Layer-by-layer self-assembled hollow titania composite nanospheres containing [60]fullerene

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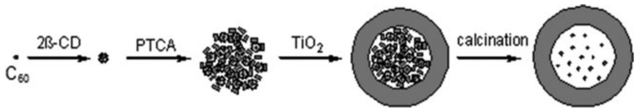
Core–shell nanospheres, titania composite nanospheres containing [60]fullerene, were fabricated with sizes of about 100 nm by a layer-by-layer self-assembly procedure, and were characterized by TGA, FT-IR and XPS spectroscopy.

Developments in nanotechnology demand building blocks of increasing structural and compositional complexity that can be reproducibly self-assembled into functional materials. In this regard, nanoparticles with core–shell morphologies represent a new type of construction unit, consisting of two dissimilar compositional and structural domains. In recent years, most attention has been paid to core–shell nanostructures[1–3] owing to their important optical, electronic, magnetic and catalytic applications, and as drug delivery carriers and nanoreactors.[4–10] In this field, layer-by-layer (LBL) self-assembly approaches have been applied to fabricate hollow composites using molecular precursors and nanoparticles as inorganic shell building blocks.[1,9,10] As kinds of photocatalytically active and photoconductive *n*-type semiconductors, numerous nanosized titania materials have been synthesized and investigated extensively.[11,12] Recently, several types of titania hollow shell have been reported using the LBL technique.[1,13] In our past work, we have fabricated C_{60}@2β-CD-TiO_2 (CD = β-cyclodextrin) nanospheres (15 nm in diameter) and investigated their properties.[14] But owing to the small cavity in the TiO_2 shell, it was difficult to observe hollow TiO_2 nanospheres with C_{60} cores. Bearing this mind, herein we introduce 3,4,9,10-perylene tetracarboxylic acid (PTCA) to form organic–inorganic C_{60}@2β-CD/PTCA/TiO_2 composite nanospheres that are 100 nm or so in diameter. By removing the organic compounds, after calcination, hollow nanospheres result.

The hollow titania composite nanospheres, containing [60]fullerene with a core–shell structure, were designed as shown in Scheme 1. [60]Fullerene is highly symmetric, representing a special class of aromatic system. Because of water insolubility and the absence of a driving force for self-assembly with orthotitanic acid, the pristine C_{60} was capped with two β-CD molecules, firstly to form a C_{60}@2β-CD inclusion complex, which was then self-assembled with PTCA to form nanoparticles. PTCA is a unique water soluble compound with four carboxyl groups and a flat π-system. Strong hydrogen bond and π–π interactions make it an ideal building block for fabricating novel nanoarchitectures. With numerous hydroxyl groups from β-CD and carboxyl groups from PTCA on the C_{60}@2β-CD/PTCA nanoparticle surface, the composite nanoparticle was further self-assembled with orthotitanic acid, resulting in C_{60}@2β-CD/PTCA/TiO_2 composite nanospheres. In the composite nanospheres, both PTCA and β-CD are thermally unstable. Hollow titania composite nanospheres containing [60]fullerene with a core–shell structure were finally obtained by calcination.

The perylene derivatives exhibited flat π-systems, as confirmed by the X-ray diffraction of several single crystals.[15,16] The strong π–π stacking and hydrogen bond interactions enabled PTCA molecules to aggregate readily to form one-dimensional nanorods of up to 400 nm in length (Fig. 1(a)). However, after being assembled with C_{60}@2β-CD, only nanoparticles of less than 80 nm in diameter were observed (Fig. 1(b)). It was noted that the morphologies and sizes of the nanoparticles heavily depended on the molar ratio of C_{60}@2β-CD to PTCA used. In general, high excesses of PTCA resulted in its dominative self-aggregation and a tendency to form rod-like nanostructures, whereas high excesses of C_{60}@2β-CD led to larger particle sizes.

