Core–Shell Nanoparticles

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The Precise Synthesis and Growth of Core–Shell Nanoparticles within a Self-Assembled Spherical Template**

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Nanoparticles with core–shell structures can exhibit unique material properties and promise a variety of applications in materials science, optics, catalysis, and biophysics.[1–11] The precise synthesis of core–shell nanoparticles is of utmost importance as the material properties depend on the constituent elements as well as the size and shape of the nanoparticles. The synthesis of core–shell nanoparticles is typically carried out by coating the surface of the core nanoparticles with metal ions or metal alkoxides in solution, where the controlled growth of the core nanoparticles and the outer shells is achieved by modulating the synthetic conditions (e.g., temperature, concentration, solvent, and pH value). However, the preparation of both the highly monodisperse core nanoparticles and the subsequent core–shell nanoparticles remains difficult. Recently, several groups have utilized hollow assemblies and media, such as reverse micelles, to control the growth of core–shell nanoparticles, in which the hollow interior acts as a template.[12–14] Unfortunately, the templating assemblies are themselves not monodisperse and thus the precise control of nanoparticle growth remained elusive. Furthermore, the large size of the template assemblies precludes the synthesis of small (< 10 nm) core–shell nanoparticles.

Recently we published the synthesis of monodisperse SiO_2 nanoparticles using structurally exact coordination spheres as templates.[15] The $M_{12}L_{24}$ spheres self-assembled from 12 Pd^{2+} ions (M) and 24 bent bridging ligands (L)[15–21] and presented a sugar-coated interior that templated the precise synthesis of highly monodisperse SiO_2 nanoparticles with diameters of 2–4 nm using the sol-gel condensation of alkoxysilanes. Herein, we describe the elaboration of monodisperse SiO_2 nanoparticles confined within the template sphere with a metal oxide (MO_2; where M = Ti or Zr) layer to generate monodisperse core–shell nanoparticles (Figure 1). The core–shell nanoparticles (SiO_2/TiO_2, SiO_2/ZrO_2) have diameters of 3 nm and preserve the highly monodisperse molecular weight distributions ($M_w/M_n < 1.01$) as characterized by TEM and MS analyses.

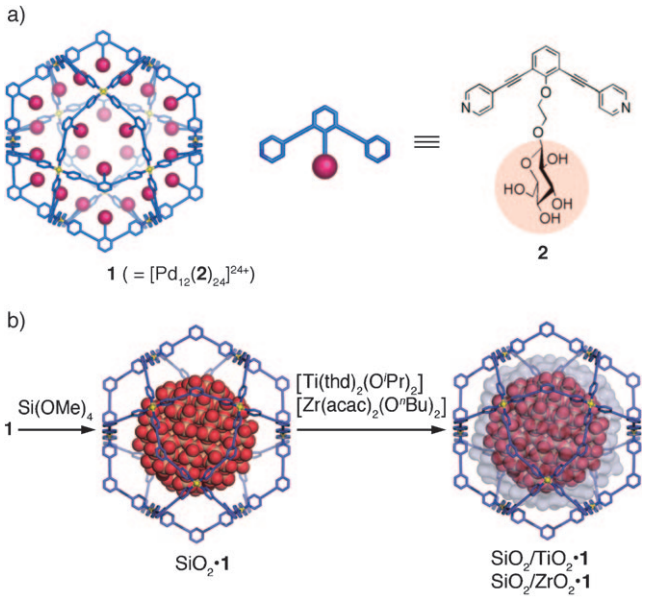

Figure 1. a) Structures of **1** and **2**. Yellow spheres in compound **1** denote Pd^{2+} ions. b) Schematic representation of the template-directed synthesis of core–shell nanoparticles within hollow sphere **1**. The $ROCH_2CH_2O$ pendant groups (R = β glucosyl) are omitted for clarity.[22]

