Large Scale Fabrication of Hollow Palladium Nanospheres by Template-free Approach

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(Received November 4, 2003; CL-031048)

In large-scale and high yields hollow palladium nanospheres with different scales were fabricated by template-free approach in one step at room temperature. The hollow nanospheres were found to form from the aggregation of small palladium nanoparticles.

The fabrication of hollow nanostructures of noble metals is of much interest because they have been shown to exhibit a range of properties superior to their solid counterparts.[1] Compared with other inorganic hollow spheres, noble metal hollow spheres reported are relatively limited. Typically, these hollow nanostructures are prepared by coating the surface of colloidal particles (e.g., silica beads, silver or gold colloids, and polymer latexes)[2] with thin layers of the desired material (or its precursors), followed by selective removal of the colloidal templates through calcinations or wet chemical etching.[3] Caruso and others have done much elegant work on noble metal hollow spheres using this approach. Recently, a novel template-engaged replacement reaction developed by Xia and co-workers[4] was used to synthesize hollow structures of noble metals, which involves the replacement reaction between the surface of silver template and the solution of an appropriate salt precursor. While these approaches have shown remarkable capabilities in preparation of hollow nanostructures, the exploration of a simple template-free route to hollow nanospheres, which is suitable for large-scale synthesis, is still a great challenge. Herein, we report a simple one-step approach to hollow palladium nanospheres at room temperature.

Hollow palladium nanospheres were obtained by reduction of $PdCl_2$ using $NaBH_4$ as reductant at the presence of Bu_4NBr.[5] High yields of hollow spheres can be achieved in two minutes after the addition of $NaBH_4$ solution to the mixture of $PdCl_2$ and tetrabutylammonium bromide, which accompanied by a color change from orange to dark-brawn and then to black in several minutes. Meanwhile, a large amount of small bubbles emerged from the solution.

In our synthesis, larger concentrations of the reactants lead to relatively smaller hollow nanospheres and the hollow spheres with diameters of 80–120 nm were found relatively uniform. Further higher concentration of the reactants leads to the mixture of hollow spheres and aggregated particles. It should be stated that quick injection of $NaBH_4$ solution favors the uniformity of the hollow nanospheres. The concentrations of the reactants for the synthesis of hollow nanospheres with different sizes were illustrated in Table 1.

The structure of the hollow Pd spheres was investigated by powder X-ray diffraction (XRD) and electron microscopy. All the peaks of the XRD pattern can be indexed to the cubic palladium (JCPDS 5-681). The transmission electron microscopic (TEM) image (Figure 1a) showed that the individual particles were composed of an empty core with a relatively uniform shell of 15 nm. The scanning electron microscopic (SEM) image of the Pd sample, shown by Figure 1b, revealed that relatively uniform spherical particles with sizes of 80–120 nm were produced. Their hollow interiors were also confirmed by the images of the broken spheres (Figure 1b, insert). The scanning electron microscopy–energy dispersive X-ray analysis (SEM–EDXA) results in Figure 2a showed the composition of the palladium hollow spheres, while the weak Cu, C, and Br energy peaks arise from the copper disc of SEM and the small amount of capping Bu_4NBr (Pd:Br:C = 98.40:0.65:0.95).

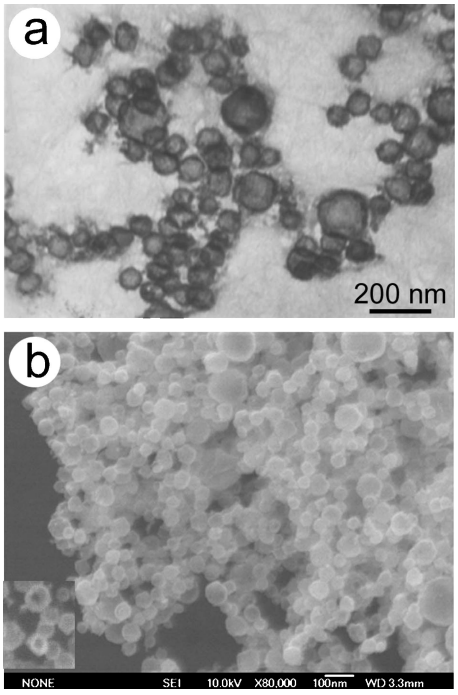

Figure 1. (a) TEM image of hollow Pd spheres with sizes of ca. 80–120 nm; (b) SEM image of hollow Pd spheres with sizes of ca. 80–120 nm, inset: broken hollow nanospheres.

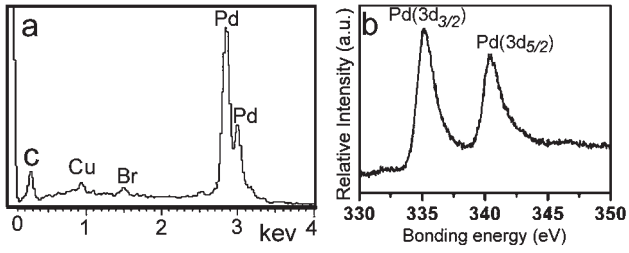

Figure 2. (a) SEM–EDXA spectrum of as-prepared Pd sample; (b) Pd(3d) XPS spectrum of as-prepared hollow Pd nanospheres.

