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Facile Fabrication of Hollow Silica and Titania Microspheres Using Plasma-Treated Polystyrene Spheres as Sacrificial Templates

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By means of a plasma technique, the surfaces of monodisperse polystyrene (PS) colloids have been modified with hydroxyl groups. Using these surface-modified PS colloids as sacrificial templates, we have fabricated silica-coated PS colloids (PS@silica) and titania-coated PS colloids (PS@titania) composite microspheres as well as hollow and mesoporous silica and titania microspheres. This process not only demonstrated a facile, low-cost, environmentally benign way to fabricate hollow oxides structures but also offered a feasible alternative to the preparation of polymer/inorganic oxide composites by templating against the polymer substrate with hydrophobic surfaces.

Introduction

The design and fabrication of hollow inorganic microspheres with well-defined structures have received considerable attention recently because of their potential applications in catalysis, anode materials, low-dielectric materials, gas sensors, the protection of biologically active agents, the encapsulation and controlled release of various substances, and the formation of photonic band gap crystals.[1–6] A variety of chemical and physicochemical procedures have been employed to fabricate hollow oxide microspheres, including the lost-wax method,[7] a microemulsion process,[8–10] nozzle reactor approaches,[11] and sacrificial-core techniques.[12]

Recently, polystyrene (PS) spheres on the micrometer scale have been demonstrated to be powerful templates for many kinds of hollow oxide spheres. In a typical procedure, surface-modified PS spheres are coated in solution either by the controlled surface precipitation of inorganic molecule precursors or by direct surface reaction utilizing specific functional groups on the cores to create core/shell composites. The template spheres are subsequently removed by selective dissolution in an appropriate solvent or calcinations at elevated temperature to generate hollow structures. In this process, one of the most crucial steps is to modify the hydrophobic, chemically inert surfaces of PS spheres with tunable chemical and physical environments, which is beneficial for inducing the favorable growth of oxide through specific interaction.

Two strategies have been reported to modify the surface of PS spheres for the fabrication of hollow oxide spheres. One is termed a prior-modification method in which the surface-modified PS spheres can be obtained by a one-pot reaction. For example,

Tissot and co-workers synthesized PS beads bearing silanol groups on the surface via emulsion polymerization using 3-(trimethoxysily)propyl methacrylate as a comonomer.[13] Using this functionalized PS bead as a template, hollow silica spheres were synthesized by co-condensation between the silanol groups on the surface of PS latex and tetraethoxysilane (TEOS), followed by the thermal degradation of the PS core. By means of a similar method, Agrawal and co-workers used β-diketone-functionalized PS beads as sacrificial templates to fabricate submicrometer-sized hollow tantalum oxide spheres by the controlled deposition of tantalum oxide nanoparticles on the functionalized template surface.[14] The other method can be defined as postmodification, which allows us to introduce functional groups onto the surface of bare PS spheres by means of physical or chemical approaches. One of the most typical examples is a layer-by-layer (LbL) self-assembly technique developed by Caruso and co-workers.[15,16] In this process, the polyelectrolytes were absorbed on the surface of PS spheres through electrostatic interaction to reverse the surface charge, which allowed the small oxide nanoparticles and inorganic molecule precursors to assemble consecutively onto PS colloids. By removing the PS template, the resulting composite can be converted into hollow oxide spheres. Concerning the chemical way, Zhong and co-workers used the sulfonating reaction technique to introduce the sulfonate groups onto the surface of bare PS colloids.[17,18] By templating against these surface-modified PS spheres, hollow titania, barium titanate, and strontium titanate spheres with tunable cavity size and crystalline phases have been successfully fabricated.[17,18]

The above-described pioneering work is very interesting; however, during all of those processes for modifying the PS surface, more chemicals such as comonomers, organic solvents, modifier agents, and other additives are indispensable. These would inevitably increase the environmental imperilment, augment the preparation cost, and add complexity to the preparation processes. Therefore, it is still challenging work to develop a facile, low-cost, environmentally benign PS surface-modification