The sample C_{60}@2β-CD/PTCA (Fig. 1(b)) was obtained using the ratio [C_{60}@2β-CD]/[PTCA] = 0.55. These nanoparticles were further coated with TiO_2 to form the C_{60}@2β-CD/PTCA/TiO_2 composite nanospheres, which were calcined at 360 °C in a vacuum overnight to yield hollow titania nanospheres containing C_{60}. The TEM images of the C_{60}@2β-CD/PTCA/TiO_2 composite nanospheres and the resulting hollow nanospheres are shown in Fig. 1(c) and 1(d), respectively. The color of the composite nanospheres was far deeper than the C_{60}@2β-CD/PTCA nanoparticles owing to the TiO_2 coating, and the sizes of nanospheres were around 100 nm in diameter. Compared to the C_{60}@2β-CD/PTCA/TiO_2 composite nanospheres, the surface of the hollow nanospheres were relatively rough after calcination. When the 360 °C calcination time was short, the composite nanospheres still had a solid core. A hollowing effect was observed for those prepared by



Scheme 1 Synthesis scheme for the hollow titania nanospheres with a [60]fullerene core.

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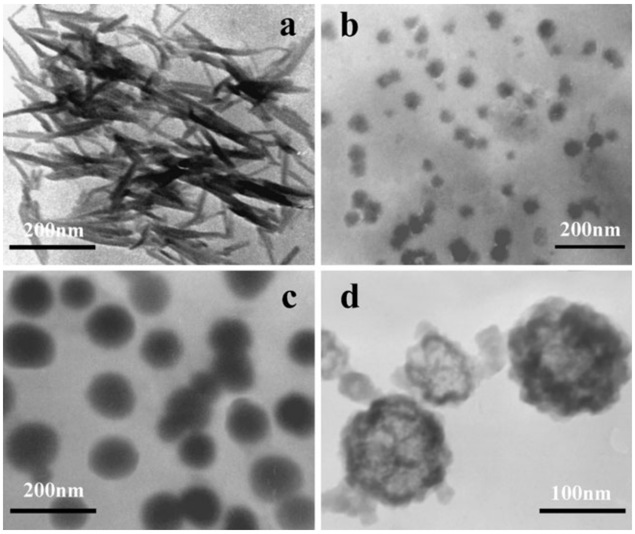

Fig. 1 TEM images of (a) PTCA nanorods, (b) C_{60}@2β-CD/PTCA nanoparticles, (c) C_{60}@2β-CD/PTCA/TiO_2 nanospheres and (d) the resulting hollow nanospheres.

calcination in a vacuum overnight. It should be mentioned that no such hollowing effect was observed in our previous work.[14]

To confirm the content and decomposition behavior of the C_{60}@2β-CD/PTCA/TiO_2 composite nanospheres and hollow nanospheres, TGA investigations were carried out at a heating rate of 5 °C min^{-1} in a nitrogen atmosphere. Fig. 2 illustrates the TGA curves of the C_{60}@2β-CD/PTCA/TiO_2 composite nanospheres and the hollow nanospheres containing [60]fullerene. The TGA trace of the C_{60}@2β-CD/PTCA/TiO_2 composite nanospheres (curve a) offers some interesting observations, and shows *ca.* 14% weight loss until 120 °C that is related to adsorbed water, but this amount could change, depending on the relative humidity. The main decomposition was found between 120 and 600 °C, and was clearly attributable to the dehydration of β-CD, PTCA and C_{60}, with a weight loss during this stage of 37%. Compared to the pristine [60]fullerene (curve c), the formation of the nanostructures resulted in a remarkably early degradation of C_{60}. Hollow nanospheres (curve b) only showed a slight, steady decrease in weight between 30 and 460 °C, amounting to no more than 4% in total. It is suggested that most of the β-CD and PTCA were decomposed by calcination. Further signals were visible from 460 °C, attributable to fullerene, with a mass reduction up to 10%. Compared with the C_{60}@2β-CD/PTCA/TiO_2 composite nanospheres, the decomposition temperature of fullerene in hollow nanospheres is similar. This result demonstrates that the hollow nanospheres containing fullerene were obtained by the calcination of β-CD and PTCA.

