Chem. Mater. **2008,** *20,* 3003–3007

Decoration of the Interior Surface of Hollow Spherical Silica Colloids with Pt Nanoparticles

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Received July 15, 2007

This paper describes the generation of Pt nanoparticles inside hollow silica colloids. Solvent etching of *a*-Se core in *a*-Se@Pt@silica double-shelled colloids transformed the thin Pt layer into a number of Pt nanoparticles, decorating the interior surface of hollow silica colloids. The release rate of *a*-Se was directly related to the formation of Pt nanoparticles. Fast dissolution of the core in solvents such as carbon disulfide (CS_2) and hydrazine (N_2H_4) produced Pt nanoparticles with diameters less than 15 nm, while slow release of *a*-Se in alcohols or in a mixture of CS_2 and water did not make any change in the Pt thin layer. At elevated temperatures (65 °C) in alcohols, the nanoparticles were aggregated and rearranged into large nanoparticles. The nanoparticles obtained in these processes were characterized single crystallites with HR-TEM analysis and electron diffraction patterns.

Introduction

Hollow colloidal particles have found widespread use in a variety of applications, including target drug delivery, controlled release of drugs, cosmetics, inks, and pigments, and protection of biologically active species.[1] The hollow spherical morphology of these aggregates should render them suitable as precursors for the preparation of size- and shape-persistent nanocontainers. A templating approach has been widely employed for the production of the hollow colloids. The surfaces of spherical colloids made of inorganic ceramics,[2] polymers,[3] and their hybrids[4] have been coated with a thin shell of desired materials, followed by selective removal of the core via calcination or chemical etching in solution. Self-assembly of lipid molecules or amphiphilic block copolymers also has been a main approach to obtain vesicles or liposomes.[5] Recent advances in emulsion/suspension polymerization have demonstrated nanometer-sized hollow polymer particles as a one-step process.[6] Dendrimers have been the topic of active research for the past decade due to their inherent formation of nanometer-scale containers as well as their easy tunability in size.[7] Very recently, ultrasonic wave was utilized to fabricate inorganic and composite hollow nanostructures.[8]

In solid colloids, the active current uses have been found from the composite-layered systems, in which active components are evenly loaded in the colloids.[9] Most latex particles or silica colloids possessing superparamagnetic nanoparticles are used in the form of the composites. The developments in surface science and technology offered new opportunities for modern engineering concepts of functionalizing the outer surface of the colloids. The main idea to load active components in colloids was to distribute inorganic nanoparticles on the outer surface of solid colloids by adjusting the surface energy of the colloids

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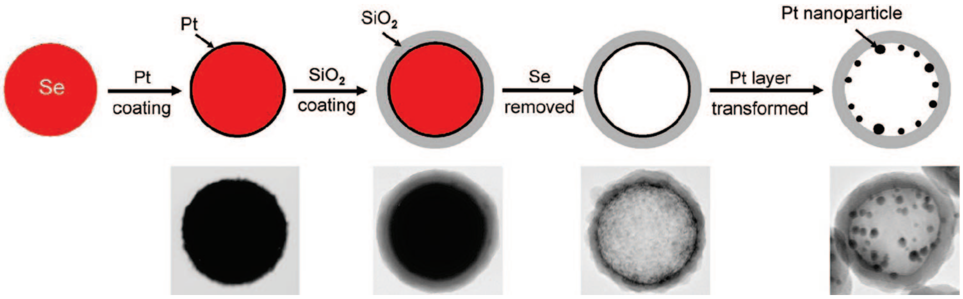

Figure 1. Schematic procedure to fabricate *a*-Se@Pt@silica double-shelled colloids, followed by selective removal of *a*-Se and the transformation of the Pt thin layer into Pt nanoparticles. The experimental results of TEM images correspond to each step.

with surfactants or by utilizing the formation of chemical bonding between the nanoparticles and the colloidal surface.[10]

In hollow colloids, main interests have been focused on encapsulation of organic active ingridents such as drugs and DNA for the expanding needs in biomedical uses.[11] On the contrary, functionalizing the interior surface of the hollow colloids has not gained much attention.[12–14] A few approaches have been tried so far to functionalize the inner part of the hollow colloids. The hollow colloids with functionalized interior were demonstated to be useful as small containers to investigate chemical diffusion through nanoscale thin shells[13] and as miniaturized reactors.[14]

In this study, we suggest a new approach to functionalize the interior surface of hollow colloids with metal nanoparticles. Fragmentation of the thin metal layer during dissolution of core material in core–shell colloids can produce metal nanoparticles inside the resulting hollow shells. As a proof-of-concept study, we decorate Pt nanoparticles on the inside surface of hollow silica colloids.