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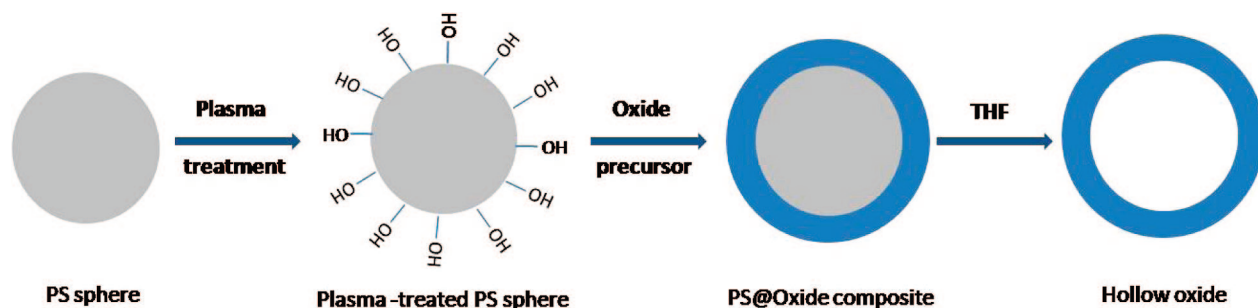(15) Caruso, F. *Adv. Mater.* **2001**, *13*, 11.
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Scheme 1. Schematic Illustration of the Fabrication of Hollow Oxides Using Plasma-Treated PS Spheres as Sacrificial Templates

method for fabricating hollow inorganic materials. Herein, we demonstrated a novel postmodification approach, plasma treatment, to modify the PS surface. To date, using plasma to tailor a PS surface to fabricate hollow oxide has remained relatively unexplored. The plasma treatment process can easily introduce hydroxyl groups onto the surfaces of PS spheres.[19] Moreover, in comparison to the previous modification approaches mentioned above, no additional solvent and chemicals are involved in this process, which can simplify the modification process, reduce the preparation cost, and decrease the hazard to the environment. Herein, we employed this simple, low-cost, environmentally benign method to introduce hydroxyl groups on the surfaces of PS spheres and use these surface-modified PS spheres as sacrificial template to fabricate silica-coated PS (PS@SiO$_2$) and titania-coated PS (PS@TiO$_2$) composites by co-condensation between hydroxyl groups with TEOS and titanium (IV) isopropoxide (TIPP) in a sol−gel process, respectively. The hollow silica and titania can be generated by the subsequent removal of the PS core using tetrahydrofuran (THF). The schematic procedure and more detailed experimental information are shown in Scheme 1 and the Experimental Details section, respectively.

Experimental Details

Monodispere PS spheres with an average diameter of 310 nm were synthesized by surfactant-free emulsion polymerization.[20] In a typical process, 200 g of water and 10 g of styrene were introduced into a double-walled glass reactor equipped with a mechanical stirrer, reflux condenser, nitrogen inlet, and temperature controller. After the reaction mixture was deoxygenated via the bubbling of nitrogen gas for 15 min, the temperature was increased to 70 °C and an aqueous potassium persulfate (0.1 g in 10 mL of water) solution was added to start the polymerization process. The reaction was allowed to proceed for another 24 h, and PS colloids were obtained as a stable dispersion in water with approximately 5% solid content. After 10 mL of the PS dispersion was centrifuged at 2000 rpm, the PS samples were collected and dried in vacuum at 80 °C overnight. The dry PS samples were subsequently subjected to grinding, and the resulting powder samples were transferred into the chamber of the plasma cleaner (Harrick Plasmer Cleaner PDC-32G). After the chamber was evacuated to low-pressure residual air (0.2 mbar), the PS samples were subject to plasma treatment at 10.5 W for 20 s. The treatment process was repeated three times to introduce hydroxyl groups homogeneously onto the surface of PS spheres. The surface-modified PS spheres (0.1 g) were transferred to a 250 mL flask containing 100 mL of absolute ethanol. After sonication for 5 min, 5 mL of ammonia water (28 wt.-%) and 0.35 mL of TEOS (0.33 g) were added to the mixture under gentle stirring. The mixture was stirred at ambient temperature for 3 h. In this sol−gel process, PS@silica core−shell composite was formed. After the PS cores

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using THF at room temperature were etched, hollow silica spheres was obtained. Following the same procedure mentioned above, the hollow titania also could be generated using titanium (IV) isopropoxide (0.2 mL, 0.19 g) as a precursor.

