

Fabrication of Controllable Ultrathin Hollow Shells by Layer-by-Layer Assembly of Exfoliated Titania Nanosheets on Polymer Templates

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Core–shell composites and titania hollow shells have been fabricated via the layer-by-layer self-assembly approach using exfoliated unilamellar titania nanosheets $Ti_{1-\delta}O_2^{4\delta-}$ ($\delta \sim 0.09$) as inorganic shell building blocks. Polystyrene and poly(methyl methacrylate) spheres with different diameters were employed as colloidal templates, and polyethylenimine was utilized to modify the surface charge of polymers. The ultrathin nature (0.75 nm) of two-dimensional nanosheets enabled tailoring the shell thickness in a nanometer-scale range by varying the coating cycles. SEM revealed the evolution of shell structures on templating cores. An X-ray diffraction peak with a periodicity of ca. 1.6 nm and its enhancement with increasing coating cycles indicated the regular growth of the shell of nanostructured $Ti_{1-\delta}O_2^{4\delta-}$ /PEI repeating pairs. Calcination at 500 °C or UV-irradiation of the core–shell composites removed the polymer cores, yielding titania hollow shells. They are characterized by their smooth curvature and extremely small thickness (as small as 5 nm). The titania hollow shells exhibited various optical properties, depending on the treatments.

Introduction

The strategy to fabricate inorganic nano-coatings or shells on colloidal particles is currently an attractive topic of investigation due to their great potential in the areas of electronics, photonics, and catalysis, as well as nanotechnology.^{1–3} The preparation process generally involves the deposition of particular precursors of desired shell materials around core particles such as polymer and microemulsion. The resulting shells coated on templating cores often afford the composites physicochemical properties significantly different from those of cores. A number of works have been focused on the fabrication of core–shell composites using molecular precursors and nanoparticles as inorganic shell building blocks in either direct surface reaction/precipitation or layer-by-layer (LBL) self-assembly approaches.^{4–8} One of the main challenges for this pathway is to obtain

uniform and controllable structures of shells. However, sensitive condensation/polymerization conditions of molecular precursors or the aggregation tendency of nanoparticles made the manipulation complicated for the purpose of preparing core–shell structures with precisely controllable thickness.

Titanium oxide has attracted much attention because of its versatile applications in electronic, photocatalytic and electrochemical systems.^{9–11} Recently the LBL procedure has been applied to fabricate titania hollow shells using nanoparticles or molecular precursors as starting materials.^{5b,7,12} A thickness as small as ~15 nm has been achieved for submicrometer-sized hollow shells. We have recently reported novel titania “nanosheets” crystallites of $Ti_{1-\delta}O_2^{4\delta-}$ ($\delta \sim 0.09$) produced by soft-chemical delamination of a layered titanate $Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$ (\square : vacancy).¹³ The nanosheet has a crystallographic thickness of 0.75 nm corresponding to two edge-shared TiO_6 octahedra. On the other hand, its two-dimensional size is usually in the range of 200–400 nm, depending on the dimensions of the starting titanate crystals. We have demonstrated the LBL assembly of

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the nanosheets on a flat substrate and interesting optical properties for the resulting ultrathin films.¹⁴ It should be of great interest if the two-dimensional delaminated nanosheets can be used as inorganic building blocks in fabrication of core–shell composites. The nanosheets may behave as pieces of “wrapping paper” when covering the template surface via the LBL assembly approach. The flexibility of nanosheets enables the reliable replication of original template morphology. Compared with titania nanoparticles or molecular precursors studied to date, the lamellar nanosheets are advantageous as building blocks for several reasons: the uniform thickness in sub-nanometer range and highly crystalline nature may lead to a well-defined shell and the precise control of its thickness. Recently, exfoliated zirconium phosphate nanosheets and silicate clay nanoplatelets have been employed as inorganic coating materials in fabricating core–shell composites.^{7,15} However, the information concerning the crystallinity or controllable structures of core–shells was limited.