Experimental Section

Materials. All the starting materials were used as purchased. Selenious acid (H_2SeO_3, 98%), hydrazine hydrate ($N_2H_4 \cdot xH_2O$, 53 wt hydrazine), polyvinylpyrrolidine (PVP, Mw = 55 000), hydrogen hexachloroplatinate (H_2PtCl_6, 99.9%), and tetraethyl orthosilicate (TEOS, 99.999%) were purchased from Aldrich. Ethylene glycol (99.9%), isopropyl alcohol (99%), and ammonium hydroxide (35% aqueous solution) was purchased from Fischer Scientific. The water used in all syntheses was purified by passing through an 18 MΩ (SHRO-plus DI) system.

Synthesis of *a*-Se Colloids. Hydrazine hydrate solution in ethylene glycol (0.35 M, 20 mL) was poured into 100 mL of ethylene glycol hosted in a 500 mL round-bottom flask. The mixture solution was placed in a cold water bath maintained at 10 °C, and it was magnetically stirred for 30 min. H_2SeO_3 solution in ethylene glycol (20 mL, 0.07 M) was poured into the mixture solution. The clear solution gradually turned to orange within 30 min. The reaction was allowed to proceed for 2 h in order to have H_2SeO_3 completely consumed.

Formation of *a*-Se@Pt Core–Shell Colloids. Vacuum distillation was conducted to eliminate residual hydrazine hydrate in the *a*-Se suspension and thus to prevent H_2PtCl_6 from being reduced directly. PVP solution in ethylene glycol (100 mL, 5 wt %) was added to the suspension to stabilize the *a*-Se colloids before coating a Pt thin layer. A total of 0.2 g of H_2PtCl_6 was put into the *a*-Se colloids in ethylene glycol in a 500 mL round-bottom flask at room temperature, and magnetic stirring was exerted for 10 min. The solution flask was placed in an oil bath at 65 °C under magnetic stirring. Ethylene glycol served as a reducing agent for H_2PtCl_6 as well as a solvent in this reaction. The color of the solution changed from orange to dark brown within 2 h. The reaction batch was taken out of the oil bath and cooled in air. The same amount of water with the product solution was added to the reaction batch to help the centrifuge of the colloids. Any Pt chunks from the reduction of H_2PtCl_6 and unreacted precursor powder were removed through a filter paper. The colloids were centrifuged, and the solution was decanted. The colloids were washed with pure water by repetitive cycles of dispersion and centrifuge to remove residual ethylene glycol and finally dried in air.

Formation of *a*-Se@Pt@Silica Double-Shelled Colloids. A small amount of the Pt-coated colloids (0.1 g) was redispersed in isopropyl alcohol (20 mL) hosted in a 50 mL round-bottom flask, followed by the addition of a small amount of PVP (50 mg) and pure water (5.0 mL). After dissolving PVP, ammonium hydroxide (0.5 mL) and tetraethyl orthosilicate (TEOS, 20 μL) were introduced successively under vigorous magnetic stirring. The reaction proceeded for 2 h, and the final product was centrifuged and washed with water three times by repetitive centrifuge and redispersion cycles.

Instrumentation. SEM images were taken using a JEOL JSM-6700F at an acceleration voltage 5–20 kV. TEM images and electron diffraction patterns were acquired from a JEOL 2100F at an acceleration voltage 200 kV.

Results and Discussion

Generation of Pt Nanoparticles on Interior Surface of Silica Hollow Shells. Figure 1 is a schematic to guide the experimental procedure. The TEM images show the representative results corresponding to each stage. Spherical *a*-Se colloids were chosen as the starting material because they can be coated with platinium through