Samples for TEM were deposited onto carbon-coated copper electron microscope grids and dried in air. TEM analysis was performed using JEOL 1200 EX at 120 keV. Samples for SEM were mounted onto a silicon plate and dried in air. After platinum coating was carried out with an Edwards S150B sputter coater, SEM analysis was carried out using a JSM-6700F microscope at an accelerating voltage of 10 kV. Thermogravimetric analysis data were recorded using TA Instruments Q500. Samples were examined over the range of 20−600 °C using a heating rate of 10 °C/min. The furnace was purged with ultra-high-purity nitrogen at a flow rate of 50 mL/min. Nitrogen adsorption/desorption isotherms were obtained on an NOVA 3200e nitrogen adsorption apparatus. All of the samples were degassed at 100 °C prior to BET measurements. The BET specific surface area was determined by a multipoint BET method using desorption data in the relative pressure (P/P_0) range of 0.05−1. The desorption isotherm was used to determine the pore-size distribution using the Barrt−Joyner−Halenda (BJH) method.

Results and Discussion

The hydroxyl groups have been successfully introduced onto the surface of PS colloids by means of plasma treatment, which can be evidenced by FTIR analysis of PS samples before and after plasma treatment (Supporting Information). By comparison, it is observed that the plasma-treated PS colloids exhibit a broad band at around 3430 cm^{-1}, which is attributed to the presence of hydroxyl groups.

Figure 1a shows transmission electron microscope (TEM) images of PS spheres used in the present study, indicating that PS particles are monodisperse in size and the average diameter is 310 nm. The same PS spheres have been successfully employed to generate hollow silica and titania spheres. The TEM and scanning electron microscope (SEM) images of PS@silica and PS@titania composites are shown in Figure 1b−e. It is observed that both the coated PS@silica and PS@titania particles remain spherical in shape and show complete shells on the surfaces of PS template spheres. Moreover, no formation of uncoated oxide nanoparticles is observed. TEM (Figure 1b) and SEM (Figure 1d) images show that the silica shells consist of a large number of silica nanoparticles with quite a broad size distribution, which roughens the surface of PS@silica spheres greatly. In comparison, the PS@titania spheres exhibit relatively smooth surface morphology (Figure 1d,e), which indicates that fine titania nanoparticles are formed and cover the surfaces of PS spheres in a uniform way.