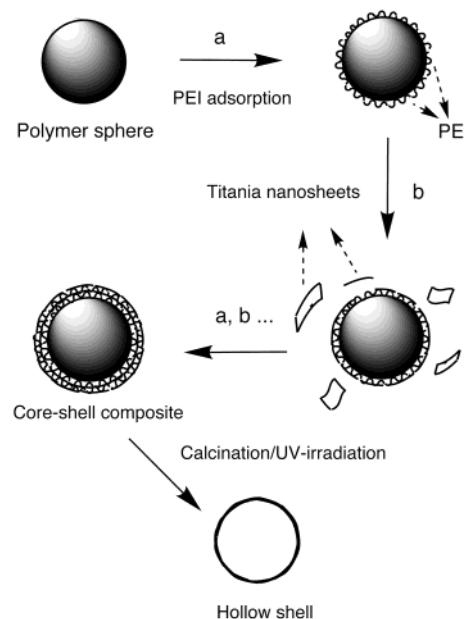
This paper describes the fabrication of ultrathin titania hollow shells with precisely controllable thickness by employing exfoliated titania nanosheets as inorganic shell starting materials. The alternate LBL assembly technique allowed the negatively charged titania nanosheets to adhere onto the surface of colloidal polymer templates to produce core–shell structures. The resulting core–shell composites could be converted into hollow spheres by heat-treatment or UV-irradiation.

Experimental Section

Materials. Two kinds of polymers used as colloidal templates, polystyrene (PS) with an average diameter of 1.3 μm and poly(methyl methacrylate) (PMMA) with an average diameter of 0.4 μm , were purchased from Soken Chemical Co., Japan. Polyethylenimine (PEI), a cationic polyelectrolyte, was purchased from Aldrich Chemical Co. and used as received. A colloidal suspension containing exfoliated titania nanosheets of the composition $\text{Ti}_{1-\delta}\text{O}_2^{4\delta-}$ ($\delta \sim 0.09$) was synthesized according to the previously reported procedure.¹³ Ultrapure water ($>17 \text{ M}\Omega \text{ cm}^{-1}$) from a Milli-Q water system was used throughout the experiments.

Fabrication of Hollow Shells. Prior to the adsorption of the negatively charged titania nanosheets, the surfaces of the PS and PMMA were modified by adsorbing PEI, an effective disperser in aqueous solution.¹⁶ In a typical synthetic procedure, 0.6 g of PS particles were dispersed in 150 cm^3 of H_2O containing 0.02 g of PEI under stirring, and then the suspension was ultrasonically treated for 10 min. Further stirring was carried out for another 15 min to ensure the saturated adsorption of PEI on the surface of the PS. Excess PEI was removed by twice repeating a cycle of centrifugation (5000 rpm, 5 min) and water washing. Afterward, the PEI-coated PS was dispersed in 150 cm^3 of H_2O again and ultrasonically treated for another 10 min. A 5- cm^3 portion of colloidal suspension of exfoliated titania nanosheets (concentration 8 mg/cm^3) was added to the turbid PS suspension under stirring. Immediately after addition of the suspension, some flocculated aggregates formed in the mixture due to the electrostatic interaction of the oppositely charged nanosheets and PS surface. After the reaction, the resulting product was sedimented, giving super-

Scheme 1. Schematic Illustration of the Fabrication Procedures for Hollow Titania Shells (Polymer Sphere, PEI, and Titania Nanosheets Are Indicated)



natant that was almost transparent. Titania nanosheets were used in excess to ensure coverage of the entire particle surface. Finally, the resulting material was recovered by the separation and washing process. The above procedure was repeated for a specified number of cycles to fabricate the PS-shell coated with alternating multilayers of $\text{PEI}/\text{Ti}_{1-\delta}\text{O}_2^{4\delta-}$.¹⁰ The preparation of PMMA-shell is similar to that of PS-shell except that the amount of the colloidal suspension of titania nanosheets was increased to 20 cm^3 because the surface area of PMMA spheres is larger than that of PS spheres. Hollow titania shells were produced either by heat- or UV-treatment of the core–shell composites. Calcination was conducted (heating rate of 1 K/min) at 500 °C in air for 2 h. UV-irradiation was carried out under a Xe lamp in an oxygen atmosphere for a specified time. The power density for the Xe lamp was about 5 mJ/cm^2 .