Infrared spectra of the hollow nanospheres, the C_{60}@2β-CD/PTCA/TiO_2 nanospheres and the C_{60}@2β-CD/PTCA nanoparticles are shown in Fig. 3. In the spectrum of the C_{60}@2β-CD/PTCA nanoparticles (Fig. 3(a)), strong vibration bands at 1614.7, 1638.7 and 1454 cm^{-1} can be attributed to C=C stretching and the aromatic perylene skeleton. The strong peak at 1659.6 cm^{-1} may be assigned to a C=O stretching mode of the carboxylic acid group, which is remarkably shifted towards a low wavenumber owing to the formation of strong hydrogen bonds. The strong vibration band at 1384.4 cm^{-1} may be assigned to the –OCH_3 group of β-CD. Weak peaks at 575.6 and 526.2 cm^{-1} can be attributed to the fullerene. After being coated with orthotitanic acid, a broad band from 450 to 700 cm^{-1} was observed, which can be assigned to TiO_2 (Fig. 3(b)). Compared with spectra a and b, the FT-IR of the hollow nanospheres after calcination was simple. Peaks corresponding to C=O, –OCH_3 from PTCA and β-CD disappeared, while the characteristic absorption peaks of [60]fullerene at 575.6 and 526.2 cm^{-1} verified the presence of fullerene. But there were also small peaks at 1618.7, 1638.6 and 1400 cm^{-1}, corresponding to a trace of perylene decomposed from PTCA.

The presence of C_{60} in the C_{60}@2β-CD/PTCA/TiO_2 nanospheres and hollow nanospheres was further confirmed by measuring binding energy spectra of the C_{1s} electrons. As shown in Fig. 4, Gaussian analysis of the XPS data of C_{1s} displayed four main components. The binding energy for C_{60} was situated at 284.5 eV. The contribution at 285.5 eV could be assigned to carbons associated with the core of the PTCA molecule. All of the C-2–C-6 carbons of the glucose units in β-CD were situated at 286.1 eV. The fourth broad contribution at 287.4 eV arose from carbonyl group carbons, hemiketal carbons (C-1 carbon of the glucose units) and a shake-up feature associated with the carbonyl groups.[17] Compared with the C_{60}@2β-CD/PTCA/TiO_2 nanospheres, the hollow

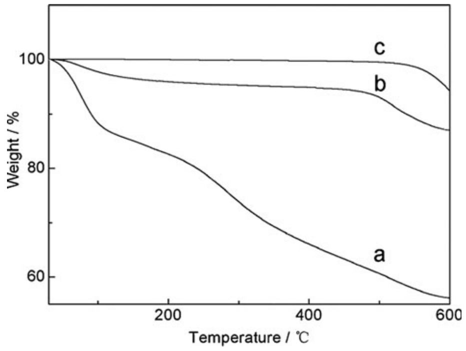

Fig. 2 TGA curves of (a) the C_{60}@2βã CD/PTCA/TiO_2 composite nanospheres, (b) the hollow nanospheres and (c) the pristine [60]fullerene.

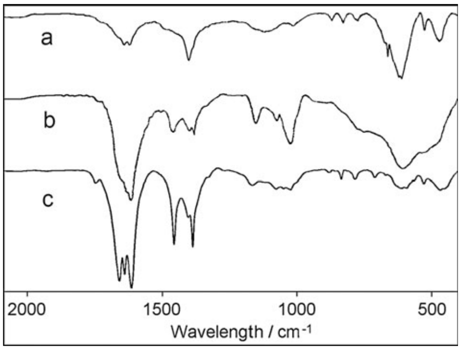

Fig. 3 FT-IR spectra of (a) the hollow nanospheres, (b) the C_{60}@2β-CD/PTCA/TiO_2 nanospheres and (c) the C_{60}@2β-CD/PTCA nanoparticles.