These results could be attributed to the combination effects of the nucleation and growth processes of oxide nanoparticles derived from precursors on the surface of each PS core. During nucleation, the precursors interact with the hydroxyl groups on the PS surface and provoke the nucleation of oxide nanoparticles
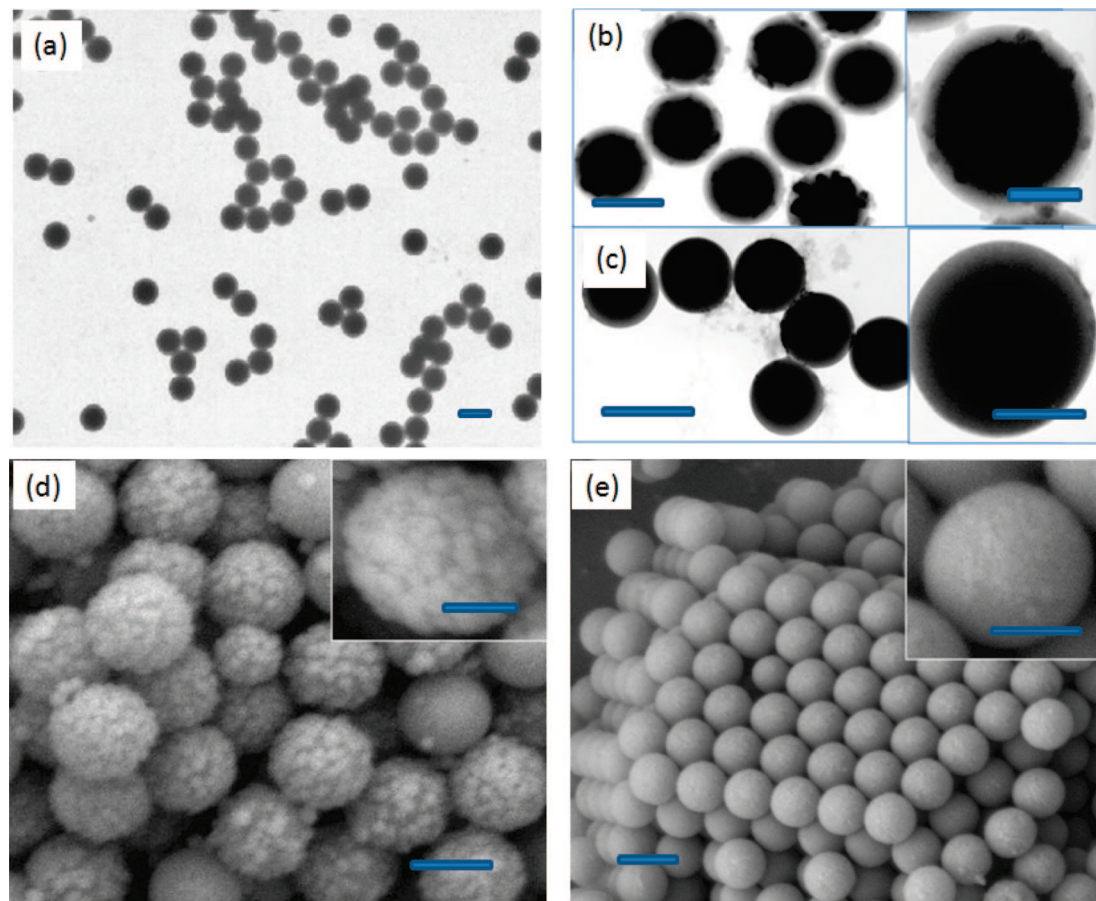
Figure 1. TEM images of (a) monodispere PS spheres, (b) PS@silica, and (c) PS@titania composite microspheres. SEM images of (d) PS@silica and (e) PS@titania composite microspheres. The scale bars are 400 nm, and the scale bars in the insets are 200 nm.

on the PS surface (surface nucleation process). Successively, these nuclei grow in size and finally fuse with each other, forming an oxide shell on the PS spheres (nuclei growth process). The final surface morphology of composite particles depends on the relative rate of nucleation and growth processes.[14] The surface-nucleation-controlled process is favorable to form smooth surfaces on composite spheres, and the nuclei-growth-controlled process is beneficial for generating rough surface morphology.[14] Therefore, it is believed that the employed reaction conditions of this study are more favorable for the nuclei-growth-controlled process for the hydrolysis process of TEOS and the surface-nucleation-controlled process for TIPP, which make the PS@silica spheres exhibit rougher surfaces than do the PS@titania spheres.