Characterization. X-ray diffraction (XRD) data were collected by a Rigaku Rint 2000 powder diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$; scattering slit, $1/2$ degree; receiving slit, 0.3 mm; divergence slit, $1/2$ degree). Scanning electron microscopy (SEM) observations were performed with a JEOL JSM-5800LV instrument operated at 15 kV. Samples were sputter-coated with Au to approximately 10 nm in thickness. A JEOL 1010 transmission electron microscope (TEM) operated at 100 kV was employed to obtain TEM images and electron diffraction patterns. Thermogravimetric measurements (TGA) were carried out under airflow using a Rigaku TG-8120 instrument at a heating rate of 1 K/min. The ultraviolet–visible diffuse-reflectance (UV–vis DR) spectra were recorded in a diffuse reflectance mode using a Hitachi U-4000 spectrometer equipped with an integrating sphere detection system.

Results and Discussion

Scheme 1 schematically displays the overall procedure for synthesis of the titania hollow shells. In the first step, the surface of the colloidal polymer spheres was modified with PEI to be positively charged. Next, the negatively charged titania nanosheets were adsorbed onto the surface of these polymer templates to form core–shell composite due to the electrostatic attraction between them. To fabricate thicker titania shells, PEI and the titania nanosheets were alternatively deposited

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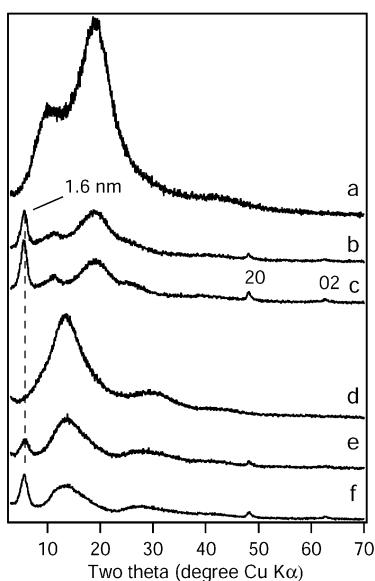


Figure 1. XRD patterns of core–shell nanocomposites. (a) Bare PS spheres; (b) PS spheres coated with 10 layer pairs of PEI/ $\text{Ti}_{1-\delta}\text{O}_2^{4\delta-}$; (c) PS spheres coated with 20 layer pairs; (d) bare PMMA spheres; (e) PMMA spheres coated with 5 layer pairs; and (f) PMMA spheres coated with 10 layer pairs. Dotted line shows the Bragg peak with an interplanar spacing of ca. 1.6 nm. All the data were collected with a similar amount of sample.

on polymer spheres for a specified number of cycles. Every deposition step involved dispersing, mixing, centrifuging, washing, and re-dispersing operations. The resulting core–shell composites were finally heated at 500 °C or treated under UV-irradiation to obtain ultrathin titania hollow shells.

Core–Shell Structures. XRD data of the PS-shells and PMMA-shells provided the information for the growth of shell structures (Figure 1). The halos from polymers suppressed considerably upon coating, suggesting the coverage of PS or PMMA cores with shell materials. Apart from the halos, diffraction features due to the multilayer shell became discernible after several sequential adsorption cycles. A peak showing an interplanar spacing of ~1.6 nm can be attributed to the repeated inorganic–organic layer pairs of $\text{Ti}_{1-\delta}\text{O}_2^{4\delta-}$ /PEI. A similar XRD result showing a Bragg peak has already been obtained for the multilayer assemblies of $\text{Ti}_{1-\delta}\text{O}_2^{4\delta-}$ /PDDA pair on a flat substrate,¹⁴ where PDDA represents poly(diallyldimethylammonium) ion. It is noteworthy that no internal nanostructure has been reported for shells with nanoparticles or molecular precursors. As mentioned above, the thickness of titania nanosheets is 0.75 nm, and the thickness of the PEI monolayer deposited under similar conditions has been determined to be 0.80 nm by ellipsometry.^{14b} Hence, the expected repeating distance of $\text{Ti}_{1-\delta}\text{O}_2^{4\delta-}$ /PEI layer pair should be ~1.55 nm, which is in good agreement with the observed XRD data. The progressive enhancement in intensity of these profiles with increasing coating cycles strongly suggested the successful LBL self-assembly of titania nanosheets on PS and PMMA surfaces. The additional two peaks that appeared at higher 2θ range can be identified as two-dimensional reflections, 20 and 02 diffraction bands which arise from intra-nanosheets periodicity of 0.38 nm × 0.30 nm.¹⁷

