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General Method for the Fabrication of Hollow Microcapsules with Adjustable Shell Compositions

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In this paper, a facile and general strategy has been proposed for the preparation of a series of microcapsules with the diverse shell compositions from silica to nonsilica (e.g., titania, zirconia, platinum, silver sulfide, cadmium sulfide, indium sulfide, and cadmium telluride) by simply alkaline treating the cationic polyelectrolyte precoated mesoporous silica spheres (MSSs) with or without the encapsulated guest species. The MSS acts both as the spherical template for the morphology of the final product and as the nanoreactor/reservoir of the nonsilica nanoparticles in their 3D-connected channels, while the cationic polymer precoated outside plays an interesting role of exonet or spherical scaffold for the construction of the shell in the final products through capturing and immobilizing the nanoparticles released during the core etching. The mechanism on the formation of the shell has also been revealed through investigating the morphology evolution of the samples during the alkaline treatment. Such a synthesis route could be extended to the fabrication of most of the alkaline-stable hollow microcapsules in principle.

1. Introduction

Hollow microcapsules with diverse shell compositions present a class of special materials that brings a series of new opportunities in the development of novel microreactors, catalysis, and optical or electrochemical architectures.[1] For examples, the hollow silica microcapsules are regarded as good candidates for the controlled drug release[2] while the hollow semiconductor microcapsules, such as CdS[3] or CdS/polystyrene[4] composites, have shown the special quantum-confined effects different either from the CdS quantum dots or the bulk counterparts. Besides, the hollow WO_3 microcapsules have been recently synthesized for the construction of the sensors to various organic gases.[5] Our group has also fabricated a series of noble metal or their oxide hollow microcapsules and found that the hollow platinum or the carbon core encapsulated platinum microcapsules have the high activity in the electrooxidation of methanol which is a fundamental reaction in the direct methanol fuel cells.[6] Up to now, three main strategies have been reported to prepare microcapsules, such as nozzle reactor process, emulsion/phase separation procedures, and sacrificial core techniques.[7] The layer-by-layer (LbL) assembly based on the sacrificial core technique is widely used for the purposeful fabrication of microcapsules with diverse shell compositions, which relies on (1) the synthesis and modification of stable monodispersed nanoparticles in dilute solution; (2) the construction of the desired shell via alternatively coating the nanoparticles and polyelectrolytes with opposite charges onto spherical template; and (3) the removal of the core through thermal or wet chemical methods.[8] However, the controlled

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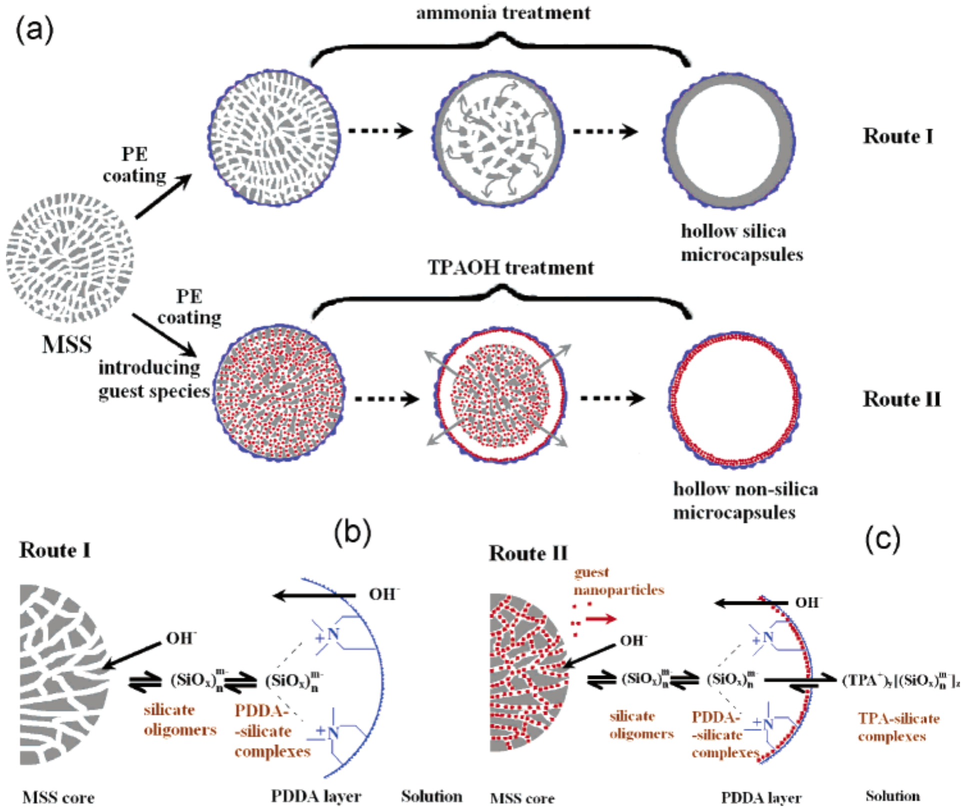
Scheme 1. Schematic Illustration for the Fabrication of Hollow Microcapsules (a), and the Formation of the Silica Shell in the Presence of Ammonia (b), and the Nonsilica Shell in the Presence of TPAOH (c) Accompanied with the Dissolution of MSS Core