The rough surface consisting of the larger nanoparticles tends to decrease the strength of the resulting of oxide shell.[3] In this study, we tried to coat the silica and titania shell on the surface of PS using the same concentration of 0.20 vol % for both TEOS and TIPP. Unfortunately, when the PS core is etched with THF, the silica shell is too fragile to keep the complete hollow structure (Supporting Information). In comparison, the titania shell can stand and keep the hollow structure intact (vide infra). To generate rigid hollow silica, we tried to increase the concentration of TEOS to 0.35 and 0.50 vol %. It was found that both resulting hollow silica spheres exhibited spherical morphology and the average shell thickness was increased from 60 to 90 and 115 nm, respectively (Supporting Information). This fact indicates that the shell thickness of the hollow silica spheres obtained by templating plasma-treated PS colloids can be controlled by changing the employed amount of TEOS. As a result, in this study, the coating reactions were carried out at concentrations
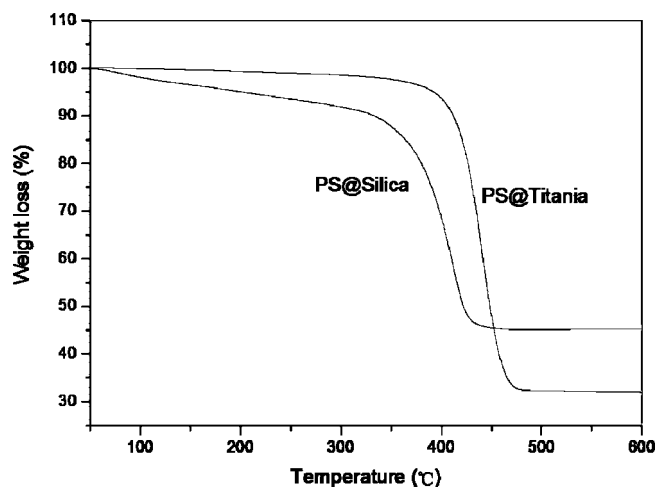

Figure 2. Thermogravimetric traces of PS@silica and PS@titania composite microspheres.

of 0.35 vol % for TEOS and 0.20 vol % for TIPP. The size of the corresponding PS@silica and PS@titania composite spheres increased from 310 (neat PS) to 490 and 360 nm, respectively (as determined by TEM and SEM, Figure 1b−e).

The compositions of PS@silica and PS@titania composite spheres were also investigated by means of thermogravimetric analysis (TGA), and the results are shown in Figure 2. In both cases, the weight loss stage below 330 °C is the result of the evaporation of physically adsorbed water and residual solvent in the samples. The major weight loss of the PS core was
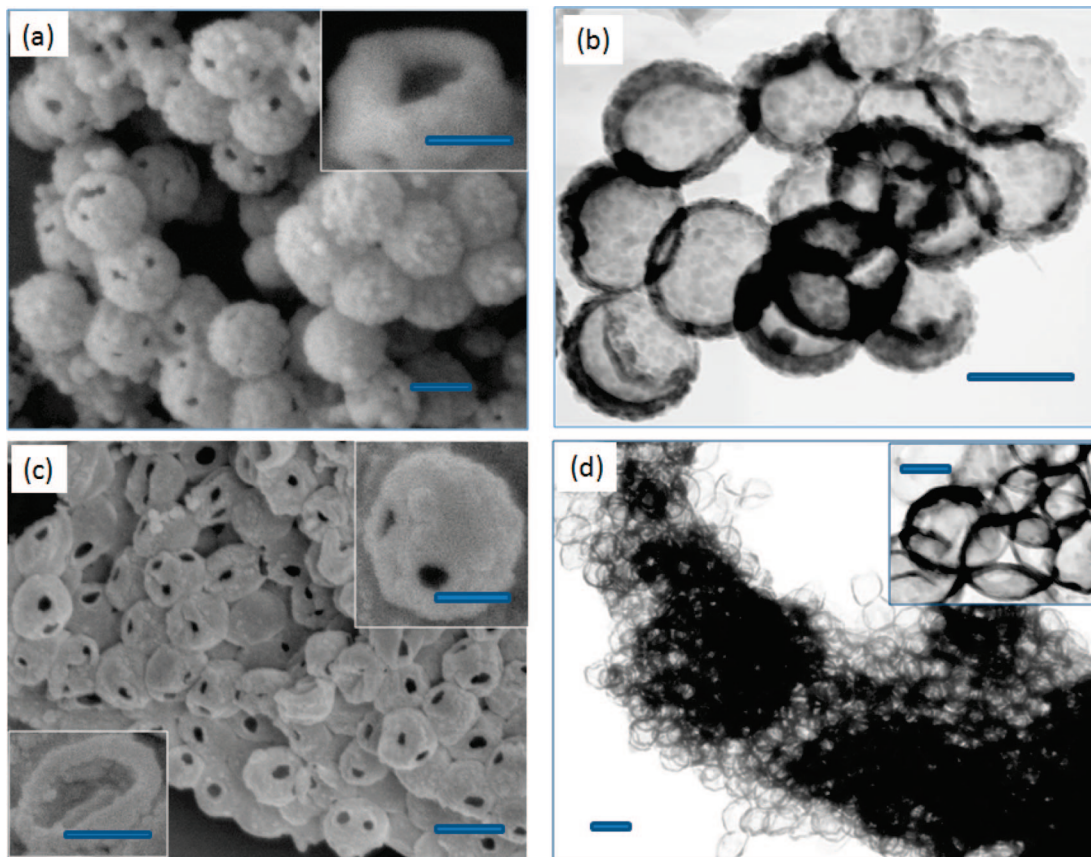
Figure 3. (a) SEM and (b) TEM images of hollow silica microspheres. (c) SEM and (d) TEM images of hollow titania microspheres. The scale bars are 400 nm, and the scale bars in insets are 200 nm.