SEM observations visualized the formation of the core–shell structures. The nearly homogeneous curvature of the spherical morphologies in the core–shell particles indicated that the fabricated shells preserved the spherical shape of the templates. As the titania nanosheet is extremely thin compared with the relatively huge diameters of PS and PMMA spheres, almost no apparent change in diameter could be distinguished during the sequential coating of shells. Only a noticeable difference for the spheres with or without shells was the surface roughness. Up to 10 cycles of coating, the surface of the PS sphere was still relatively smooth (see Figure 2a), which is similar to that of a bare PS sphere, and only a very small amount of splinters was identified in high-magnification observations. In contrast, the roughness of the spherical surface became pronounced after 20 cycles (Figure 2b). Partial peeling off of shells from the core surface was observed.

Titania Hollow Shells. The core–shell samples were calcined to remove the polymer cores. To avoid the fracture of shells due to combustion of a large amount of organic polymer, the heat-treatment was performed using a slow heating rate of 1 K/min. The shells prepared from the PS-shell composite coated with 20 bilayers of $\text{PEI}/\text{Ti}_{1-\delta}\text{O}_2^{4\delta-}$ kept virtually intact as that observed in the uncalcined core–shell composite. Some broken spheres provided clear evidence for hollow spherical structures (Figure 2c). SEM observations revealed that hollow shell structures could also be observed in the sample coated with 10 bilayers, although a larger proportion of broken shells was present. TEM images (Figure 2d) of titania shells further confirmed the hollow nature of materials. High-magnification TEM image of a typical area of one hollow shell prepared with 20 layers showed that the thickness of the shell was around 15–20 nm (Figure 2e). As mentioned above, the thickness of a nanosheet is 0.75 nm. Hence, the expected thickness of 20 layers of stacked nanosheets after removal of intercalated PEI molecules should be ~15 nm. This is very consistent with the TEM result, strongly suggesting the feasibility of our strategy in precise control of shell thickness. The smooth curvature of the shell structure may also be taken as an advantage in comparison with the uneven surface of hollow shells prepared from nanoparticles. The electron diffraction pattern of shells (Figure 2f) was composed of a series of sharp diffraction rings that are attributable to anatase, one of the polymorphs of TiO_2 . The indices and spacings for the diffraction rings 1–6 were (1) 101, 0.353 nm; (2) 004, 0.236 nm; (3) 200, 0.189 nm; (4) (105 + 211), 0.167 nm; (5) 204, 0.151 nm; and (6) 116, 0.134 nm, respectively. The XRD profile (Figure 3) also confirmed the formation of anatase. It is rather surprising that high crystallinity was achieved even by calcination at a relatively low temperature of 500 °C. Anatase crystallized at this temperature is usually in poor crystallinity.

