A Bis(*p*-sulfonatophenyl)phenylphosphine-Based Synthesis of Hollow Pt Nanospheres

J. Yang,[†] **Jim Yang Lee,***[†,‡] **Heng-Phon Too,**[‡,§] **and S. Valiyaveettil**[∥]

Department of Chemical and Biomolecular Engineering, National University of Singapore,
10 Kent Ridge Crescent, Singapore 119260, Singapore−MIT Alliance, 4 Engineering Drive 3,
National University of Singapore, Singapore 117576, Department of Biochemistry,
National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, and
Department of Chemistry, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

We report herewith the synthesis of hollow Pt nanospheres by using bis(*p*-sulfonatophenyl)phenylphosphine to selectively remove the Ag cores of Ag−Pt core−shell nanoparticles. Core−shell Ag−Pt nanoparticles were first obtained by the successive reduction method with a discontinuous Pt shell to allow the BSPP passage. Transmission electron microscopy imaging of the core−shell Ag−Pt nanoparticles before and after BSPP dissolution showed little changes in the particle size, indicating that the removal of the Ag cores had occurred isomorphously. The hollow Pt nanospheres, together with the predecessor Ag−Pt core−shell particles of the same size, were transferred from water to toluene and surface modified by dodecylamine in toluene. This allows the catalytic activities of solid and hollow Pt particles in room temperature methanol oxidation reaction to be compared under conditions of identical particle size and the same surface environment. The measured higher specific activity of the Pt hollow nanospheres could then be attributed unambiguously to the larger specific surface area prevalent in the porous hollow structure.

Introduction

The synthesis of uniform hollow spheres with nanometer dimensions and tailored structural, optical, and surface properties is of interest to a wide range of applications, as the products are potentially useful as photonic crystals, drug delivery vehicles, fillers, and catalysts.[1] While a number of hollow nanospheres have been fabricated from sacrificial templates of polymer and inorganic spheres,[2−4] liquid droplets,[5] vesicles,[6] and microemulsion droplets,[7] these common templates are too large for the preparation of hollow Pt nanospheres. Liang and co-workers[8] took a different approach recently, using the replacement reaction initially developed by Xia and co-workers[9] to successfully produce hollow Pt nanospheres. In their implementation, Pt ions in H_2PtCl_6 were reduced by preformed Co nanoparticles. The authors reported enhanced catalytic activity in the room-temperature electro-oxidation of methanol and attributed the increase to the larger surface areas available in hollow nanospheres. Another method of Pt nanosphere preparation, which has better preservation of the particle geometry and surface conditions, is reported here. In this new method, bimetallic core−shell Ag−Pt nanoparticles are first synthesized by the successive reduction of Ag and Pt precursor salts. This is followed by the selective dissolution of the Ag cores with bis-(*p*-sulfonatophenyl)phenylphosphine (BSPP), leaving behind hollow Pt nanoparticles with nearly the same size as their core−shell predecessors. The new synthesis method has several notable advantages compared to the replacement reaction approach: (1) The BSPP synthesis can be carried out at room temperature amid a greater ease of control. On the contrary, the replacement reaction approach requires elevated temperatures. (2) The replacement reaction is more predisposed to forming alloy nanoshells,[9] whereas the BSPP synthesis forms only pure Pt nanoshells. In addition, as will be described in detail later, the BSPP synthesis can be combined with a phase transfer procedure to standardize the surface conditions of Pt hollow spheres and their solid counterparts, thereby allowing the catalytic activities of hollow and solid Pt nanospheres to be compared under well-controlled conditions to keep the experimental uncertainties to a minimum.

Experimental Section

$AgNO_3$, K_2PtCl_4, and dodecylamine (98%) from Aldrich, sodium borohydride, sodium citrate (98%), and ethanol (99%) from Merck, toluene from Baker, BSPP dihydrate dipotassium salt (97%) from Strem Chemicals were used as received. Deionized water was distilled by a Milli-Q water purification system. All glassware and Teflon-coated magnetic stir bars were cleaned with aqua regia, followed by copious rinsing with distilled water before drying in an oven.

