Size controllable self-assembly of titania nanospheres cored with fullerenol/fullerene

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The core–shell nanospheres fullerenol–TiO_2 and C_{60}@2β-CD–TiO_2 were fabricated by a layer-by-layer self-assembly procedure seeding with fullerenols and C_{60}@2β-CD respectively, the nanospheres ranging in size from 40 to 80 nm and 10–20 nm in diameter respectively. The presence of fullerenols in the nanostructures was confirmed by XPS and FT-IR spectroscopy, and the XRD patterns prove both the titania shells on fullerenol and C_{60}@2β-CD are rutile and anatase phases.

Core–shell nanostructures[1–3] are of increasing interest owing to their potential applications in optical, electronic, magnetic, and catalytic science and in drug-delivery and nanoreactors.[4–10] In these areas, layer-by-layer (LBL) self-assembly approaches have been applied to fabricate core–shell composites using molecular precursors and nanoparticles as inorganic shell building blocks.[1,9,10] As a kind of photocatalytic active and photoconductive n-type semiconductor, numerous nanosized titania materials have been synthesized and investigated extensively.[11–14] However, fabrication of titania nanospheres has so far achieved only limited success due to the intrinsically anisotropic growth of crystalline titania. The resulting shells coated on templating cores often afford the composites physicochemical properties significantly different from those of the cores. Recently several hollow titania shells have been reported using LBL techniques.[1,15] One of the main challenges of this method is to obtain uniform structures and controllable shell sizes. The sensitive condensation conditions of molecular precursors or the aggregation tendency of nanoparticles made manipulation complicated for the purpose of preparing core–shell structures with precisely controllable thickness.

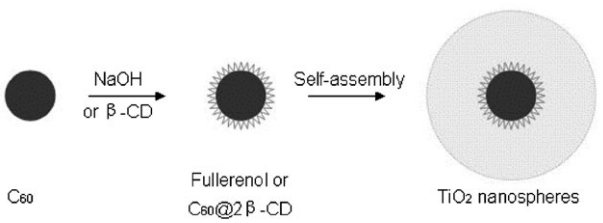
Herein, we report the size controllable self-assembly of titania nanospheres with core–shell structures based on fullerene using LBL techniques. Hydroxide modified fullerene (fullerenols)[16] or surface hydroxyl coated fullerene (C_{60}@2β-CD, obtained by coating fullerene molecules with 2β-cyclodextrin molecules)[17] was used as a seed to fabricate the fullerene–TiO_2 host–guest nanostructures. With an electron acceptor–spacer–donor structure, C_{60}@2β-CD–TiO_2 nanospheres are about 10–20 nm in diameter, which is very near the quantum size (10 nm or less).

To seed the self-assembly of titania nanospheres, the core must have two characteristics. First, the core must be water or polar organic solvent soluble, so it tends to dissolve to provide multiple seeds; second, there must be a strong chemical or physical interaction between the surface of the core and the precursor orthotitanic acid, which is the driving force for the self-assembly. Fullerene was herein enabled as a rational core by: (1) being modified to fullerenols, (2) being coated with two β-CD molecules. Scheme 1 illustrates the schematic procedure for the self-assembly of titania nanospheres.

The morphologies and sizes depending on the concentrations and the molar ratio of Ti-source to fullerenol were investigated. $TiCl_4$ and diethylamine (DEA) were kept unchanged at effective concentrations as reported,[18] whereas the concentration of fullerenols was systematically changed. Detailed experimental conditions for the Ti-hydroxide coating of fullerenol are given in Table 1. Compared with most nanoparticles, nanospheres were seldom observed when the fullerenol was too dilute as in T1 conditions (Fig. 1a). Along with the increase in fullerenol concentration, dominating nanospheres were formed and the sizes became smaller from 80 nm in T2 (Fig. 1b) to 40 nm in T4 (Fig. 1d), but the morphologies also changed, becoming more irregular. As shown in Fig. 1, the morphology of the self-assembled fullerenol–TiO_2 nanospheres obtained under T3 conditions is not as uniform as that of T2 nanospheres; and the T4 nanospheres are not as regular as T2 nanospheres. It was also noted that DEA plays a key role in the morphology control of the assemblies. In the case of absence of DEA, only nanoneedles were observed.