Note that the shrinkage of the PS-shell upon calcination is quite small, being only about 5–10% compared with the corresponding size of uncalcined core–shell composites. More than 10%, or even around 30%, shrinkage could occur in comparable hollow shells or macroporous structures prepared from nanoparticles

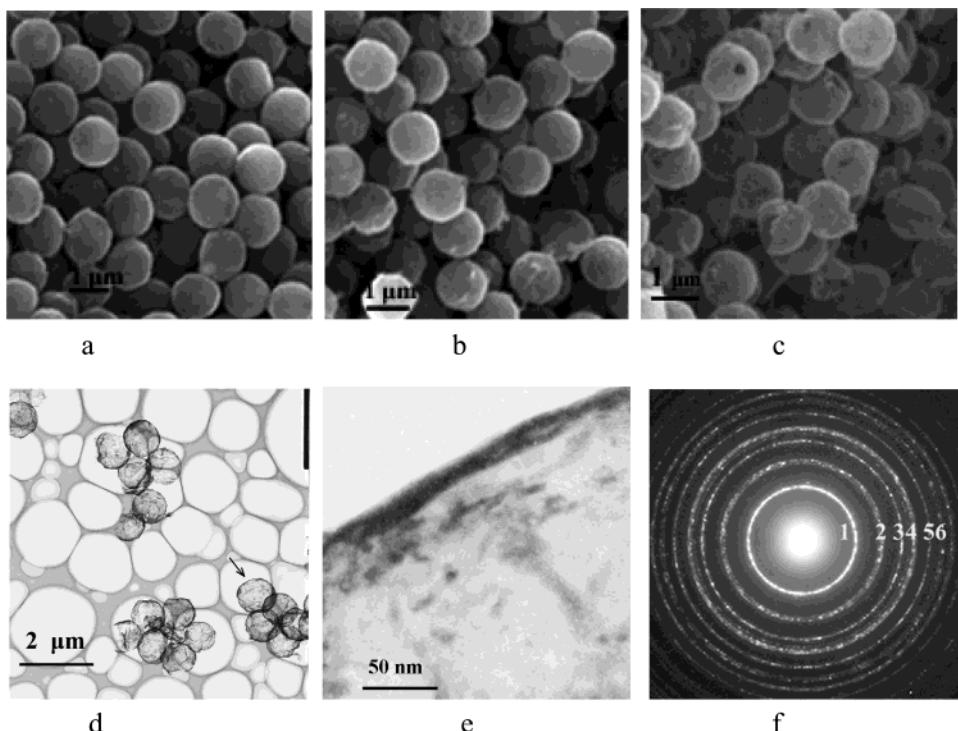


Figure 2. SEM images of PS-shell composites prepared with (a) 10 and (b) 20 layer pairs of PEI/Ti_{1- δ} O₂^{4 δ -}; SEM image (c) and TEM image (d) of hollow shells obtained after calcination of the PS-shell coated with 20 layer pairs; (d) high-magnification TEM (marked area by arrow in Figure 2c) showing the wall structure; (e) electron diffraction pattern from hollow shells.

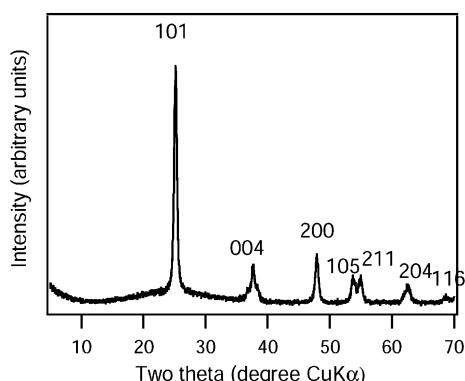


Figure 3. XRD pattern of titania hollow shells prepared with calcination at 500 °C for 2 h.

and molecule precursors,^{7a,18} which might be due to the sintering contraction of nanoparticles or further condensation/polymerization of molecular precursors upon calcination. In contrast, titania nanosheets with high two-dimensional anisotropy made it unique and relatively stable upon heat treatment. The slight shrinkage of hollow shells might be a consequence of the removal of PEI molecules between the nanosheets. The shell without significant shrinkage should be favorable in applications that require accurately controllable sizes.

