Nanoparticles

Pt Hollow Nanospheres: Facile Synthesis and Enhanced Electrocatalysts**

Han-Pu Liang, Hui-Min Zhang, Jin-Song Hu, Yu-Guo Guo, Li-Jun Wan, and Chun-Li Bai**

Considerable attention has been paid to alternative energy sources such as hydrogen and fuel cells as energy sources in an attempt to relieve the pollution and energy crisis. Among various candidates, Pt has stimulated considerable research into its use as a catalyst in the production of hydrogen from methane, in automobile catalytic converters, and particularly in the direct methanol fuel cell (DMFC).[1] However, a critical problem with Pt-based catalysts is their prohibitive cost. Therefore, economical and effective alternative catalysts are required and cost-effective routes are being sought to make more-efficient Pt catalysts. To date, efforts have focused on the development of techniques to produce Pt catalysts with a high surface area to achieve high catalytic performance and utilization efficiency.[2]

Hollow metallic nanospheres exhibit catalytic activities different from their solid counterparts with the advantages of low density, saving of material, and reduction of costs. For example, Hyeon and co-workers reported that hollow Pd spheres show good catalytic activities in Suzuki cross-coupling reactions and can be reused many times without the loss of catalytic activity.[3] Traditional ways to fabricate hollow spheres have focused on various sacrificial templates, including polystyrene spheres,[4] silica spheres,[3,5] resin spheres,[6] vesicles,[7] liquid droplets,[8] and microemulsion droplets.[9] The common procedures of these methods relate to the removal of the core template or two immiscible liquid phases. The procedures are technically complicated, which limits their application to some extent. Recently, Xia and co-workers reported a one-step approach to produce metallic hollow nanospheres with average diameters of ≈50 nm by combining Ag nanoparticles with a solution of an appropriate salt precursor.[10] However, an AgCl precipitate was formed in the procedure, which made the procedure complicated and influenced the yield of hollow nanospheres. Herein we described a facile, efficient, and economical route to the

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[*] H.-P. Liang,[+] H.-M. Zhang, J.-S. Hu,[+] Y.-G. Guo,[+] L.-J. Wan, C.-L. Bai
Center for Molecular Science, Institute of Chemistry
Chinese Academy of Sciences
Beijing 100080 (China)
Fax: (+86) 10-6255-8934
E-mail: wanlijun@iccas.ac.cn
clbai@iccas.ac.cn

[+] Also at the Graduate School of Chinese Academy of Sciences
Beijing 100064 (China)

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large-scale synthesis of Pt hollow nanospheres with an average diameter of 24 nm. The synthesized Pt hollow nanospheres, composed of discrete Pt nanoparticles, show good electrocatalytic activity in the oxidation of methanol.

The key idea of our method for the synthesis of the Pt hollow nanospheres is to exploit the replacement reaction between Co nanoparticles and H_2PtCl_6. The fabrication of Co nanoparticles is an important step. The formation of Co particles is easily determined, as the solution undergoes a color change from transparent to dark. Citrate is present as a capping agent to prevent the growth of Co nanoparticles through repulsive forces between negatively charged cobalt nanoparticles. To avoid the oxidation of Co nanoparticles in the presence of atmospheric oxygen, nitrogen is bubbled through the solution during the whole procedure (see Experimental Section for details). As the standard reduction potential of the $PtCl_6^{2-}/Pt$ redox pair (0.735 V vs. the standard hydrogen electrode (SHE)) is much higher than that of the Co^{2+}/Co redox pair (−0.277 vs. SHE), Co nanoparticles are immediately oxidized to cobalt ions when the solution of Co nanoparticles is added to the H_2PtCl_6 solution. The H_2PtCl_6 solution turns from pale yellow to black at the same time, which suggests the oxidation of Co nanoparticles and the formation of Pt hollow nanospheres. As this replacement reaction occurs rapidly, the Pt atoms nucleate and grow into very small particles, eventually evolving into a thin shell around the cobalt nanoparticles. The shell should have an incomplete porous structure because Co^{2+} and $PtCl_6^{2-}$ continuously diffuse across the shell until the Co nanoparticles have been completely consumed. Spherical Pt materials were fabricated on a large scale (see Figure S1 in the Supporting Information). If $NaBH_4$ reduces all the Co^{2+} to Co nanoparticles, the solutions of Co nanoparticles should react completely with H_2PtCl_6 on the basis of the stoichiometric relationship in Equation (1).