The FT-IR spectrum of the fullerenol–TiO_2 nanospheres is dominated by bands associated with the titania, however, a weak typical band is observed at 578 cm^{-1}, which consistent with the presence of a fullerene skeleton.

The electronic structures of fullerenols were analyzed by measuring the binding energy spectra of C1s electrons. The



Scheme 1 Synthesis scheme for titania nanospheres with a fullerene/fullerenol core.

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Table 1 Detailed synthesis conditions depended on for morphology and size control of the fullerenol-TiO_2 nanostructures

	T1	T2	T3	T4
[$TiCl_4$]	0.016 M	0.016 M	0.016 M	0.016 M
[DEA]	0.115 M	0.115 M	0.115 M	0.115 M
[Fullerenol]	2.4×10^{-5} M	4.8×10^{-5} M	1.92×10^{-4} M	7.68×10^{-4} M
Morphology	Nanoparticles	Nanospheres	Nanospheres	Nanospheres
Mean diameter	40 nm	80 nm	60 nm	40 nm

results are given in Fig. 2. The main line of XPS spectra shows a broad and asymmetric shape. This is different from the symmetric main line of C_{60}: it is well-known that the detailed XPS spectrum of C1s regions of pristine C show only a single Gaussian profile located at 284.7 eV.[12] The Gaussian analysis of XPS data of C1s showed the presence of four components (indicated by broken lines named C═C, C–O, O–C–O and C═O, respectively). The C1s binding energies observed for sp^2 nonfunctionalized carbons (C═C) are centered at 284.5 eV, and those for hydroxylated (C–OH) carbons are centered at 285.8 eV. A small peak at 287.8 eV is assigned to traces of deoxygenated carbon (hemiketal carbon, O–C–O).[19] The smallest peak at 288.5 eV is assigned to traces of absorbed CO_2. All of the three fullerenol peaks are different from that for free fullerenols (284.8, 286.6 and 288.3 eV, respectively) in value.[20,21] It can be assumed that the fullerenol in TiO_2 nanospheres is isolated in a nanocavity by the TiO_2 nanoshell, resulting in a different chemical environment of the isolated fullerenol from that of the free one. The intensities of the C1s components were estimated from integration of the peak area under each broken line. The relative intensities for sp^2 nonfunctionalized carbon, hydroxylated carbon, and deoxygenated carbon groups obtained by normalizing them to the total area were 60%, 37%, and 3%, respectively. Accordingly, the number of hydroxylated carbons estimated from XPS data is 24, which is in good agreement with experimental result.[16]

The crystal structure of titania nanospheres was confirmed by X-ray diffraction analysis. Owing to the absence of a calcination step, the titania shell didn't crystallize well. As shown in Fig. 3a, the XRD of the fullerenol–TiO_2 nanospheres obtained under T2 conditions exhibits peaks associated with rutile and anatase phases. The strong peak at $2\theta = 24.2^\circ$ proves an anatase phase, and two peaks at $2\theta = 27.9^\circ$ and 34.2° indicate the presence a of rutile phase. Several weak peaks are mixed peaks for anatase and rutile.[22–24]

Compared with fullerenols, C_{60}@2β-CD seems to be a preferred seed for the self-assembly of titania nanospheres. First, the diameter of C_{60}@2β-CD is estimated to be about 2 nm according to previous reports,[17,21] which is larger than that of fullerenols (about 1 nm). Larger seeds are in theory easier to coat or deposit by molecular precursors. Second, the number of surface hydroxyl groups for C_{60}@2β-CD is 42,[17] whereas the average number for the fullerenols used in this work is about 26. Accordingly, the core–shell interactions for C_{60}@2β-CD are stronger than those for fullerenols. Third, the complex of C_{60}@2β-CD is uniform, whereas the fullerenols are a mixture. Most of all, the C_{60}@2β-CD complex seed keeps the fullerene molecule undamaged. Fig. 1e shows the image of C_{60}@2β-CD–TiO_2 nanospheres obtained under similar conditions to T2 but with a DMF solution of C_{60}@2β-CD instead of aqueous fullerenols. It is observed that the size of the C_{60}@2β-CD–TiO_2 nanospheres ranges from 10 to 20 nm in diameter, which is far smaller than fullerenol–TiO_2 nanospheres. A notable difference between C_{60}@2β-CD–TiO_2 synthesis and fullerenol–TiO_2 synthesis is that most of the C_{60}@2β-CD–TiO_2 nanospheres are fabricated suspended in solution, resulting in a sol, instead of aggregating to a gel as in the case of fullerenol–TiO_2. As for the gel formed, dominant amorphous floccules were observed in the TEM image. Peaks at 27.9° and 34.2° in XRD pattern (Fig. 3b) proved a dominating rutile phase of the titania shell, and some weak peaks for anatase were also observed. Two weak typical bands at 576 and 527 cm^{-1} in the FT-IR spectrum of the C_{60}@2β-CD–TiO_2 nanospheres indicated the presence of fullerene.