Removal of Cores via UV-Irradiation. Calcination and solvent extraction have been the methods commonly used to remove organic cores in core–shell nanocomposites. In this work, UV irradiation was attempted to decompose the polymers in core–shell powders. UV illumination is considered as a promising “green” pathway due to the advantage of mild low-temperature

reaction conditions.¹⁹ To eliminate organic species in the core–shell nanocomposite, a small amount of sample was dispersed well in a glass container and then was exposed to UV light in oxygen atmosphere for a specified time. TGA analysis on the irradiated sample revealed that organic species could be decomposed. The degree of decomposition was dependent on the polymer-particle size and UV-treatment time. In the case of the PS-shell, less than half of the PS could be removed after one week, whereas the smaller-sized polymers (PMMA) were more easily decomposed, e.g., more than 75% of polymer in PMMA-shell could be removed by UV illumination for one week. Further treatment for two weeks might lead to polymer-free shells. TEM observations revealed that both hollow shells and intermediate form of shells accommodating partially decomposed cores could be observed, which depends on UV treatment time. Figure 4a shows a TEM image of hollow shells obtained via UV-irradiation of PMMA-shells coated with 5 layer pairs of Ti_{1- δ} O₂^{4 δ -}/PEI. Most shells preserved the spherical morphologies despite their extremely thin shells. Note that calcination of the same sample gave the broken shells as majority, suggesting that UV-irradiation is a more promising route in preparing intact ultrathin hollow shells. XRD data of the UV-treated sample (Figure 5) revealed almost loss of the halo pattern from PMMA.

What is the mechanism of polymer removal? Recently, Thurn-Albrecht et al. reported that pristine PMMA could be decomposed, whereas PS tended to cross-link under dense UV-irradiation (power density 25 J/cm²).²⁰

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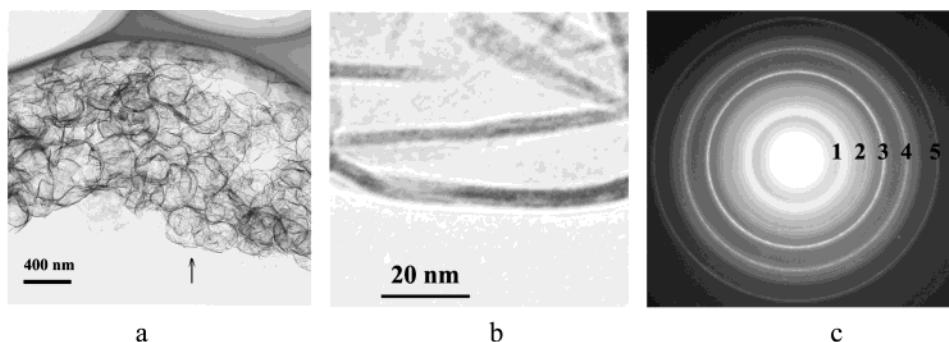


Figure 4. (a) TEM image of hollow shells obtained after UV-irradiation of PMMA-shell with 5 layer pairs of PEI/Ti_{1- δ} O₂^{4 δ -}; (b) high-magnification TEM image (marked area by arrow in Figure 3a) showing the shell structure; (c) electron diffraction pattern from hollow shells. The indices and spacings for diffraction rings 1–5 can be indexed as 10 (0.377 nm), 11 (0.235 nm), 20 (0.189 nm), 02 (0.151 nm), and 22 (0.118 nm), respectively, of the two-dimensional unit cell (0.38 nm × 0.30 nm) for the nanosheet.²¹

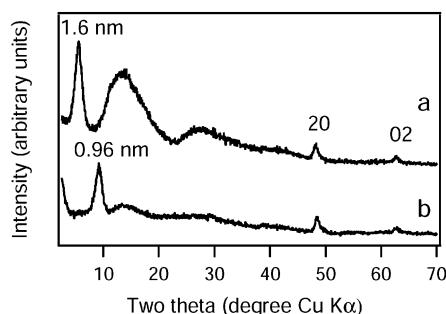


Figure 5. XRD patterns of PMMA-shells coated with 10 layer pairs (a) before and (b) after UV-irradiation for one week.