$$2\,Co + PtCl_6^{2-} = Pt + 2\,Co^{2+} + 6\,Cl^- \qquad (1)$$

The structure and morphology of these Pt hollow nanospheres were investigated by transmission electron microscopy (TEM). Figure 1 a is a typical large-scale TEM image. It was found that the centers of the spheres are brighter than the edges. The structural details are revealed in high-magnification TEM (Figure 1 b). The individual Pt spheres are composed of an empty core with a shell, that is, a hollow structure. The thickness of the shell is ≈2 nm. The average diameter of the nanospheres was statistically calculated to be 24 ± 2 nm. From the high-magnification TEM image in Figure 1 b, the shells of the Pt hollow nanospheres seem to be rough and consist of Pt nanoparticles with a size of ≈2 nm. Another feature is that the shell is incomplete and porous, not solid. This feature endows the Pt hollow nanospheres with a high surface area.

To evaluate the electrocatalytic activity of the Pt hollow nanospheres, solid Pt nanoclusters with roughly the same diameter as that of the Pt hollow nanospheres were fabricated by a seeding growth strategy. The morphology and structure of the solid Pt nanocluster was characterized by TEM. Figure 1 c and d are the low- and high-magnification TEM images, respectively. In Figure 1 c, well-dispersed Pt nanoclusters are observed. The average diameter of the clusters was statistically measured to be ≈29 ± 3 nm. From the high-magnification TEM image in Figure 1 d, it can be seen that each cluster is composed of small nanoparticles with a size of ≈4 nm. The crystalline feature was confirmed by microelectronic diffraction pattern (see Figure S2). Both the Pt hollow nanospheres and nanoclusters adopt a typical face-centered-cubic polycrystalline structure.

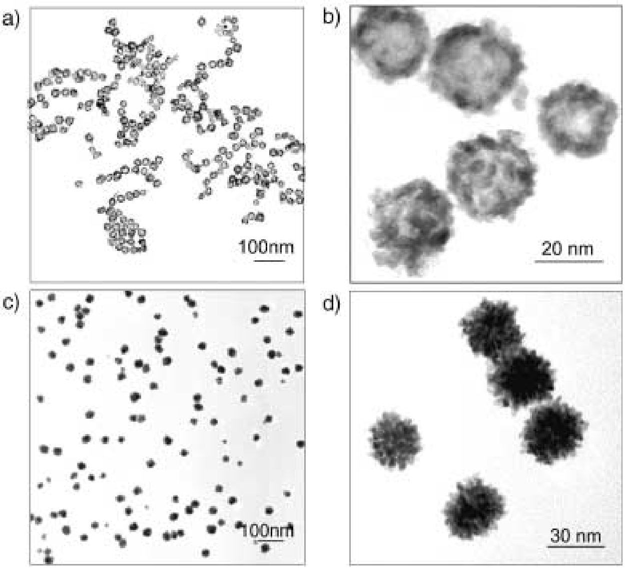

Figure 1. TEM images of Pt hollow nanospheres (a) and (b), and solid nanoclusters (c) and (d).

The electrocatalytic activity of the Pt hollow nanospheres for the oxidation of methanol was demonstrated and compared with that of solid Pt nanoclusters by using a well-used electrochemical reaction in a solution of H_2SO_4.[11] A glassy carbon disk electrode with a diameter of 3 mm was used. The loading of the hollow nanospheres and the solid nanoclusters on the electrode surface was the same ($0.0175\ mg\,cm^{-2}$). From the voltammograms in Figure 2, both the Pt hollow nanospheres and nanoclusters show catalytic behavior for the electrooxidation of methanol by the appearance of an oxidation current in the positive potential region. The consistent appearance of the two voltammograms can be seen in the figure. The onset potentials are around 0.3 V (vs. SCE). The peak potentials for the oxidation of methanol are approximately 0.65 V (vs. SCE), in agreement with literature values.[11] The peak currents of the nanosphere and nanocluster catalysts are 54 μA and 19 μA, respectively. From the current measurements, it is clear that the catalytic activity of the Pt hollow nanospheres is twice that of the solid Pt nanoclusters. The remarkably high oxidation current for the hollow-sphere catalysts is directly related to the high surface area. Since Pt hollow nanospheres are coreless, a larger number of Pt nanospheres were obtained relative to that found with the same loading of solid Pt nanoclusters. Furthermore, the incomplete shell of hollow nanospheres may provide the interior surface for the catalytic reaction. If we assume that the inner and outer surfaces of a hollow