synthesis of stable monodispersed nanoparticles of many compositions is relatively complicated and sometimes very difficult. As an improvement of this approach, Caruso et al.[9] recently reported an exquisite way called core-mediated LbL method for the preparation of two-component microcapsules (PSS/dMF and Ca^{2+}/algnate) by alternative deposition of PE from solution and the component from the decomposed core via a selective interaction between PE and guest species. Very recently, Wu et al.[4] have introduced a one-step strategy for the synthesis of hollow CdS/polystyrene composite microcapsules by in-situ transformation of Cd^{2+}, S^{2-}, and styrene monomer in the water/oil (W/O) emulsion under γ−ray radiation. However, the special requirements for the above processes (e.g., the special PE/core couple with characteristic interaction in Caruso's work and γ−ray sensitive species in Wu's work) make such methods suitable to those systems with aboratively designed compositions, which may limit their generality. Therefore, the development of facile and general methods for the formation of microcapsules with desired shell composition remains a challenge to the scientists.

Porous sphere is an ideal template for the fabrication of hollow microcapsules. Besides the spherical morphology, its highly porous interior offers great opportunity for the pre-encapsulation of functional guest species. By taking porous spheres as the template, Volodkin et al.[10] and our groups[1h,11] have successfully fabricated polyelectrolyte and zeolitic microcapsules containing organic and inorganic species, respectively. In this paper, a general approach is developed for the fabrication of microcapsules with diverse shell compositions. By precoating one layer of cationic poly-(dimethyldiallylammonium chloride) (PDDA) on mesoporous silica spheres (MSSs) and subsequently treating in ammonia solution, the hollow silica microcapsules could be obtained as a result of the interaction between the anionic silicate oligomers and the cationic polyelectrolyte shell (Scheme 1, route I). If the pore channels of MSS are purposefully pre-incorporated with guest species and the weak alkaline ammonia is substituted by the strong alkaline tetrapropylammonium hydroxide (TPAOH) for removal of silica, a variety of microcapsules with the nonsilica shell including oxides, metals, sulfides, or tellurides can be fabricated through the similar method (Scheme 1, route II). The combination of both the porous silica sphere and the surface-coated PDDA layer endows this method with some unique advantages compared with the previously reported techniques: (1) the abundant mesopores in the MSS act as the nanoreactor/reservoir for the formation of various nanoparticles and consequently bypass the difficult step for presynthesis of highly dispersive nanoparticles in traditional LbL process; (2) besides the spherical template effect of the silica core for the microcapsule formation in the initial stage, the

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cationic polymer coated outside plays an interesting role of the exonet or spherical scaffold for the shell construction via catching and immobilizing the nanoparticles which are released during the silica core etching process; and (3) the dissolution of the silica core and the formation of the shell occur in one step, which greatly simplifies the fabrication procedures.