Successive reduction, or the seed-mediated growth method, was used to prepare bimetallic Ag−Pt nanoparticles with the core−shell structure. Citrate-stabilized Ag seeds were obtained from the $NaBH_4$ reduction of $AgNO_3$. Briefly, 1.6 mL of 40 mM aqueous sodium citrate solution was added to 20 mL of 1 mM aqueous $AgNO_3$ solution. Under vigorous stirring, 0.4 mL of 100 mM aqueous $NaBH_4$ solution was added dropwise to prepare a Ag hydrosol in which citrate ions served as the stabilizers. The molar ratio of $NaBH_4$ to $AgNO_3$ was kept above 5 to ensure the complete reduction of Ag (I) to metallic silver. The Ag hydrosol was left to age for 6 h after the $NaBH_4$ addition to completely decompose the residual $NaBH_4$. For the preparation of bimetallic core−shell Ag−Pt nanoparticles, 20 mL of

* To whom correspondence should be addressed. Fax: 65 6779 1936. Tel: 65 6874 2899. E-mail: cheleejy@nus.edu.sg.
† Department of Chemical and Biomolecular Engineering.
‡ Singapore−MIT Alliance.
§ Department of Biochemistry.
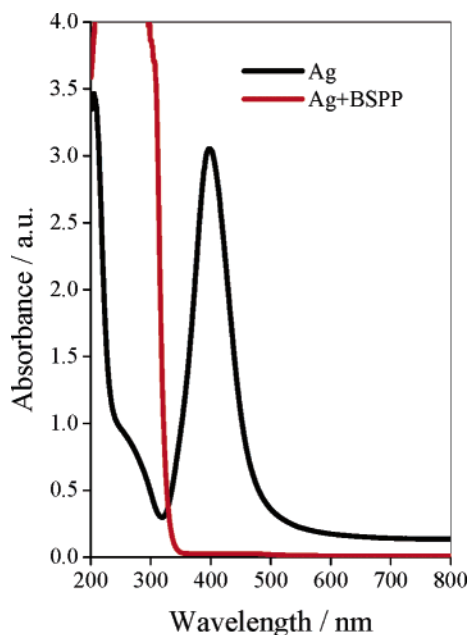∥ Department of Chemistry.

Figure 1. UV−visible spectra of Ag hydrosol before the addition of BSPP and 3 h later.

aqueous K_2PtCl_4 solution was refluxed at 110 °C for 1 h, and then the Ag hydrosol prepared above, together with 1.6 mL of 40 mM sodium citrate solution, was added. The mixture was refluxed for one more hour, and a reddish-brown solution of core−shell Ag−Pt nanoparticles was obtained.

For the preparation Pt hollow nanospheres, 50 mg of solid BSPP was added to 20 mL of the core−shell Ag−Pt prepared

above, and the mixture was aged for 4 h or more to completely oxidize the Ag cores. The phase transfer of BSPP-stabilized Pt hollow nanospheres from the aqueous phase to toluene was carried by a previously reported procedure.[10,11] Briefly, 20 mL of the hydrosol of Pt hollow spheres were mixed with 20 mL of ethanol containing 400 μL of dodecylamine. After 1 min of stirring, 10 mL of toluene was added, and stirring continued for 3 more minutes. Phase transfer of the dodecylamine-stabilized Pt hollow nanospheres from water to toluene occurred quickly with nearly 100% efficiency, as shown by the complete bleaching of the color in the aqueous phase.

A JEOL JEM2010 microscope was used to obtain transmission electron microscopy (TEM) images of the nanoparticles. For TEM measurements a drop of the nanoparticle solution was dispensed onto a 3-mm copper grid covered with a continuous carbon film. Excess solution was removed by an adsorbent paper, and the sample was dried under vacuum at room temperature. UV−visible spectroscopy of Pt hollow nanospheres and the core−shell Ag−Pt nanoparticles was carried out on a Shimadzu UV-2450 spectrophotometer. The nanoparticles before and after BSPP treatment were also analyzed by energy-dispersive X-ray (EDX) analysis on a JEOL MP5600 SEM. Samples were drawn from particles recovered in the aqueous phase by centrifugation, which were then washed copiously with distilled water and vacuum dried at room temperature.