Self-assembled nanosphere **1** (nitrate salt unless otherwise noted) with the templating glucose interior lining was prepared from sugar-appended ligand **2** and $Pd(NO_3)_2$ in DMSO. With sphere **1** as a template, silica (SiO_2) core nanoparticles were prepared as follows: tetramethoxysilane (TMOS, 100 equiv) was added to sphere **1** (80 μM, $CDCl_3$/[D_6]DMSO 9:1) and the mixture was stirred at room temperature for four days. Upon hydrolysis and condensation of TMOS inside **1**, NMR signals of the sphere framework significantly broadened because of the growth of SiO_2 nanoparticles within the inner cavity (Figure 2a,b). Under laser desorption ionization mass spectrometry (LDI-MS) conditions, the shell framework of **1** was destroyed and we could directly confirm the formation of highly monodisperse silica nanoparticles with molecular ion peaks of $[SiO_2]^+$ centered at $m/z = 7840$ (ca. 100 SiO_2 units) and a polydispersity index (PDI; M_w/M_n) of 1.006 (Figure 3a). The nanosphere template **1** utilizes solvophobic effects to sequester the hydrophilic intermediate silanols from the relatively nonpolar $CDCl_3$/[D_6]DMSO 9:1 solvent mixture into the sugar-coated hydro-

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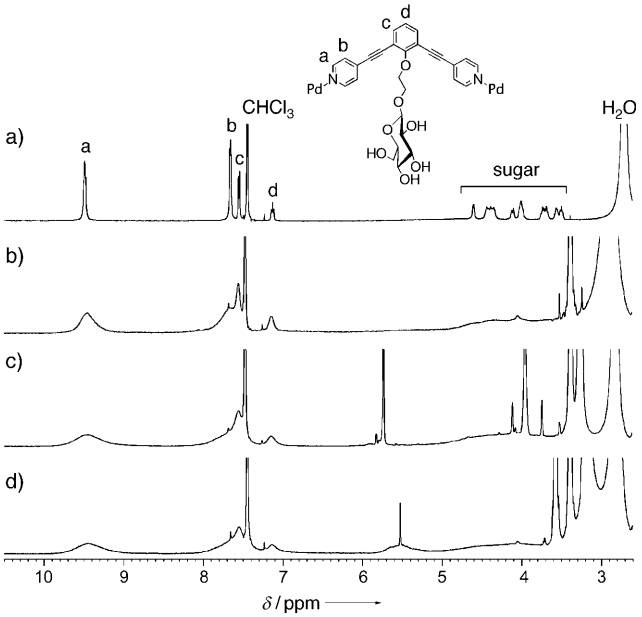

Figure 2. ^{1}H NMR spectra (500 MHz, $CDCl_3$/[D_6]DMSO 9:1, 300 K). a) Sphere **1**. b) SiO_2·**1** produced by condensation of TMOS (100 equiv) in the presence of sphere **1** at room temperature for four days. c) (SiO_2/TiO_2)·**1** produced by condensation of $Ti(thd)_2(OiPr)_2$ (40 equiv) in the presence of SiO_2·**1** at room temperature for four days. d) (SiO_2/ZrO_2)·**1** produced by condensation of [$Zr(acac)_2(OiPr)_2$] (40 equiv) in the presence of SiO_2·**1** at room temperature for four days.