2. Experimental Section

2.1. Materials. The PDDA (Mw = 200 000), poly(sodium 4-styrene sulfonate) (PSS, Mw = 70 000), poly(*N*-vinyl-2-pyrrolidone) (PVP, Mw = 40 000), zirconium (IV) isopropoxide (ZrIP), titanium (IV) isopropoxide (TiIP), 3-amino-propyltriethoxysilane (APS), and 3-mecapto-propyltriethoxysilane (MPTS) were purchased from Aldrich. The noble metal precursor H_2PtCl_6 was supplied from Shanghai July Chemical Company. Concentrated ammonia solution ($NH_3 \cdot H_2O$, 26∼28 wt %), KBH_4 (94 wt %), cadmium chloride ($CdCl_2 \cdot 4H_2O$), indium chloride ($InCl_3 \cdot 3H_2O$), silver nitrate ($AgNO_3$), triethylchlorosiliane (Et_3SiCl), tetrapropylammonium hydroxide (TPAOH, 25 wt % in water), orthosilane (TEOS), ethanol, toluene, and cyclohexane were obtained from Shanghai Chemical Reagent Company. All chemicals were used without further purification. MSS was synthesized according to the method reported by Unger's group.[12] CdTe nanoparticles (2 nm) were synthesized according to the literature.[13] The monodispersed nonporous silica spheres were synthesized according to the well-documented Stöber method.[14]

2.2. Fabrication of Hollow Silica Microcapsules. The silica microcapsules were prepared by simply treating PDDA-precoated MSS in ammonia solution as illustrated in Scheme 1a, route I. Typically, 1 g of MSS was dispersed in 10 mL of 0.2 wt % PDDA solution at room temperature and sonicated for 30 s to coat a PDDA layer onto MSS. After being centrifuged and washed by deionized water three times, the PDDA-coated MSS was added to 80 mL of 1 M ammonia solution and heated at 90 °C under static conditions for 7 h. The resulted product was isolated, washed with deionized water several times, and dried at room temperature. The organic species was removed by calcination in air at 550 °C for 4 h. To illustrate the effect of PDDA for the formation of silica shell, the same procedure was also applied to PSS and PVP-precoated MSS spheres which were pre-prepared by dispersing 1 g of MSS in 10 mL 0.2 wt % PSS and PVP solution, respectively. Furthermore, the PDDA-coated nonporous silica spheres were also treated under the same conditions to prove the effect of mesopores in MSSs.

2.3. Fabrication of the Hollow Microcapsules with Nonsilica Shell. *2.3.1. Pre-incorporation of Guest Species.* To incorporate enough quantity of guest species into MSS mesopores for the formation of the continuous shell, the MSSs were premodified with ethyl-, NH_2-, and SH-groups by, respectively, mixing 1 g of MSS into 20 mL dry cyclohexane, ethanol, and dry toluene solutions containing 1 wt % of Et_3SiCl, APS, and MPTS, stirring for 6 h at ambient temperature, and then washing with corresponding solvents and drying at 80 °C. The introduction of zirconia or titania was conducted by dispersing 1 g of ethyl-modified MSS into 20 mL of cyclohexane containing 20 wt % ZrIP or TiIP and stirred for 7 h under room temperature. The final products are separated by centrifugation, washed by cyclohexane, and dried at 80 °C, followed by calcination at 600 C for 3 h in air. Platinum is introduced by adding 1 g of NH_2-modified MSS into 10 mL of 0.4 M aqueous solution of H_2PtCl_6 stirred at room temperature for 30 min, and then treated by 10 mL of 0.01 M KBH_4 solution till no more bubbles are observed. After being centrifuged, washed, and dried, the samples are calcinated in air at 600 °C for 3 h. The sulfide incorporation is formed by dispersing 1 g of SH-modified MSS into 30 mL 10 wt % $CdCl_2 \cdot 4H_2O$, $InCl_3 \cdot 3H_2O$, or $AgNO_3$ aqueous solutions and stirring for 30 min, followed by centrifugation and washing; the final products are obtained by calcination at 350 °C in nitrogen. Cadmium telluride (CdTe) is introduced by treating NH_2-modified MSS with a solution containing 2 nm CdTe nanoparticles followed by washing and drying.

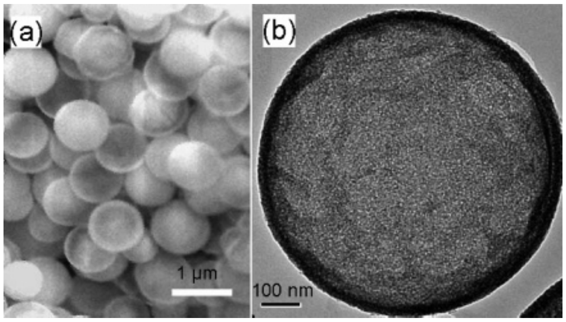

Figure 1. SEM (a) and TEM (b) images of the hollow silica microcapsules obtained by treating PDDA-precoated MSSs with 1 M ammonia solution.