Electrochemical measurements were performed in a standard three-electrode electrochemical cell at room temperature. The working electrode was a 5-mm glassy carbon disk, polished with Al_2O_3 paste and washed in distilled water. The surface area of the vitreous carbon disk was 0.1962 cm^2. Before electrochemical measurements, Pt hollow spheres and core−shell Ag−Pt nano-
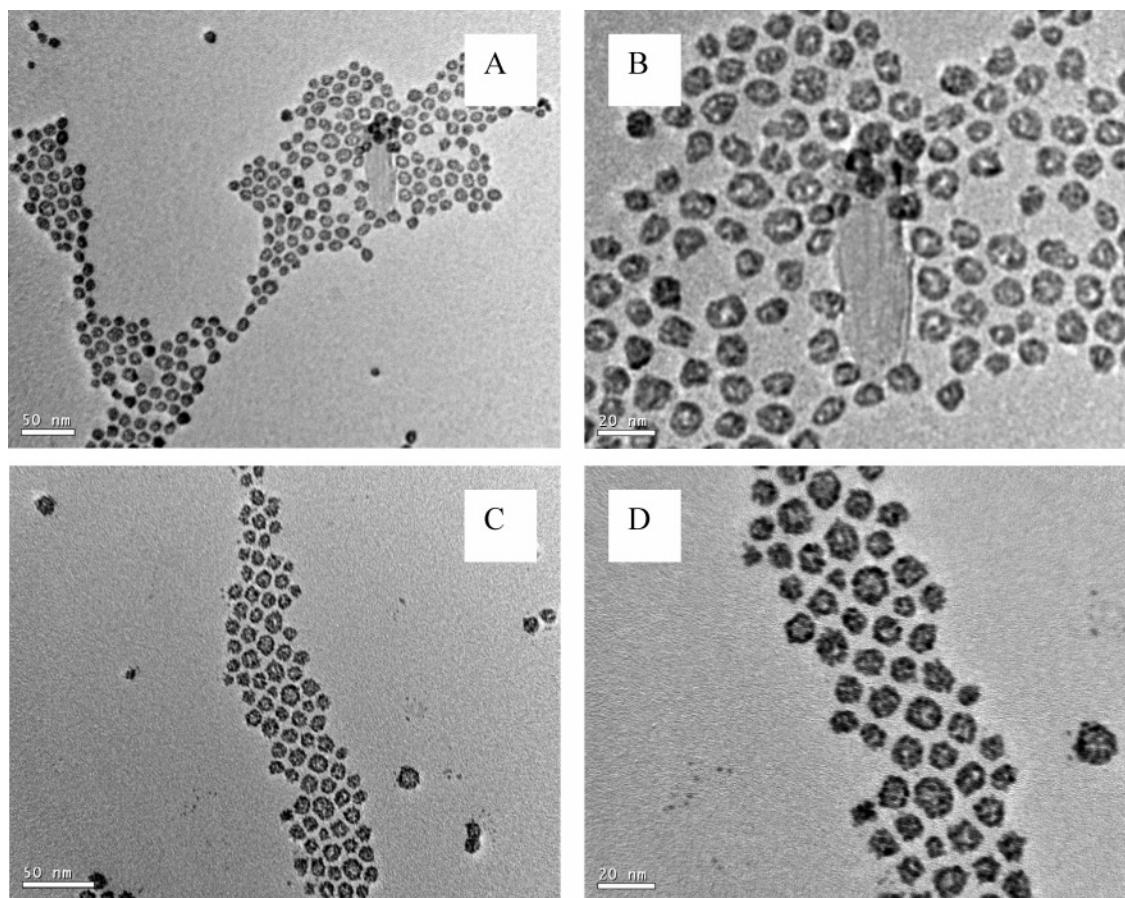

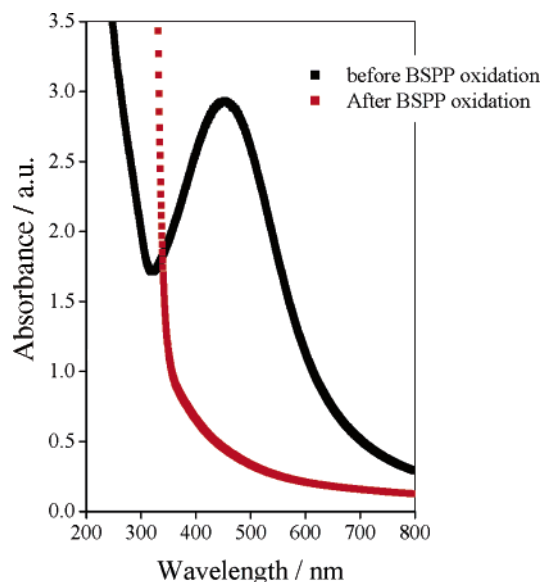**Figure 2.** A and B, TEM images of core−shell Ag−Pt nanoparticles; C and D, Pt hollow nanospheres.

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Figure 3. UV−visible spectra of core−shell Ag−Pt nanoparticles before (black trace) and after (red trace) BSPP oxidation.