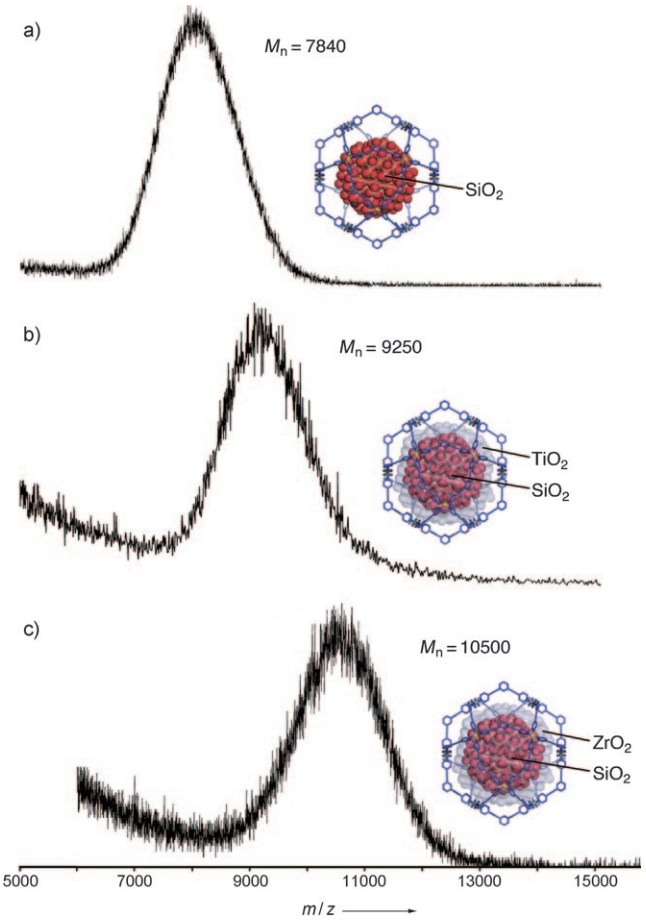

Figure 3. LDI mass spectra of nanoparticles. a) SiO_2 core nanoparticles (M_n = 7840) within **1**. b) SiO_2/TiO_2 core–shell nanoparticles (M_n = 9250) within **1**. c) SiO_2/ZrO_2 core–shell nanoparticles (M_n = 10500) within **1**.

philic interior of **1**, which, by virtue of the exact molecular structure of nanosphere **1**, produces well-controlled SiO_2 nanoparticles (denoted as SiO_2·**1**).

With monodisperse SiO_2 nanoparticles in hand, the surfaces of the nanoparticles were then covered with TiO_2 shells. Initial attempts with $Ti(OiPr)_4$ as the TiO_2 precursor were unsuccessful because hydrolysis and condensation were too fast and the partially hydrolyzed intermediates did not penetrate the sphere scaffold. $Ti(thd)_2(OiPr)_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate), however, is less reactive than $Ti(OiPr)_4$ and facilitated the fabrication of TiO_2 layers onto the inclusion complex SiO_2·**1**. A mixture of SiO_2·**1** (80 μM) and 40 equivalents of $Ti(thd)_2(OiPr)_2$ in $CDCl_3$/[D_6]DMSO 9:1 was stirred for four days at room temperature and the SiO_2/TiO_2 core–shell nanoparticles were characterized by ^{1}H NMR and LDI-MS. ^{1}H NMR signals of the framework of **1** in SiO_2/TiO_2·**1** were further broadened relative to SiO_2·**1** as the growth of a TiO_2 shell upon the surface of SiO_2 core further restricts the degrees of freedom for the framework (Figure 2c). LDI-MS analysis revealed the molecular weights of the nanoparticles increased from 7840 (core nanoparticle of ca. 100 SiO_2 units) to 9250 for SiO_2/TiO_2·**1** and thus confirmed the formation of SiO_2/TiO_2 core–shell nanoparticles (Figure 3b). The increase in molecular weight (ΔM_n = 1410) corresponds to approximately 18 TiO_2 units and accordingly SiO_2/TiO_2 100:18 core–shell nanoparticles.[22] Elemental analysis by inductively coupled plasma atom emission spectroscopy (ICP-AES) analysis indicated the Si/Ti ratio to be 100:19, in consistency with the LDI-MS study. More importantly, the SiO_2/TiO_2 nanoparticles exhibited a very high monodispersity (M_w/M_n = 1.005), hence showing that the original accuracy of SiO_2 core nanoparticles was preserved and that shell growth was also strictly controlled. The SiO_2/TiO_2 nanoparticles are quite stable in solution within the protective framework of template **1**: neither aggregate formation nor changes in molecular weight were observed even after several months in solution.

After core–shell formation, a new band at 951 cm^{-1} appeared in FTIR and can be attributed to the Si–O–Ti stretching vibration at the interface of the SiO_2/TiO_2 core–shell structures (Figure 4b).[23] TEM images showed uniformely sized and well-separated nanoparticles with diameters of 3.0 nm (Figure 4a). Unfortunately, the interface of core–shell structures was not clearly distinguishable because of the relatively low-contrast images. Nevertheless, in combination with the LDI-MS data, these results demonstrate that Si–O–Ti bonds bind a TiO_2 shell to the surface of monodisperse SiO_2 nanoparticles.