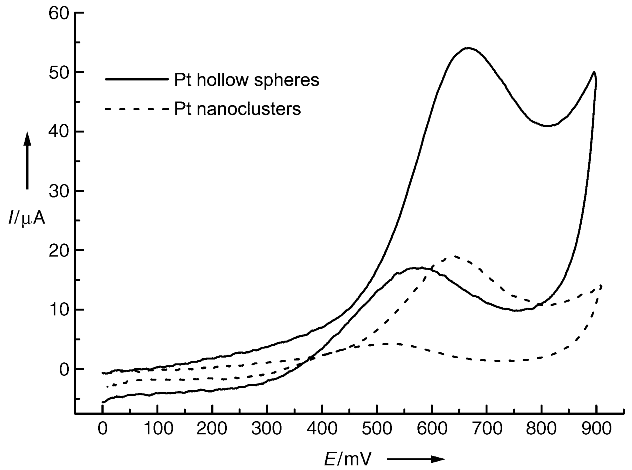

Figure 2. Cyclic voltammograms of Pt solid nanoclusters (dashed line) and hollow nanospheres (solid line) on a glass carbon disk electrode in H_2SO_4 (0.5 M) and methanol (0.6 M). The same loading of nanospheres and solid nanoclusters was applied to the electrodes (0.0175 mg cm^{-2}). Scan rate = 50 mV s^{-1}.

nanosphere can participate in the catalytic reaction, the surface area of the single hollow nanosphere is approximately 1.16 times as that of a single solid nanocluster. The higher surface area of Pt nanospheres results in a higher catalytic activity. Consequently, our results suggest a simple route to enhance the catalytic efficiency of Pt catalysts by a simple improvement of the morphology. Therefore, enhanced electrocatalysts can be obtained as hollow nanospheres without changing catalyst loadings.

In summary, a facile procedure for the large-scale synthesis of Pt hollow nanosphere catalysts was developed. The catalysts can be simply prepared at room temperature in a homogeneous solution with Co nanoparticles as sacrificial templates. The method presented herein is more cost-effective than previous methods. The incomplete and porous shells of the Pt hollow nanospheres have a higher surface area and therefore exhibit enhanced electrocatalytic performance. This approach was successfully extended to the fabrication of Au, Pd, and their bimetallic hollow nanospheres. These metallic hollow nanospheres could be useful in industrial applications including catalytic nanoreactors, plasmonic devices, and near-infrared absorbers.

Experimental Section

Cobalt chloride, $NaBH_4$, H_2PtCl_6, and citric acid were obtained from Beijing Chemical Reagent Ltd. and were used without further purification. The Co nanoparticles were fabricated by the addition of a solution of $CoCl_2$ (0.4 M; 0.1 mL) to a deaerated aqueous solution (100 mL) of $NaBH_4$ (4 mM) and citric acid (0.4 mM). For the preparation, a solution of citric acid and $NaBH_4$ was first prepared. $NaBH_4$ should be freshly dissolved. H_2 was evolved during the reaction and continued for several minutes. When gas evolution ceased, the resulting solution (100 mL) was immediately added to a stirred solution of H_2PtCl_6 (1 mM; 30 mL) at room temperature.

The obtained solution was centrifuged, and the precipitate was collected, washed, and dispersed by ultrasonic treatment, dropped onto a carbon-coated copper grid, and characterized by transmission electron microscopy (TEM, Philips TECNAI-20). A Hitachi S-4300F scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyzer (Phoenix) was used to determine the morphology and the composition of the hollow nanospheres.

Pt solid nanoclusters with roughly similar diameter were prepared by a seeding growth strategy. Pt seeds with diameters of ≈4 nm were fabricated according to Teranishi et al.[12] Briefly, a mixture of aqueous H_2PtCl_6 (6.0 mM; 5 mL; 30 µmol of Pt), water (4.5 mL), and poly(*N*-vinyl-2-pyrrolidone) (PVP; 30 µmol) in methanol (40.5 mL) was heated at reflux in a 100-mL flask for 3 h under air to synthesize the PVP-protected Pt nanoparticles. The above solution (1 mL) was added to the H_2PtCl_6 solution (1 mM; 10 mL). Excess ascorbic acid (100 mM; 1.2 mL) was added to the stirred solution. The reaction was continued until the solutions turned black in color, suggesting the formation of Pt nanoclusters.

Electrochemical measurements were conducted in an electrochemical cell with a three-electrode configuration at room temperature. The working electrode was a glassy carbon disk with a diameter of 3 mm, polished with Al_2O_3 paste and washed ultrasonically in Millipore water. The electrode was loaded with Pt nanospheres and nanoclusters. The same loading (0.0175 mg cm^{-2}) was used for the two catalysts. Electrocatalytic oxidation measurements were carried out in a solution of H_2SO_4 (0.5 M) and methanol (0.6 M) on a Basic Electrochemical System from EG&G instruments, Princeton Applied Research (PAR).

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