2.3.2. Formation of the Nonsilica Hollow Microcapsules. The formation of microcapsules with nonsilica shell was achieved by TPAOH treating PDDA-coated MSSs which were pre-incorporated with corresponding guest nanoparticles (Scheme 1, route II). The PDDA coating step was the same as that for the fabrication of hollow silica microcapsules as described in 2.2. The TPAOH treatment was realized by adding 0.1 g PDDA-precoated sample into 20 mL 1.5 wt % TPAOH aqueous solution at 100 °C for 5 h to remove the silica ingredient from the sample. The final products are collected by centrifugation, washing, and dispersing in distilled water for further characterization.

2.4. Characterization. X-ray powder diffraction (XRD) patterns were taken on a Rigaku D/MAX-IIA diffractometer using Cu Kα radiation. SEM and TEM studies were performed on Philips XL 30 and JEOL 200 with the accelerate voltage of 20 and 200 kV, respectively. The selected-area electron diffraction (SAED) patterns were obtained via the electron diffraction instrument attached to TEM.

3. Results and Discussion

3.1. Fabrication of Hollow Silica Microcapsules. Figure 1a and b shows the SEM and TEM images of the discrete hollow silica spheres after calcination at 550 °C, respectively. The spherical morphology of the MSS was well retained after ammonia treatment, and the hollow structure in TEM image (Figure 1b) and the semitransparent shells in SEM images (Figure 1a) clearly indicate that the silica template cores have been completely dissolved. The mean diameter of the product is ca. 800 nm and the shell thickness is ca. 50 nm. The well-retained structure after calcinations at 550 °C proved their high thermal stability.

During the synthesis, we found that the coating of PDDA layer, the ammonia concentration, and the porous structure of MMS play important roles in the fabrication of silica hollow microcapsules. Without being coated with PDDA,

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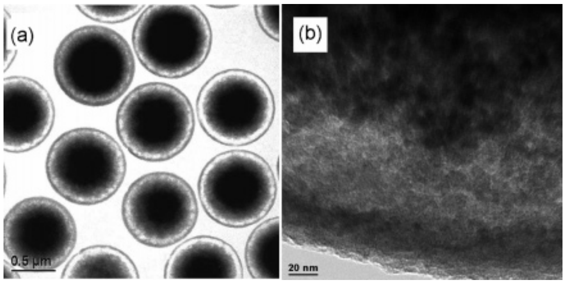

Figure 2. TEM images of the core−shell silica microcapsules obtained by treating PDDA-precoated MSSs with 0.1 M ammonia solution (a), and its high magnification image (b).

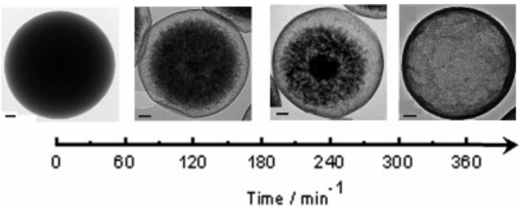

Figure 3. TEM images of the PDDA-precoated MSSs in the different period of 1 M ammonia solution treatment (scale bar = 100 nm).

the same treatment only led to the decrease of the MSS particle size as well as the collapse of mesopores. Furthermore, when the PDDA coating is replaced by the neutral polymers (e.g., PVP) or negative charged polyelectrolytes (e.g., PSS) and followed with the same ammonia treatment, only little amount of hollow morphology could be observed, and their shells were very loose and obscure compared with those prepared from PDDA-coated MSSs (Supporting Information), indicating that the use of the positively charged polymer is crucial for the formation of compact silica shell. At relatively lower ammonia concentration (e.g., 0.1 M $NH_3 \cdot H_2O$), only core−shell silica spheres instead of the hollow microcapsules were obtained at the same reaction time (Figure 2a). The residue core inside is featured by a coarse surface (Figure 2b), which could be attributed to the corrosion effect of the alkali treatments. The diameter of the core gradually decreases with the increasing of the concentration of alkali and finally disappears completely when the ammonia concentration reaches 1 M. The porous structure of the MMS is also quite necessary for the formation of the microcapsules. If the nonporous silica spheres were used as templates, only few shell structures were observed under the same condition. Furthermore, if the pore channels of MSS are blocked (e.g., in the case of zirconia pre-incorporated MSS), the expected shell structures could hardly be obtained even at higher ammonia concentration (e.g., 3 M) and higher treatment temperature (e.g., 100 C) (Supporting Information).