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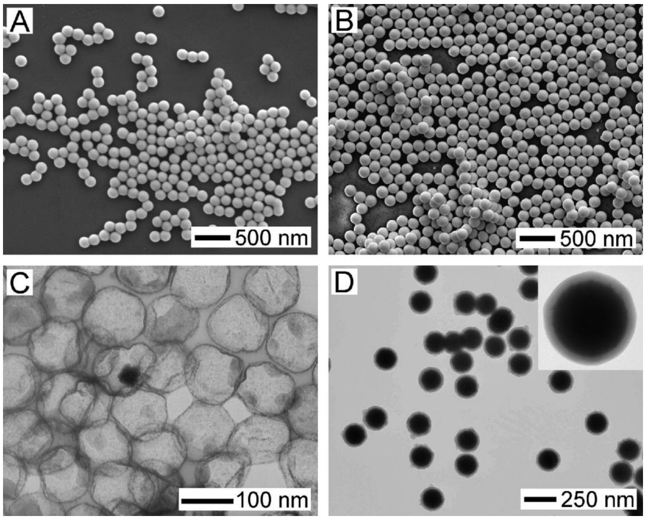

Figure 2. SEM (A, B) and TEM (C, D) images showing the procedure to obtain *a*-Se@Pt@silica double-shelled colloids. (A) *a*-Se, (B) *a*-Se@Pt, (C) Pt thin shells obtained by evaporating *a*-Se core by focusing electron beam during TEM observation, and (D) *a*-Se@Pt@silica double-shelled colloids with magnified image in the inset.

chemical reduction in ethylene glycol or alcohols.[15] The thickness of Pt layer is controllable by adjusting the degree of the reduction of platinium precursors. Xia and coworkers already demonstrated that a thick layer of Pt can be coated on Se colloids or nanowires, resulting in core−shell structured colloids or nanocables. Selective removal of the Se core led to Pt hollow spheres or Pt nanotubes.[15] Different from their research, this study investigates thin layers of Pt coated on *a*-Se colloids. The Stöber process[16] with tetraethyl orthosilicate (TEOS) can provide a silica shell on the Pt-coated *a*-Se colloids under a slightly basic condition.[15b] The *a*-Se core in the core−shell colloids is readily dissolved by several organic solvents such as hydrazine, carbon disulfide, or phosphine oxides.[15] Alcohols also slowly dissolve *a*-Se and transform it into *t*-Se nanowires.[17] When the dissolution of Se is carried out slowly, the Pt thin layer can be conserved without damage. However, fast dissolution of the core or incubation at an alleviated temperature might destroy the Pt thin layer and lead to transformation into Pt nanoparticles inside the hollow silica shells. The TEM images positioned below each step represent a Pt-coated *a*-Se colloid (*a*-Se@Pt), a double-shelled *a*-Se@Pt@silica, double-shelled colloids after selectively removing the *a*-Se core, and a silica hollow shell decorated with Pt nanoparticles on its interior surface.

Figure 2 shows the experimental procedures to obtain the double-shelled *a*-Se@Pt@silica colloids. Anhydrous ethylene glycol, selenious acid, and hydrazine hydrate were used to synthesize monodisperse *a*-Se spherical colloids.[15b] Since hydrizine used as a reducing agent is too powerful to reduce Se precursors in a short time at room temperature, the temperature was fixed at 10 °C to slow down the rate of reduction, which produced *a*-Se colloids with smaller diameter. For SEM investigation of the *a*-Se colloids, 1 mL of water was mixed with one drop of the colloidal suspension in a small vial, followed by air drying on a Si wafer. The as-synthesized *a*-Se colloids were monodisperse with a diameter of 160 nm, as shown in Figure 2A. The residual hydrazine in the colloidal suspension of *a*-Se in ethylene glycol was vacuum degassed for 2 h at 30 °C because a small amount of hydrazine can quickly reduce platinium precursors and form a large aggregation of Pt. Polyvinylpyrrolidone (PVP) solution in ethylene glycol was added to the suspension to stabilize the *a*-Se colloids. Due to the low glass transition temperature of Se, the *a*-Se suspension was kept in a refrigerator to prevent any shape change.