Table 1. Concentrations of the reactants and sizes of produced hollow nanospheres

	$PdCl_2$	Bu_4NBr	$NaBH_4$	Hollow spheres
I	0.01 M	2.5 mM	0.05 M	200–400 nm
	0.8 mL	40 mL	0.5 mL	
II	0.01 M	5 mM	0.1 M	100–300 nm
	1.6 mL	40 mL	0.5 mL	
III	0.01 M	10 mM	0.1 M	80–120 nm
	3.2 mL	40 mL	1 mL	

The product purity and elemental composition were determined by X-ray photoelectron spectroscopy (XPS). No peaks of other elements except Pd, C, O, Br were observed on the survey spectrum. The peaks for O can be attributed to the O_2, CO_2, or H_2O adsorbed on the surface of the sample, whereas weak C and Br peaks can be attributed to capping surfactant Bu_4NBr. XPS Pd($3d_{5/2}$) and Pd($3d_{3/2}$) peaks (Figure 2b) were observed at binding energy values of 335.9 and 341.2 eV, respectively. Such binding energy values are similar to that reported for Pd metals in the literature.[6]

Figure 3a shows the TEM image of hollow spheres with external diameters of ca. 100–300 nm. The TEM image at high magnification showed that the shell is composed of ≈5 nm Pd nanoparticles (Figure 3b). The lattice distances that correspond to the strongest reflection ring of ED pattern (Figure 3b, inset) can be assigned to the (111) lattice plane of metallic palladium. The TEM results also revealed that the sizes of the small palladium nanoparticles were nearly uniform and ca. 5 nm for almost all of the hollow spheres although external diameters of these hollow spheres were different.

On the basis of these observations, an aggregation mechanism to form hollow palladium nanospheres was proposed, which is similar to the preparation of SiO_2, TiO_2,[7] or ZnSe[8] microspheres. In the reaction, Pd(II) was reduced into Pd(0) easily by $NaBH_4$ whereas $NaBH_4$ turned into H_2. After the initial nucleation, the monomers grew into nanocrystals, which could stay relatively stable at the presence of the surfactant Bu_4NBr. These nanocrystals have a tendency to aggregate, and at the same time, lots of newly formed nanobubbles of H_2 produced in the reaction provide the aggregation centers. Driven by the minimization of interfacial energy, small Pd nanoparticles may aggregate around the gas–liquid interface between H_2 and water and finally hollow palladium nanospheres form. The hollow spheres with different diameters were probably resulted from different bubble sizes. It is probable that higher concentration of reactants leads to dense and small bubbles whereas lower concentration leads to relatively loose and larger ones.

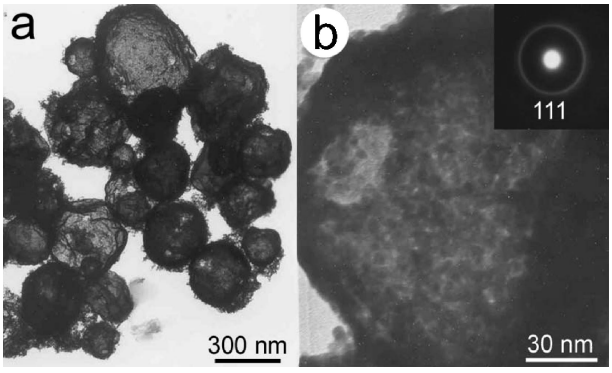

Figure 3. TEM image of hollow Pd nanospheres with external diameters of ca. 100–300 nm (a) and TEM at high magnification (b) showing the small Pd particles of ca. 5 nm.

In conclusion hollow palladium nanospheres with different sizes were fabricated, in large-scale and high yields by template-free approach in one step at room temperature. Compared to other template-synthetic methods, the use of gas bubble produced during the reaction to provide aggregation centers is a novel and effective method for large-scale fabrication of hollow nanospheres. This simple template-free approach might be extended to other solution system in which easily aggregated monodispersed nanocrystals are produced during the reaction.

This work was supported by the National Natural Science Foundation of China, and Chinese Ministry of Education.

References and Notes

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5 Hollow palladium nanospheres with external diameters of 80–120 nm were synthesized as follows: $PdCl_2$ solution (0.01 M, in acetonitrile) 3.2 mL was mixed with tetrabutylammonium bromide solution (0.01 M, in water) 40 mL to form a turbid mixture, which was stirred for 5 min. Freshly prepared water solution of $NaBH_4$ (0.1 M) 1 mL was added quickly. The color turned from yellow-orange to dark-brawn and then to black in several minutes. The final mixture was kept at room temperature for several minutes and the product was collected through centrifugation and then redispersed into water.
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Published on the web (Advance View) January 26, 2004; DOI 10.1246/cl.2004.244