On the basis of the above experimental results, a mechanism for the shell formation could be described as follows. During the ammonia treatment, the hydroxyl ions (ionized by $NH_3 \cdot H_2O$) permeated through the PDDA layer and attacked the silica sphere and generated the dissolved silicate oligomers (Scheme 1b). Such oligomers with negative charge tend to immigrate and deposit onto the positively charged PDDA layer because of the electrostatic interaction. With increasing the amount of the silicate oligomers deposited on the PDDA exonet and the decrease of the alkalinity in the solution (the pH value decreased from ca. 11 to 9 since the hydroxyl ions were gradually consumed by the digestion of the silica core), the silicate oligomers begin to cross-link and finally form a continuous and compact silica−PDDA complex shell. Herein, the PDDA plays a role just like the catcher which captured the silica species dissolved from MSS core and enriched them onto its surface. By investigating the TEM images of the solid product separated from the reaction mixture at certain time intervals, more information about the shell formation process could be obtained (Figure 3). In the initial stage of the alkaline treatment (about 120 min), the silica near the surface of MSS is first attacked and the dissolved silicate oligomers are immediately captured by the PDDA layer. The resulting thin shell of PDDA−silicate complex prevented the deformation or collapse of the flexible PDDA layer when it lost the support of the MSS. With prolonging the duration of the treatment, the core diminishes and finally disappears while the thickness of the shell increases through the dissolution−polymerization equilibrium of the silica species (Scheme 1b). Such a process is similar to the natural biosilification process in most of the diatom cells in which the biomolecules capture the silicate species from the aqueous environment through organic−inorganic interactions and direct the formation of various morphologies.[15] In this work, the essential driving force for the fabrication relies on the interaction between the silicate oligomers and PDDA exonet which leads to the formation of the silica−PDDA composite shells. If the PDDA exonet is not applied, no microcapsule could be obtained. When the neutral polymer or negatively charged polyelectrolyte was used instead of PDDA, both the dissolution and deposition of silica species are not favored because of the less interaction or even repulsion between the polymer exonet and the negatively charged silica oligomer as well as the hydroxyl anions. The porous structure in MSS also greatly facilitated the formation of the shell because the abundant peripheral pore opening around the MSS offers additional spaces for the accommodation of the PDDA chain, and their three-dimensionally (3-D) connected pores is beneficial for the diffusion of hydroxyl ions and silicate oligomer during the dissolution process.

3.2. Fabrication of Hollow Microcapsules with Nonsilica Shell. The microcapsules with the nonsilica shell compositions have wider applications than those with the silica shells;[1,5,6] thus, the fabrication of the hollow microcapsules with nonsilica shell is more attractive and important. As reported in the previous literature,[1h,11] the 3-D mesopores in MSS could provide the excellent reservoir for various nanoparticles. By using such guest pre-incorporated MSS[1h,6,11] as the starting materials, the above method was also attempted to be extended into the fabrication of the microcapsules with nonsilica shells. However, two problems should be considered: (1) because of the blockage effect of the pre-incorporated guest particles within the pore of MSS (cf. 3.1),

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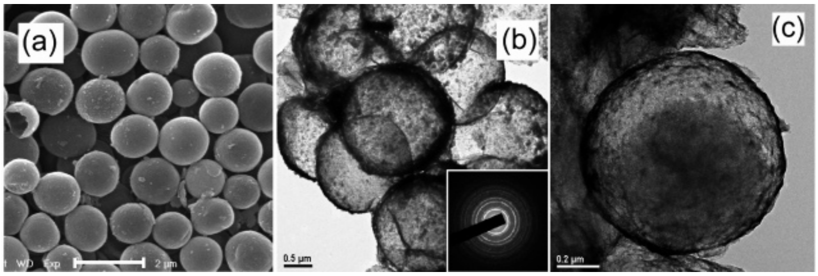

Figure 4. SEM (a) and TEM (b) images of the hollow zirconia microcapsules (inset of b is their SAED pattern) and the TEM image of the carbon-encapsulated zirconia microcapsules (c).