completed around at 450 °C for PS@silica and 480 °C for PS@titania, where the mass fractions of 45 and 32% corresponding to the silica and titania remain, respectively. This fact indicated that the amount of the inorganic component can be increased by increasing the dosage of precursors (TEOS and TIPP) in the sol−gel process.

The hollow silica and titania spheres were generated successfully by the selective removal of PS cores from PS@silica and PS@titania composite spheres using THF. As shown in Figure 3a−d, most of the resulting silica and titania hollow spheres keep their initial spherical structures of PS templates. The SEM images of broken hollow spheres in Figure 3a,c show that the shell thicknesses of the hollow silica and titania spheres are around 90 and 25 nm, respectilvey. By comparing the surface morphologies of hollow silica and titania with those of corresponding composites (Figure 3a,c and Figure 1d,e, respectively), it is clearly observed that the PS core etching process creates several pores on the surface of hollow spheres. These pores might be generated by the swelling of the PS core before dissolving in THF. When the mechanical strength of the inorganic shells is not high enough, the swelling effects would rupture the shells, resulting in the generation of pores within the shells. The pore diameter is less than 60 nm for silica and 90 nm for titania by calculating over 100 hollow spheres. However, the etching processes have no effects on the surface roughness of the corresponding hollow oxides.

To determine the specific surface area and pore structure of the resulting composite samples and the corresponding hollow silica and titania spheres, Brunauer−Emmett−Teller (BET) analyses were performed. As shown in the inset of Figure 4A, the adsorption and desorption isotherms of PS@silica and hollow silica spheres reveal a type-ν physisorption isotherm (BDDT

classification)[21] with an increase in nitrogen uptake at high relative pressure $P/P_0 = 0.9-1.0$ and a wide hysteresis loop at $P/P_0 = 0.2-0.9$ indicating a typical mesoporous solid with larger pores.[22] This fact is consistent with the corresponding pore diameter distribution determined by the Barrett−Joner−Halenda (BJH) method based on desorption isotherms (Figure 4A), which suggests that both samples possess a broad pore size distribution in the mesoporous region (2−50 nm).[21] As far as the adsorption and desorption isotherms of PS@titania and the corresponding hollow titania are concerned, both samples showed type-ν isotherm behavior and exhibited a hysteresis loop in the relative pressure range of 0.4−0.8 (inset of Figure 4B), which indicates the presence of a typical pore size distribution in the mesoporous region.[1,23] This result is supported by the corresponding pore diameter distribution determined by the BJH method (Figure 4B), which clearly shows a narrow peak centered at 3.5 and 3.7 nm for PS@titania and hollow titania spheres, respectively. This fact is different from the case of silica, which could be associated with the textural mesopores of the oxides. In general, the textural mesopores are assigned to the interparticle spacing,[24] and the size of textural mesopores decreases with a reduction of the grain size of the mesoporous oxide.[24] Thus, the silica shell is expected to be composed of larger silica nanoparticles with varied size, and the titania shell consists of much finer nanograins (Figure 3a,c), so the hollow silica possesses a much broader textural mesopore distribution than does titania.