Platinium coating was performed by using the chemical reduction of hydrogen hexachloroplatinate (H_2PtCl_6) at room temperature in ethylene glycol. The reduction is known to produce Pt nanoclusters that is readily adsorbed on the surface of Se nanostructured materials.[15b] The repetitive adsorption of Pt nanoclusters leads to conformal coating of Pt. The coating process has been reported to occur via two discrete reactions, which include the initial reduction of the Pt salt by a Se template itself at the interface and the reduction of the Pt salt by the solvent. The Pt layer could continue to grow until the reaction is finished as the Pt salt is completely consumed or the reaction is intentionally stopped. The diameter of Pt nanoparticles in this process is limited by a few nanometers, which can produce a Pt coating with a very smooth surface. This is a good reason why Se is considered as a great template for the coating of Pt, compared with other inert materials such as polystyrene beads or silica colloids. Figure 2B shows the *a*-Se colloids coated by a thin layer of Pt. The size change of the colloids was not discernible by the SEM images, but Pt-coated colloids showed improved hardness. While centrifuge of *a*-Se colloids at 10 000 rpm resulted in their aggregation stuck to the wall of the centrifuge tube due to their low glass transition temperature, Pt-coated colloids were stable during centrifuge at any rpm. Compared with *a*-Se colloids in Figure 2A, Figure 2B demonstrates the improvement in hardness. The *a*-Se colloids were slightly deformed on contact with each other during the solvent evaporation; however, Pt-coated ones maintained spherical shape and played as excellent building blocks for the hexagonal packing via self-assembly. Figure 2C is a TEM image taken after evaporating the *a*-Se core by focusing the electron beam on a small region of the sample. Due to the low boiling point, *a*-Se quickly evaporated and left behind a thin Pt shell folded or torn apart. The thickness of the Pt shell is considered to be less than 5 nm. For the silica coating, a small amount of Pt-coated colloids was redispersed in isoporpyl alcohol to apply the Stöber proces. Silica could not be directly coated on the surface of Se colloids without a Pt layer. The thickness of the silica layer was ∼23 nm on average, as displayed in the TEM image of Figure 2D. The higher magnification in the inset clearly shows the silica coating with smooth and uniform thickness.

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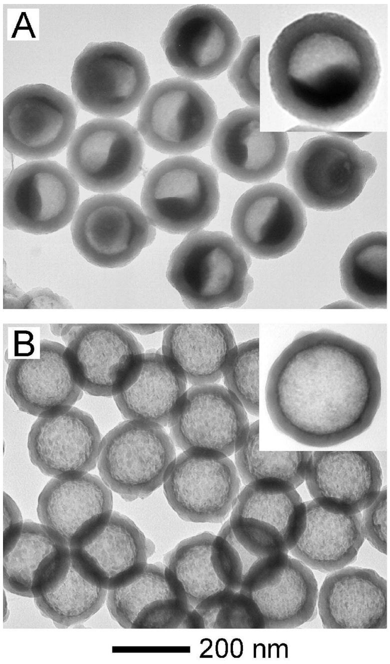

Figure 3. Release of the *a*-Se core in *a*-Se@Pt@silica, depending on the time of soaking in ethanol at room temperature. (A) Partial removal of *a*-Se at room temperature in 24 h, (B) complete removal of *a*-Se in 48 h.

Temperature Effect on the Transformation of the Pt Thin Layer. Figure 3demonstrates the selective removal of *a*-Se by ethanol at different temperatures and the accompanying change of the Pt layer. Gentle magnetic stirring was exerted to the colloidal suspensions during the removal. Figure 3A shows the partial removal of the *a*-Se core in 24 h at room temperature. The degree of dissolution of the core was readily controlled by the soaking time. The *a*-Se was completely removed in 48 h, as exhibited in Figure 3B. The thin Pt layer was maintained as prepared without experiencing damage.

When the double-shelled colloids were subjected at 40 °C in ethanol for 24 h, however, all the *a*-Se was dissolved out and the Pt layer was torn apart into small pieces as shown in Figure 4A. On the incubation of the double-shelled colloids in ethanol at 65 °C for 6 h, the *a*-Se was completely removed and the Pt layer transformed into 4−6 nanoparticles inside each silica hollow shell. The TEM image in Figure 4B indicates the size of the Pt nanoparticles ranged from ∼10 to ∼60 nm. When the samples in Figure 3B were incubated at 65 °C in ethanol, the Pt layer also transformed into nanoparticles as shown in Figure 4B. The same results were observed in iso-propanol instead of ethanol. The *a*-Se core was slowly dissolved and left a thin layer of Pt shell at room temperature, but relatively large nanoparticles were produced in 65 °C. The slow dissolution of the *a*-Se core by alcohols at room temperature results in the slow in/out diffusion of the solvents through the grain boundaries of the Pt layer. The slow material flux is considered to prevent severe deformation of the Pt layer. In contrast, raising the temperature enhances the dissolution of *a*-Se and the diffusion of the solvents toward the hollow core, leading to cracks and fragmentation of the Pt layer. And the lowered sintering temperature of the Pt clusters with very small size (usually below 1−2 nm) is considered to allow the rearrangement of the Pt clusters and the transformation into larger aggregates.