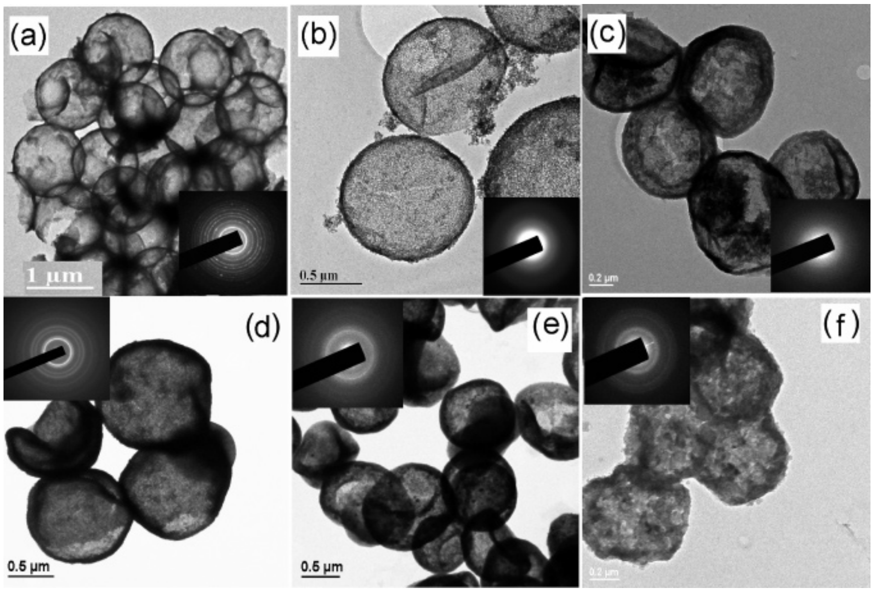

Figure 5. TEM images of the prepared TiO_2 (a), CdTe (b), In_2S_3 (c), Pt (d), Ag_2S (e), and CdS (f) microcapsules with their SAED patterns.

the dissolution of MSS core becomes very slow under the treatment of the weak alkali such as ammonia so that a stronger alkali is required for the dissolution of MSS and (2) according to the mechanism discussed in 3.1 (Scheme 1b), because of the strong interaction between the anionic silicate oligomers and cationic PDDA exonet, the silica would be collected onto the polymer shell even if the MSS core was completely dissolved, therefore, an extract agent for the removal of silica species from the product is needed in the reaction system. Here, the TPAOH is used instead of ammonia not only because it could provide the high hydroxyl ion concentration but more importantly, its tetra-alkyl-ammonium ions (TPA^+) have the special interaction with silica oligomers as reported in the literatures concerning the synthesis of zeolites.[16] Such strong alkaline and special interaction of TPAOH might favor the dissolution and removal of siliceous species from the samples, leading to the release of the pre-incorporated guest nanoparticles and the following formation of the nonsilica shell through the deposition of these guest nanoparticles onto the PDDA exonet (Scheme 1c).

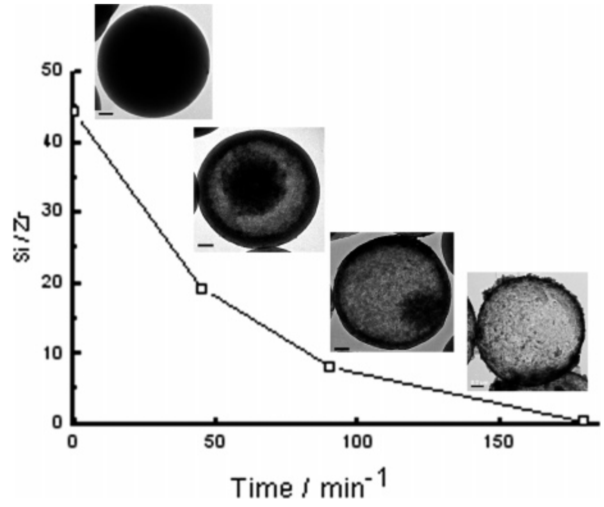

Figure 6. The time-resolved silica content variation curve of the zirconia microcapsules with the corresponding TEM images (scale bar = 200 nm).