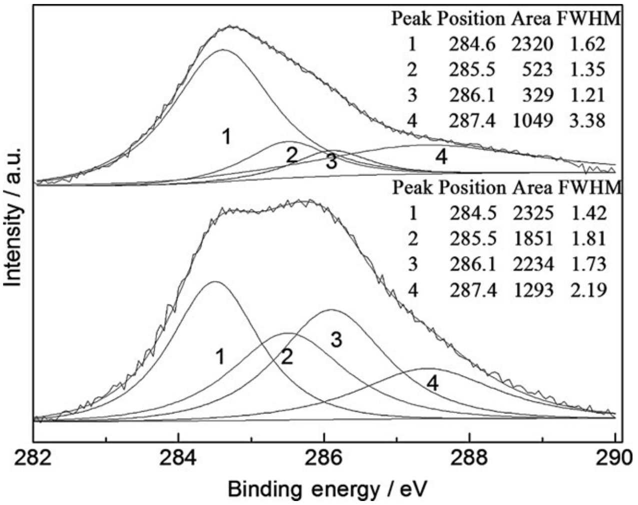

Fig. 4 C_{1s} binding energy XPS spectra of the C_{60}@2β-CD/PTCA/TiO_2 composite nanospheres (bottom) and hollow nanospheres (top). FWHM = full width at half maximum.

nanospheres exhibited only traces of PTCA and β-CD components. The C_{60} in the hollow nanospheres detached from the β-CD molecules after calcination, and its binding energy shifted to 284.6 eV, closer to pristine C_{60} (284.7 eV).[18] These results indicate that the C_{60} structure in the hollow nanosphere skeleton was retained.

In conclusion, core–shell composite nanospheres, hollow titania composite nanospheres containing [60]fullerene, were fabricated successfully using a layer-by-layer self-assembly strategy. The sizes of the nanospheres were about 100 nm in diameter. The skeleton of [60]fullerene was retained undamaged, and is expected to be an ideal object for performing investigations of [60]fullerene in nanospace.

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Experimental

Reagent grade chemicals titanium tetrachloride ($TiCl_4$, 99.9%, Aldrich) and *n*-butanol (99.9%, Shanghai Chemical Co., China) were used as the Ti source and solvent, respectively.

The preparations of C_{60}@2β-CD and PTCA have been detailed in previous reports.[19,20] In a typical experiment, C_{60}@2β-CD (34.6 mg) was dissolved in 50 mL DMF and PTCA (11 mg) was dissolved in 50 mL distilled water. Next, the PTCA aqueous solution was added dropwise to the C_{60}@2β-CD DMF solution, and the mixture kept stirring at room temperature for 3 d. Thereafter, the resulting mixture was centrifuged at 4000 rpm for 30 min. After the supernatant liquid had been discarded, the product was again dispersed in DMF by sonication. This washing process was repeated three times. The precipitates were dried at room temperature under vacuum for 1 d.

A typical procedure for the preparation of C_{60}@2β-CD/PTCA/TiO_2 nanospheres was as follows. First, a clear $Ti(OH)_4$ stock solution was obtained by dissolving 50 μL $TiCl_4$ in a mixture of 125 μL H_2O and 175 mL *n*-butanol cooled in an ice bath with stirring for 20 min. Next, 23.9 mg C_{60}@2β-CD/PTCA nanoparticles were dispersed by sonication in 175 mL *n*-butanol and added to the cold $Ti(OH)_4$ stock solution, and the mixture stirred at room temperature for 4 d. The resulting solution was transferred to a Teflon-lined autoclave and aged at 120 °C for 24 h in order to grow the titania nanospheres. Thereafter, the resulting mixture was centrifuged at 4000 rpm for 30 min, and finally the supernatant liquid was discarded. The precipitates were washed three times with DMF and acetone, and were dried at room temperature under vacuum for 1 d. The powder was then calcined at 360 °C in a vacuum overnight.

The morphology and size of the samples were observed using a Hitachi H-800 transmission electron microscope (TEM) at an accelerator voltage of 200 kV. Products were analyzed in a Perkin-Elmer TGA7 under a dynamic nitrogen atmosphere (20 mL min^{-1}) and a heating rate of 5 °C min^{-1} using platinum crucibles. The temperature range used was from 20 to 650 °C. FT-IR spectra were recorded on a Bruker Tensor-27 instrument. X-Ray photoelectron spectroscopy data were obtained using an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al-Kα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C_{1s} line at 284.8 eV of adventitious carbon.

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