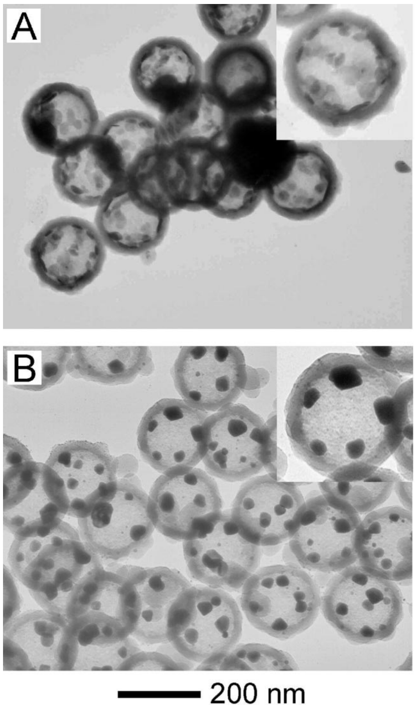

Figure 4. Removal of *a*-Se core and the accompanying change of the Pt thin layer at different temperaturesin ethanol. (A) Removal of *a*-Se and deformation of Pt layer at 40 °C in 24 h and (B) removal of *a*-Se and the transformation of the Pt layer into Pt nanoparticles at 65 °C in 6 h.

Solvent Effect on the Size of Pt Nanoparticles. The material flux through the thin Pt layer can be controlled by adjusting the solubility of the *a*-Se core in solvents, in addition to varying the temperature as demonstrated in Figures 3 and 4. The changes of the Pt layer in pure CS_2 and a mixture of water and CS_2 are displayed in Figure 5. The TEM result in Figure 5A was obtained by selectively dissolving the *a*-Se core by pure carbon disulfide (CS_2, Aldrich, 99.9%) at room temperature. CS_2 is known to dissolve *a*-Se quickly. A small amount of the dry double-shelled colloids were redispersed in 1 mL of pure CS_2 hosted in a small centrifuge tube. A few seconds of ultrasonication were exerted to help the dispersion. The *a*-Se core dissolved quickly in CS_2 and changed the color of the suspension to light yellow within a few minutes. After 10 min, the colloids were centrifuged and experienced three cycles of wash and centrifuge with pure water. Figure 5A indicates that the Pt thin layers were fragmented and formed into many small nanoparticles. The result is different from Figure 3A in which the Pt layer was stable enough to sustain the coated state. The size of the Pt nanoparticles in Figure 5A is less than 15 nm, which is much smaller than the Pt nanoparticles obtained in ethanol via incubation at 65 °C as shown in Figure 4B. By comparing the results, the Pt nanoparticles once obtained are considered stable at room temperature, while incubation at 65 °C leads to aggregation between the nanoparticles.

The degree of dissolution of the *a*-Se core can be controlled by using a mixture with a poor solvent for *a*-Se. CS_2 was mixed with water to slow down the dissolution rate.

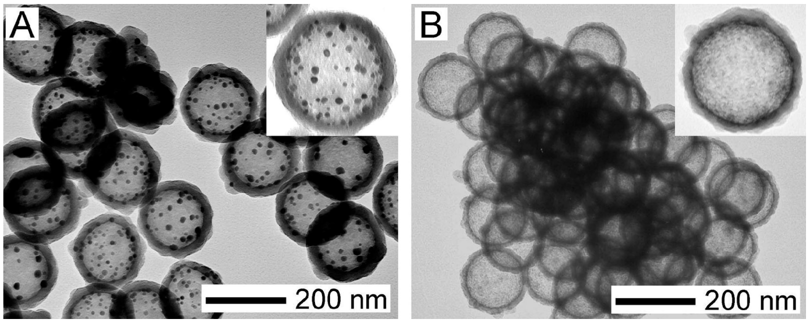

Figure 5. TEM images after removal of *a*-Se in (A) pure CS_2 and (B) a mixture of CS_2 and water (1:4, v/v). While the Pt layer transformed into many fine nanoparticles in pure CS_2 as magnified in the inset of Figure 4A, the mixture solvent did not damage the Pt thin layer.