In the same way, SiO_2/ZrO_2 core–shell nanoparticles were prepared within **1** by treating SiO_2·**1** (M_n of SiO_2 = 7840) with 40 equivalents of [$Zr(acac)_2(OnBu)_2$] at room temperature for four days (Figure 2d). The obtained SiO_2/ZrO_2 nanoparticles (M_n = 10500) also exhibit a very high monodisper-

sity by LDI-MS ($M_w/M_n = 1.006$, Figure 3c). Judging from $\Delta M_n = 2660$, roughly 22 equivalents of $[Zr(acac)_2(OiPr)_2]$ were incorporated into the sphere. Consistently, elemental analysis by ICP-AES indicated the Si/Zr ratio to be 100:27.

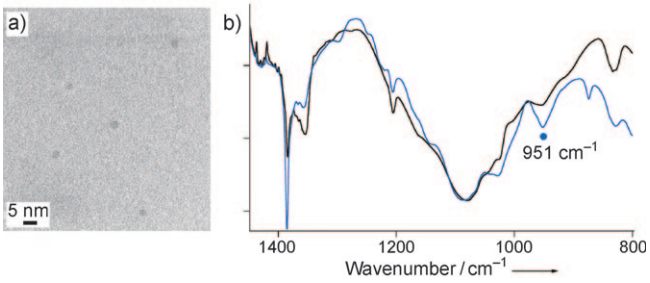

Figure 4. Structural analyses of SiO_2/TiO_2 core–shell nanoparticles. a) TEM image of SiO_2/TiO_2 nanoparticles within **1**. b) FTIR spectra of SiO_2·**1** (black line) and (SiO_2/TiO_2)·**1** (blue line). Band at 951 cm^{-1}, which corresponds to Si—O—Ti bonds, is marked with a blue circle.

In summary, we have developed an efficient method for the precise growth of core–shell nanoparticles by using a self-assembled hollow sphere complex as a template. Unlike the previous, ill-defined template assemblies, the structurally exact sphere complex generated core–shell SiO_2/TiO_2 and SiO_2/ZrO_2 nanoparticles with high monodispersity ($M_w/M_n <$ 1.01). We envision that this facile and precise synthetic method will be applied to the synthesis of further nanoparticles with core–shell structures suitable for novel applications in various research and industrial fields.

Experimental Section

NMR spectra were obtained on a Bruker DRX 500 spectrometer equipped with a 5 mm BBO Z-gradient probe, or on a Bruker AV 500 spectrometer equipped with a 5 mm TCI CryoProbe. The chemical shift values reported herein are with respect to an internal TMS standard. Spectra of CSI-MS (cold-spray ionization mass spectrometry) were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700C, JEOL) equipped with a CSI source. Spectra of LDI-TOF MS were measured with a time of flight (TOF) mass spectrometer (Applied Biosystems Voyager DE-STR) without matrix. IR measurements were carried out with KBr pellets using a DIGILAB Scimitar FTS-2000 instrument. X-ray fluorescence spectra were measured with JSX-3400R II (JEOL), and the ratio of Pd and Si was calculated by the thin-film fundamental parameter (FP) method. TEM images were obtained at 200 kV with a JEOL JEM-2010HC instrument on carbon-film-coated copper grids (thickness of carbon film was 6 nm). ICP-AES analyses were performed on a Thermo Fisher iCAP6300DUO.

Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma–Aldrich Co. All chemicals were of reagent grade and were used without any further purification.