A pathway is suggested to explain the formation of fullerenol–TiO_2 core–shell nanospheres. After the seeds were

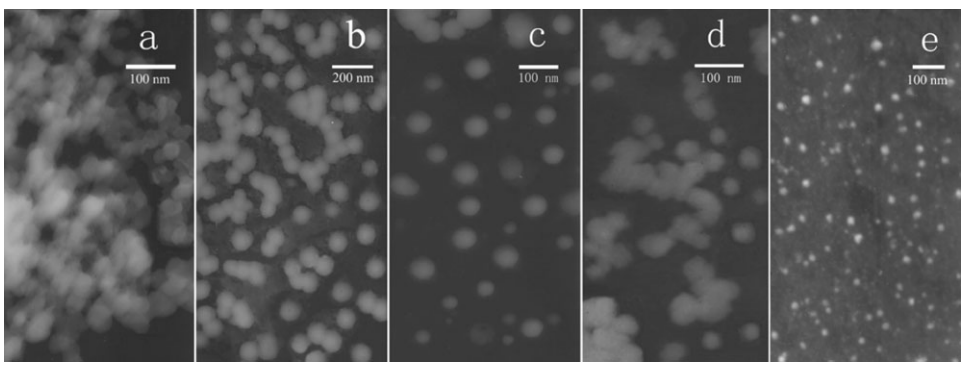

Fig. 1 TEM images of (a) fullerenol–TiO_2 nanospheres obtained under T1 conditions, (b) fullerenol–TiO_2 nanospheres obtained under T2 conditions, (c) fullerenol–TiO_2 nanospheres obtained under T3 conditions, (d) fullerenol–TiO_2 nanospheres obtained under T4 conditions, (e) C_{60}@2β-CD–TiO_2 nanospheres.

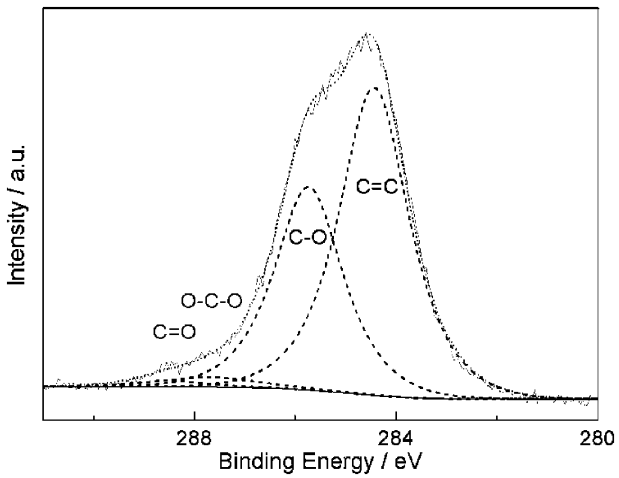

Fig. 2 XPS spectrum of the C1s binding energy of fullerenol in a shell of TiO_2 and the curve-fitting analysis showing the oxidation states of carbon.

dispersed into the cold [$Ti(OH)_4$] stock solution, $Ti(OH)_4$ precursors around the seeds deposited immediately to the surface hydroxyls. Concomitant with the temperature increase to room temperature, a portion of $Ti(OH)_4$ self-aggregated to small particles, which were ultimately deposited to form a larger core–shell particle. This mechanism was supported by the TEM images of the fullerenol–TiO_2 obtained after 1 day's reaction, in which lots of far smaller particles were observed. It is readily understood that more seeds result in smaller assemblies. As a result, the diameters of core–shell nanospheres decreased from T2 to T4 with the concentration increase of fullerenols. However, owing to the scarcity of seeds in T1, most of the self aggregated $Ti(OH)_4$ particles grew independently instead of being deposited to give a core–shell structure. With a larger size and more hydroxyls, the C_{60}@2β-CD seed grew quickly. The core–shell structure had been formed by deposition of the $Ti(OH)_4$ precursor as a dominating molecular species before the small $Ti(OH)_4$ particles self-aggregated. Accordingly, the C_{60}@2β-CD–TiO_2 nanospheres are far smaller than fullerenol–TiO_2 nanospheres.