Figure 4. Digital photos of core−shell Ag−Pt hydrosol before (A) and after (B) BSPP oxidation.

particles were first extracted to toluene to standardize the surface conditions for the two types of nanoparticles and then recovered from toluene by 15 min of centrifugation at 15 000 rpm. Pt hollow nanospheres (0.07 mg) and 0.11 mg of core−shell Ag−Pt nanoparticles were used to keep the number of hollow spheres and core−shell nanoparticles approximately the same on the electrode. The room-temperature oxidation of methanol was carried out in a mixture of 0.5 M H_2SO_4 and 0.6 M methanol using an EG&G model 273 potentiostat/galvanostat.

Results and Discussion

We have discovered recently that Ag nanoparticles could be oxidized by BSPP. Figure 1 shows the change in the UV−visible spectra of Ag nanoparticles before the addition of BSPP and 3 h after the addition. The surface plasmon resonance (SPR) of Ag nanoparticles at 397 nm was completely obliterated after 3 h, indicating the oxidation of Ag nanoparticles. The oxidized Ag could be easily reduced by $NaBH_4$, with full restoration of the characteristic yellowish-brown color and the SPR of Ag at 397 nm. The oxidation of Ag nanoparticles by BSPP is central to the preparation of Pt hollow nanospheres reported here. In this method, bimetallic core−shell Ag−Pt nanoparticles are first prepared by the successive reduction of Ag and Pt precursor salts. This is followed by the removal of Ag by BSPP oxidation, leaving behind Pt hollow nanoparticles with the same particle size as their core−shell predecessors. While HNO_3 can also be used to remove Ag from the core−shell Ag−Pt nanoparticles, it induces the aggregation of the nanoparticles as an undesirable side effect.

The preparation of core−shell Ag−Pt nanoparticles is an important step preceding the preparation of Pt hollow nano-spheres. Parts A and B of Figure 2 show the TEM images of the core−shell Ag−Pt nanoparticles prepared in this study. The core−shell structure was also confirmed by a phase transfer method described elsewhere.[11] This method leverages on the different binding characteristics of Pt-rich and Ag-rich surfaces for an affinity agent (phase-transfer agent) and using the latter to transfer the nanoparticles from the aqueous phase to an organic phase, causing visually detectable changes in the solution color. Figure 2A is a typical low magnification TEM image of the core−shell Ag−Pt nanoparticles, showing distinct
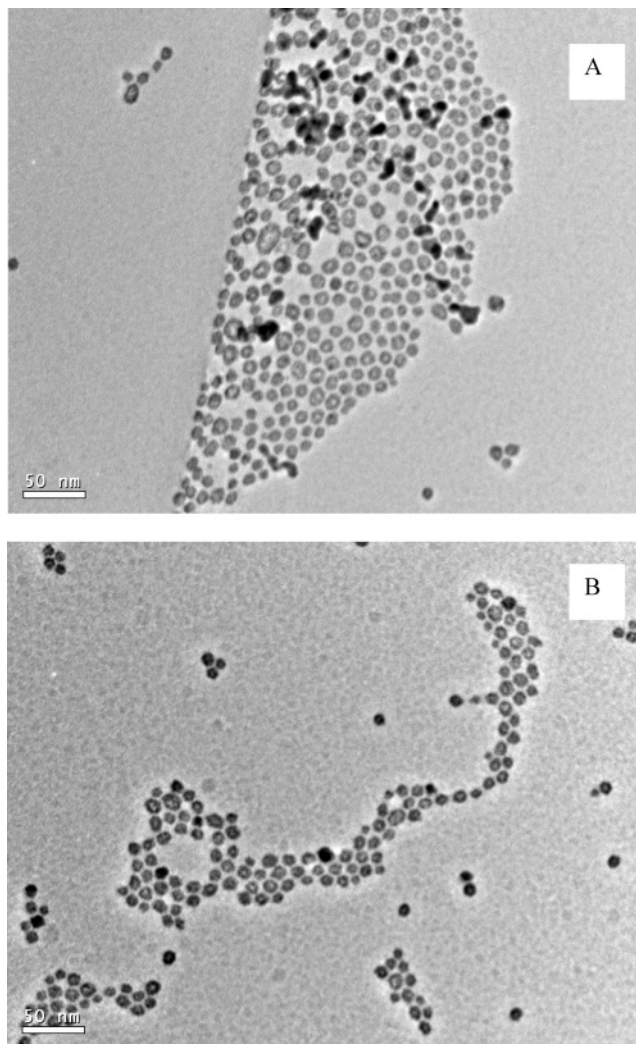