Synthesis of SiO_2 core nanoparticles within sphere **1**: Sphere **1** (0.64 μmol) in DMSO (0.80 mL) was diluted with H_2O (2.2 μL) and $CHCl_3$ (7.2 mL), and treated with tetramethoxysilane (64 μmol, 9.5 μL, 100 equiv for **1**) at RT for 4 days. As reaction time progressed, ^{1}H signals of **1** changed to broad signals in ^{1}H NMR spectra, which indicated the formation of silica nanoparticles within **1** (denoted as SiO_2·**1**). After all $Si(OCH_3)_4$ were hydrolyzed, SiO_2·**1** was analyzed by ^{1}H NMR spectroscopy, DOSY NMR spectroscopy, and LDI-MS. After removal of $CHCl_3$ by evaporation, ethyl acetate and diethyl ether were added to the resulting solution to obtain the pale yellow precipitate of SiO_2·**1**. Diffusion coefficient $D = 1.5 \times 10^{-10}$ m^{2}s^{-1} ($CDCl_3$/[D_6]DMSO 9:1, 300 K) by ^{1}H nuclei. LDI-MS: $M_n = 7840$, $M_w = 7890$ ($M_w/M_n = 1.006$). XRF analysis: number of Si atoms per **1** was 95 (Pd/Si 1:7.9).

Synthesis of SiO_2/TiO_2 core–shell nanoparticles within sphere **1**: SiO_2·**1** (0.080 μmol, M_n of $SiO_2 = 7840$) in $CDCl_3$/DMSO 9:1 (1.0 mL) was treated with $Ti(OiPr)_2(thd)_2$ (3.2 μmol, 1.7 mg, 40 equiv for SiO_2·**1**) at RT for 4 days. As reaction time progressed, ^{1}H signals of **1** became even broader in ^{1}H NMR spectra, which indicated the formation of TiO_2 shells around SiO_2 nanoparticles within **1** (denoted as (SiO_2/TiO_2)·**1**). After four days, (SiO_2/TiO_2)·**1** was analyzed by ^{1}H NMR spectroscopy, DOSY NMR spectroscopy, and LDI-MS. Diffusion coefficient $D = 1.3 \times 10^{-10}$ m^{2}s^{-1} ($CDCl_3$/[D_6]DMSO 9:1, 300 K) by ^{1}H nuclei. LDI-MS: $M_n = 9250$, $M_w = 9300$ ($M_w/M_n =$ 1.005). Elemental analysis by ICP-AES: Si/Ti 100:19. Before ICP analysis, (SiO_2/TiO_2)·**1** was once precipitated from the solution by evaporating $CHCl_3$ and adding Et_2O and AcOEt to be separated from unreacted titanium alkoxide in solution. The precipitated (SiO_2/TiO_2)·**1** was then dissolved in DMSO-aqueous NaOH solution and subjected to ICP-AES analysis. Since sphere **1** was decomposed under basic conditions and Pd^{II} ions were partially precipitated as their hydroxide, Pd/Si could not be determined by the ICP-AES analysis.

Synthesis of SiO_2/ZrO_2 core–shell nanoparticles within sphere **1**: $[Zr(OnBu)_2(acac)_2]$ was prepared by mixing aectylacetone (4.0 mmol, 413 μL) and Zr(O*n*Bu) solution (80wt% in 1-butanol, 2.0 mmol, 914 μL) at RT under argon atmosphere. SiO_2·**1** (0.12 μmol, M_n of $SiO_2 = 7840$) in $CDCl_3$/DMSO (9:1, 1.5 mL) was treated with $[Zr(OnBu)_2(acac)_2]$ (4.8 μmol, 2.9 μL, 40 equiv for SiO_2·**1**) at RT for four days. As reaction time progressed, ^{1}H signals of **1** became even broader in ^{1}H NMR spectra, which indicated the formation of ZrO_2 shells around SiO_2 nanoparticles within **1** (denoted as (SiO_2/ZrO_2)·**1**). After four days, (SiO_2/ZrO_2)·**1** was analyzed by ^{1}H NMR spectroscopy, DOSY NMR spectroscopy, and LDI-MS. Diffusion coefficient $D = 1.4 \times 10^{-10}$ m^{2}s^{-1} ($CDCl_3$/[D_6]DMSO 9:1, 300 K) by ^{1}H nuclei. LDI-MS: $M_n = 10500$, $M_w = 10560$ ($M_w/M_n = 1.006$). Elemental analysis was done by ICP-AES in a similar procedure as above: Si/Zr 100:27.

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