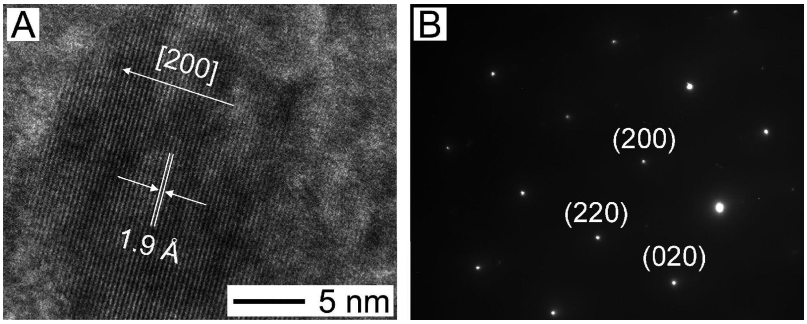

Figure 6. (A) High resolution TEM image of a nanoparticle made inside the wall of the silica colloids. The lattice fringes are spaced ~1.9 Å, which is in good agreement with the lattice spacing of (200) planes of the fcc Pt crystal structure. (B) A selected area electron diffraction (SAED) image of an individual nanoparticle. The pattern can be indexed as the diffraction from the [001] zone axis.

When a mixture of CS_2 and pure water (CS_2/water = 1:4, v/v) was used as the etchant for the *a*-Se core at room temperature, the Pt thin layer was preserved without severe fragmentation as displayed in Figure 5B. Complete dissolution of the *a*-Se core in the mixture solvent took 6 h, which is much slower than the case of pure CS_2. Replacing CS_2 with hydrazine hydrate led to the same results. Pure hydrazine hydrate produced fine nanoparticles of less than 10 nm, while a mixture solvent with water (1:4, v/v) did not damage the Pt layer. The results in Figure 5 indicate that the transformation of the Pt layer can be greatly enhanced by increasing the dissolution power of the solvent. The abrupt in/out flux of the solvents and Se atoms causes a lot of cracks in the Pt layer and leads to a small size of Pt fragments. The small fragments seem to experience rearrangement into spherical colloids even at room temperature.

Analysis of Crystal Sturcture. The nanoparticles generated inside hollow silica shells in CS_2 (Figure 5A) were characterized by high-resolution TEM images and electron diffraction patterns, as detailed in Figure 6. For thorough analysis of the Pt nanoparticles, the silica shells possessing Pt nanoparticles were etched with HF solution (1%, in water) on a TEM grid. Figure 6A shows an HR-TEM image of a Pt nanoparticle. The fringes indicate a period of around 1.9 Å, which was consistent with the spacing in {200} lattice of fcc crystal structure of Pt. The well-resolved continuous fringes with the same orientation implies that the Pt nanoparticles are single crystallites. Figure 6B shows the selected area electron diffraction (SAED) pattern of an individual nanoparticle inside the hollow silica shell, which was taken along the [001] zone axis. The diffraction pattern confirmed the FCC crystal sturucture of the Pt nanoparticles.

Conclusions

We proposed a novel approach to decorate the interior surfaces of hollow colloids with fine metal nanoparticles. Double-shelled colloids consisting of soluble core, metal layer, and outer metal oxide layer were employed. Fragmentation of the thin metal layer during dissolution of the core material produced metal nanoparticles via rearrangement of the metal thin layer. The validity of the concept was proved by utilizing *a*-Se@Pt@silica double-shelled colloids. The key factors for the transformation of the Pt thin layer was the control of dissolution rate and incubation temperature. Fast dissolution of the *a*-Se core inducing high material flux through the thin Pt shell produced fine Pt nanoparticles with diameters less than 15 nm. However, using solvents with low dissloution power did not damage the Pt layer. Incubation of the hollow double-shelled colloids at an elevated temperature (65 °C) led to fragmentation of the Pt layer and then transformation into relatively big aggregates. The silica hollow shells including Pt nanoparticles inside is useful as a catalytic nanoreactor for various organic reactions. Pt nanoparticles inside the silica shell can slow down undesirably explosive reactions, and the easy retrieval through centrifuge or filtration can minimize the loss of the expensive catalyst. We are sure that this approach is applicable for a variety of metal layers in hollow shells made of polymers, ceramics, and their composites.

Acknowledgment. This work was supported partially by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2006-311-D00411) and the IT R&D program of Korean Ministry of Information and Communication (MIC/IITA) [2007-S-078-0].

CM7036475