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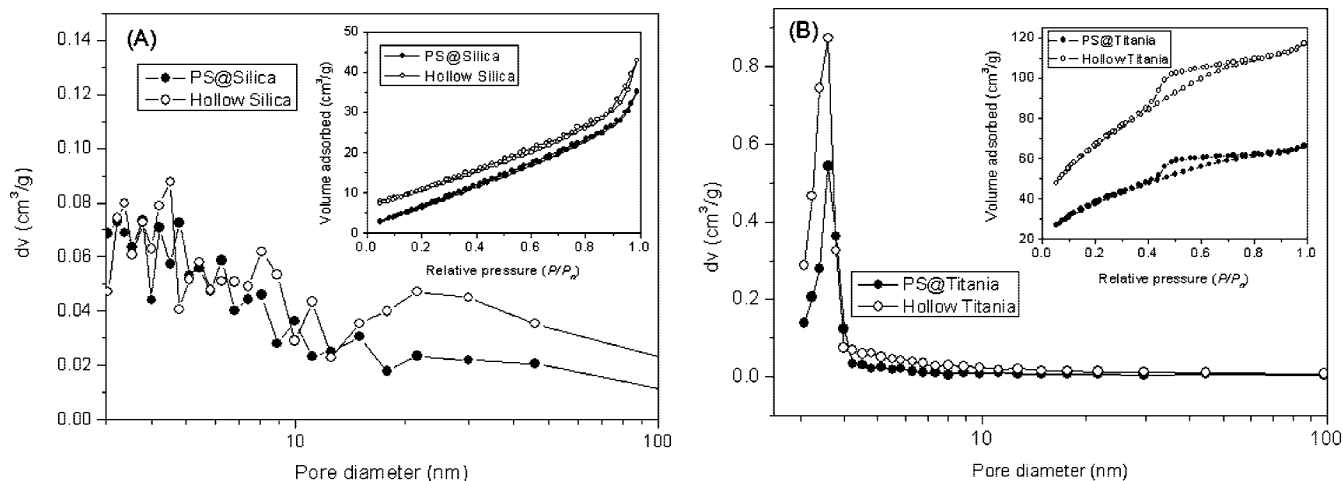(24) Ikari, K.; Suzuki, K.; Imai, H. *Langmuir* **2004**, *20*, 11504.

Figure 4. Pore size distribution curves and nitrogen adsorption and desorption isotherms (inset) of (A) the PS@silica composite and hollow silica microspheres as well as (B) the PS@titania composite and hollow titania microspheres.

The BET analysis results also gave surface area values of 27.46 and 38.33 m^2/g for PS@silica and hollow silica microspheres, respectively, and 38.55 and 67.84 m^2/g for PS@titania and hollow titania microspheres, respectively. In comparison, the composite microspheres have a smaller surface area than does the corresponding hollow structures, which was attributed to the formation of hollow structures after etching PS templates. Additionally, it is observed that hollow titania microspheres possess a larger surface area than do hollow silica microspheres, which is derived from the size of nanoparticles composed of oxide shells. Compared with titania, the larger silica nanoparticles tend to decrease the surface area of hollow silica.

Conclusions

We have demonstrated a facile, low-cost, environmentally benign way to fabricate hollow and mesoporous titania and silica microspheres using plasma-treated PS spheres as sacrificial templates. The hollow titania microspheres were characterized by the smoother surface, larger surface area, and much narrower pore diameter distribution than for the corresponding hollow silica microspheres. We are expanding our study by utilizing polymer spheres with different sizes and various metal oxide precursors. It is worth noting that this procedure offers a promising alternative to the creation of polymer/inorganic oxide composites and the corresponding hollow inorganic oxides structures by templating against the polymer substrate with hydrophobic surfaces.

Supporting Information Available: FTIR spectra of PS spheres before and after plasma treatment and SEM images of hollow silica spheres with varied shell thickness. This material is available free of charge via the Internet at http://pubs.acs.org.

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