Figure 5. TEM image of core−shell Ag−Pt nanoparticles (A) and Pt hollow nanospheres (B) after the phase transfer.
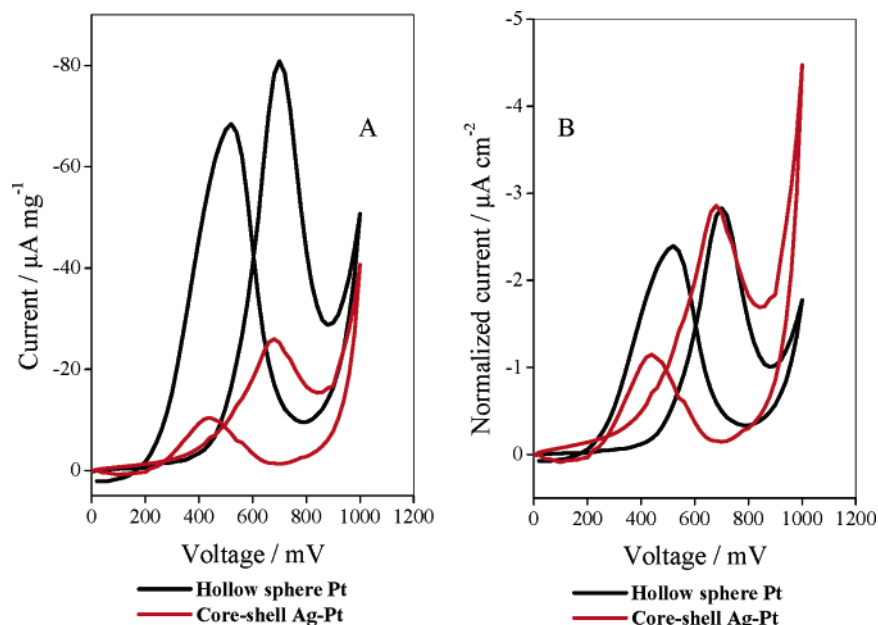
Figure 6. (A) Cyclic voltammograms of Pt hollow nanospheres (black line) and core−shell Ag−Pt nanoparticles (red line) on a glassy carbon disk electrode in an electrolyte of 0.5 M H$_2$SO$_4$ and 0.6 M methanol. Catalyst loading: 0.07 mg cm^{-2} for Pt hollow nanospheres and 0.11 mg cm^{-2} for the core−shell nanoparticles. Scan rate = 50 mV s^{-1}. (B) Renormalization of cyclic voltammograms by the available surface areas of the catalysts.

brightness differences between the inner and outer regions of the particles. Additional structural details are revealed by the high-magnification TEM image in Figure 2B. The discontinuous Pt shell with an average thickness of 2.2 nm was made up of individual Pt spheres decorating on the 9.5-nm Ag core. The formation of a discontinuous Pt shell on the Ag core is important, as it permits BSPP penetration to oxidize the underlying Ag core. Another interesting property of the Ag−Pt core−shell particles is the retention of the SPR activity of the Ag cores (black trace in Figure 3) in the presence of a Pt shell (which has no SPR features).[11] This allows the core−shell particles to be tracked by the Ag SPR signal. The large red shift (ca. 54 nm) of the Ag SPR band in Figure 3 (black dots) nevertheless indicates the influence from the Pt shell.

Four hours after the addition of BSPP, the color of the Ag−Pt nanoparticle solution was changed from reddish brown (Figure 4A) into yellowish brown (Figure 4B) and the SPR of the Ag core was no longer visible (red trace in Figure 3). These are indirect indications of the elimination of the Ag cores from the core−shell Ag−Pt nanoparticles. More direct evidence was provided by the disappearance of the Ag signal in the EDX analysis of the core−shell particles after the BSPP treatment (see Supporting Information). A comparison of TEM images of the core−shell Ag−Pt nanoparticles before (parts A and B of Figure 2) and after (parts C and D of Figure 2) BSPP oxidation shows virtually no change in the particle size. The removal of the Ag cores from the core−shell Ag−Pt nanoparticles therefore did not lead to the collapse of the spherical geometry. It should be noted that BSPP served not only as the oxidant to remove the Ag core but also as the substitute stabilizer for the initially citrate-stabilized (see Experimental Section) core−shell particles. The Pt hollow spheres formed in the process were protected by BSPP and nonaggregating, making it possible to implement the following phase transfer and surface modification procedures to standardize the particle surface conditions.