In this work with much milder treatment (5 mJ/cm²), we found that bare polymer PMMA could also be decomposed, but to a lesser extent than the sample coated with titania shell. Furthermore, negligible weight loss was observed for bare PS spheres, contrasting to ~30% loss for the PS polymers in PS-shell composites. These data indicate that photocatalytic action of titania nanosheets dominantly contributes to removal of polymer cores under UV-irradiation.

Besides the core removal, the multilayer repeat spacing was contracted to ~0.96 nm. Recently we reported similar behavior for PDDA/Ti_{1- δ} O₂^{4 δ -} multilayer film on substrates;²¹ polyelectrolytes were photocatalytically degraded to form NH₄⁺ as charge-balancing ions. In contrast, 20 and 02 diffraction bands remained unchanged, indicating the intactness of titania nanosheets. No phase transformation into anatase took place because the polymer removal proceeded at ambient temperature. A high-magnification image (Figure 4b) showed that the thickness of shell was in the range 4–5 nm, which is in agreement with the expected thickness of 4.8 nm (= 0.96 × 5) for 5 stacked nanosheets derived from XRD data, again supporting the advantage of our approach in precise control of shell thickness. To the best of our knowledge, no shell in this thickness has been achieved before using nanoparticles or molecular precursors as coating materials. The electron diffraction pattern of the shells prepared via UV treatment also gave a series of concentric diffraction rings (Figure 4c), but was apparently different from that of the hollow shell obtained by calcination. The diffraction rings were

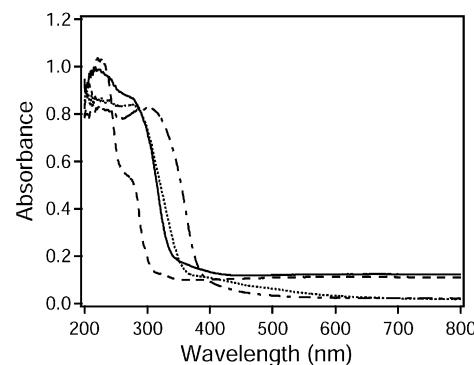


Figure 6. Diffuse reflectance UV-visible spectra of bare PMMA spheres (dashed line), PMMA-shells coated with 10 layer pairs (solid line), (c) hollow shells prepared with UV-illumination (dotted line), and (d) hollow shells prepared with calcination at 500 °C (dashed-dotted line).

attributable to the two-dimensional lattice of the nanosheets, compatible with the XRD data.^{13c,17}

Optical Properties. Figure 6 shows the diffuse reflectance UV-vis spectra for core–shell composites and titania hollow shells. A strong absorption band centering at around 220 nm with a shoulder at ca. 270 nm is diagnostic of PMMA polymers. The absorbance at ~270 nm enhanced markedly for core–shell composites, which is attributable to the coverage of the polymer surface with titania nanosheets having a UV-absorption peak at 265 nm. The spectral profile for hollow shells prepared by calcination was apparently red-shifted compared with those for core–shell composites, which is due to the transformation of nanosheets with a molecular thickness to anatase phase. In contrast, the absorbance band position of hollow shells prepared with UV-irradiation was almost unchanged from that for core–shell nanocomposites, whereas the contribution from PMMA decreased considerably. The optical data are consistent with the structural and compositional characterizations described above. The ultrathin titania hollow shells showing various optical properties may be promising in photochemical fields.

Conclusions

The fabrication of hollow shells has been demonstrated using sequential adsorption of PEI and exfoliated Ti_{1- δ} O₂^{4 δ -} on PS and PMMA spheres. The ultrathin nature of titania nanosheets enabled control of the thickness of titania shells in the step of nanometer-

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scale, providing a new alternative route in fabricating core–shell composites with finely controllable ultrathin coating. UV irradiation has been proved to be a feasible and clean approach in decomposing organic substances. The highly crystalline nature and stable hierarchical structures of the shells with varied optical properties make them promising in a range of applications. One

can also expect to prepare heterocomposite shells with different kinds of nanosheets and to find unique properties from these novel sandwiched structures. Experiments with other alternative exfoliated sheets are currently underway.

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