As expected, a series of hollow microcapsules with nonsilica shells were obtained by treating the guest-pre-incorporated PDDA-coated MSS in the TPAOH solution (Figures 4 and 5). As an example, Figure 6 exhibits the shell formation process of the hollow ZrO_2 microcapsules. Besides the gradual dissolution of the MSS core like the case of silica microcapsules (Figure 3), the Si/Zr molar ratio of the sample dramatically drops from 44.5 to 0.2 with increasing the duration of such alkaline treatment, indicating that silicate oligomers dissolved from the MSS cores have been effectively removed by TPAOH while the originally incorporated zirconia nanoparticles remain on the PDDA exonet to form the ZrO_2 shell. To further prove the efficiency of the TPAOH on the removal of silica species, the PDDA-

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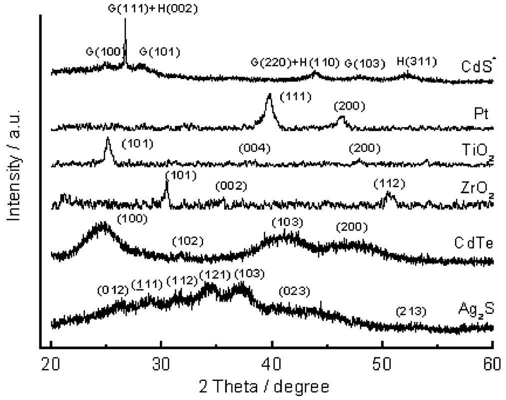

Figure 7. XRD patterns of the prepared microcapsules. (* A mixture of greenockite (G) and hawleyite (H) is observed in CdS sample.)

precoated MSSs without guest incorporation was also treated in the TPAOH solution. It was found that the reaction mixture become pellucid and no solid product could be recovered after reaction.

Figure 4 depicts the SEM and wider-field TEM images of the prepared zirconia microcapsules. The final product well keeps the spherical morphology of the initial MSS template (Figure 4a), and its shell gives a ringlike SAED pattern (Figure 4b, inset) and a characteristic XRD pattern of tetragonal crystalline structure of ZrO_2 (Figure 7). More interestingly, when MSS was prefilled with continuous carbon phase in its interior 3D-connected pores,[6,11] a sphere-in-shell structure (mesoporous carbon sphere/zirconia shell) can be obtained via the same procedures (Figure 4c). Such a structure would display the cooperative functions of shells and the interior material, leading to new applications in material science.

Besides zirconia, microcapsules with other types of shell compositions including noble metals, sulfides, and tellurides can be obtained as well by using their corresponding precursors preintroduced MSSs as the template. Figure 5a−f displays the prepared microcapsules with shells of anatase titania (TiO_2), cadmium telluride (CdTe), platinum (Pt), acanthite silver sulfide (Ag_2S), cadmium sulfide (CdS), and amorphous indium sulfide (In_2S_3, the chemical composition is proved by EDS). The crystalline structures of the prepared samples are proved by their SAED (insets of Figure 5) and XRD patterns (Figure 7). The contents of Si remaining in all samples are below 2.5 wt %, indicating that most of the silica ingredient inside the samples has been successfully removed during the process of the shell formation.

4. Conclusions

To summarize, we have demonstrated a versatile strategy to fabricate hollow microcapsules with adjustable shell compositions including oxides, noble metals, sulfides, and tellurides. The mesopores in MSS behave as reserviors/nanoreactors for the guest nanoparticles while the PDDA coated outside of MSS acts as spherical scaffold/exonet for the formation of the shell. The possible mechanisms on the formation of these structures have been discussed. The applications of such materials in catalysis, optics, and electrochemistry are yet to be explored.

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Supporting Information Available: The SEM and TEM images of the MSS template. The TEM images of the products by treating PVP- and PSS-precoated MSSs in 1 M ammonia solution, and those prepared by treating PDDA-coated zirconia-pre-incorporated MSSs in 3 M ammonia solution (PDF). These materials are available free of charge via the Internet at http://www.pubs.acs.org.

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