Both the core−shell Ag−Pt nanoparticles and the Pt hollow nanospheres could be transferred from water to toluene and be stabilized in the latter by dodecylamine using a previously developed method.[10,11] TEM examinations showed no apparent

change in the particle size, morphology, or structure before and after the phase transfer (Figure 5). The phase transferability of core−shell Ag−Pt nanoparticles and hollow Pt nanospheres allows the surface of the nanospheres to be modified according to the needs of the intended application.

The electrocatalytic activities of Pt hollow nanospheres and core−shell Ag−Pt nanoparticles in the room-temperature methanol oxidation reaction were measured in a H$_2$SO$_4$-acidified electrolyte.[12] After the phase-transfer treatment, the Pt hollow nanospheres and the core−shell Ag−Pt nanoparticles of the same size would have the same stabilizer molecules (dodecylamine) adsorbed on their surfaces. A consistent basis for comparing the catalytic activities of hollow and solid Pt nanoparticles (the Ag cores of the core−shell Ag−Pt nanoparticles are catalytically inactive in methanol oxidation) is therefore established. The only difference between hollow Pt and solid Ag−Pt core−shell nanoparticles is the existence of a hollow interior in the former. The available surface area per particle is therefore higher in the hollow nanospheres. The discontinuous Pt shells in Pt hollow nanospheres ensure that the internal surface of the latter is accessible to reactants, and is as extensively aminated as the external surface.

Voltammograms of methanol oxidation shown in Figure 6A were obtained in the potential window of 0−1 V at a swept rate of 50 mV s^{-1}. The current densities in the voltammograms were normalized with respect to the weight of Pt. The voltammetric features are typical of methanol electrooxidation reported in the literature:[12a,13] Methanol oxidation on the Pt catalysts commenced at ∼0.3−0.4 V (vs standard calomel electrode, SCE) and a fully developed oxidation peak was formed at ∼0.7 V (vs SCE). The peak current densities associated with methanol oxidation in the forward and reverse scan were −80.4 and −68.2 μA mg^{-1} for the Pt hollow nanospheres and −26.1 and −10.8 μA mg^{-1} for the core−shell Ag−Pt nanoparticles. From the comparison of current densities in Figure 6A, it is obvious that the specific activity of the Pt hollow nanospheres is higher than that of the core−shell Ag−Pt nanoparticles. However, when the current densities in the voltammograms were normalized by the accessible surface areas in hollow and solid nanaoparticles instead (Figure 6B, it is

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assumed that both the inner and outer Pt surfaces are equally accessible to methanol and have the same intrinsic catalytic activity; the surface area per Pt hollow nanosphere is calculated to be approximately 1.52 times that of a corresponding solid Ag−Pt particle), the two voltammograms collapsed into a common one within experimental errors, demonstrating convincingly that the higher catalytic activity of the Pt hollow nanospheres is purely a surface area effect. It is noteworthy to state that although the conclusion is not unexpected and has been suggested previously by Liang and co-workers,[8] the more rigorous experimental protocol adopted here allows the comparison to be made under controlled particle size and surface conditions. On the contrary, Liang and co-workers[8] had used different stabilizers to protect the hollow and solid Pt nanoparticles (citrate ions for the former and poly(vinylpyrrolidone) for the latter) and one cannot rule out, a priori, the interference from different stabilizer molecules on the catalytic property of Pt.

Conclusions

In summary, a BSPP oxidation protocol to prepare Pt hollow nanospheres has been developed and reported in detail. Core−shell Ag−Pt nanoparticles were first synthesized and the discontinuous Pt shell on the Ag core allowed BSPP to diffuse through the shell to dissolve the underlying Ag core, leaving a Pt shell with the spherical geometry largely intact. The Pt hollow nanospheres prepared this way could be easily transferred from water to toluene for surface modification by dodecylamine, which standardized the surface conditions of the Pt hollow spheres and core−shell Ag−Pt nanoparticles, allowing the comparison of catalytic activities of the two in methanol oxidation reaction to be made under conditions of the same particle size and the presence of the same stabilizer molecules on the surface. Electrochemical measurements showed that the higher specific activity of the Pt hollow nanospheres in methanol oxidation reaction could be understood on the basis of a surface area effect alone.

Supporting Information Available: EDX analyses of core−shell Ag−Pt nanoparticles before and after BSPP treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

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