z. Chen, X. Huang and X. Tang, Chem. Commun., 2010, 46, 6563.
- 29 S. A. Dergunov, K. Kesterson, W. Li, Z. Wang and E. Pinkhassik, *Macromolecules*, 2010, 43, 7785.
- 30 Y. Wang, C. Tang, Q. Deng, C. Liang, D. H. L. Ng, F. L. Kwong, H. Wang, W. Cai, L. Zhang and G. Wang, *Langmuir*, 2010, 26, 14830.
- 31 M. Feyen, C. Weidenthaler, A. H. Lu and F. Schüth, J. Am. Chem. Soc., 2010, 132, 6791.
- 32 A. H. Lu, W. C. Li, G. P. Hao, B. Spliethoff, H. J. Bongard, B. B. Schaack and F. Schüth, *Angew. Chem. Int. Ed.*, 2010, 49, 1615.
- 33 P. M. Arnal, M. Comotti and F. Schüth, Angew. Chem., Int. Ed., 2006, 45, 8224.
- 34 F. Zhang, G. B. Braun, Y. Shi, Y. Zhang, X. Sun, N. O. Reich, D. Zhao and G. Stucky, J. Am. Chem. Soc., 2010, 132, 2850.