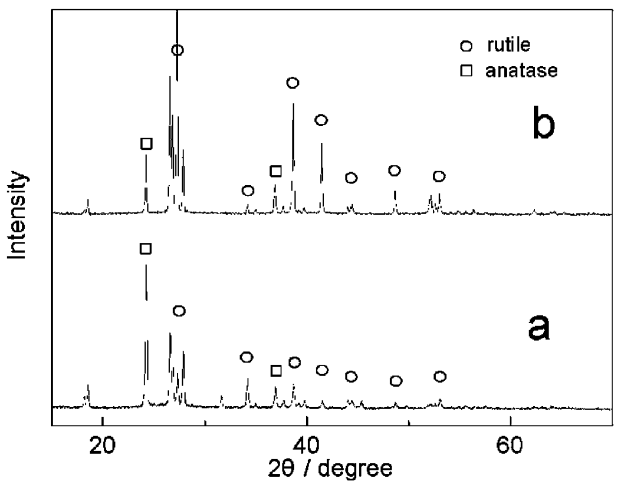

Fig. 3 XRD patterns of (a) fullerenol–TiO_2 nanospheres obtained under T2 conditions, (b) C_{60}@2β-CD–TiO_2 nanospheres.

The core–shell nanospheres fullerenol–TiO_2 and C_{60}@2β-CD–TiO_2 were fabricated successfully using a layer-by-layer self-assembly strategy. The size of the nanospheres is controllable and depends on the species and concentration of the seeds. Herein, the core–shell structure is also a host–guest or electron donor–acceptor structure. Especially for C_{60}@2β-CD–TiO_2 nanospheres, not only was the [60]fullerene skeleton kept undamaged as an intrinsically good electron acceptor, but also the sizes of the host–guest structure are very near the quantum-size. It was expected to be an ideal host–guest object to perform the investigation of photo-induced charge transfer.

Experimental

Reagent grade chemicals, titanium tetrachloride ($TiCl_4$, 99.9%, Aldrich), diethylamine (DEA, 99.9%, Shanghai Chemical Co., China), methanol (99.9%, Shanghai Chemical Co., China) were used as the Ti-source, shape controller, and solvent, respectively. Fullerenols[16] and a water-soluble β-cyclodextrin–[60]fullerene inclusion complex (C_{60}@2β-CD)[17] were prepared as detailed in previous reports.

A typical procedure for the preparation of fullerenol–TiO_2 nanospheres was as follows. First, a stock solution of orthotitanic acid [$Ti(OH)_4$], fullerenol solution (60 mg in 5 ml H_2O) and C_{60}@2β-CD solution (50 mg in 15 ml DMF) were prepared, respectively. A clear [$Ti(OH)_4$] stock solution was obtained by dissolving 60 μl $TiCl_4$ in a mixture of 60 μl H_2O and 15 ml methanol cooled in an ice bath under stirring for 15 min. Then, a solution of fullerenols and DEA were added to the cold [$Ti(OH)_4$] stock solution and the mixture was kept stirring at room temperature for 4 days. Thereafter, the resulting mixture was centrifuged at 6000 rpm for 30 minutes. After the supernatant liquid was discarded, the viscous product was redispersed in methanol by sonification. This washing process was repeated six times. Finally, the resulting gel in methanol was transferred to a Teflon-lined autoclave and aged at 120 °C for 24 h to nucleate and grow the titania nanospheres. Four synthesis experiments carried out with various resulting fullerenol concentrations were named as T1, T2, T3 and T4, respectively.

The C_{60}@2β-CD–TiO_2 nanospheres were synthesized with the same procedure as the synthesis of fullerenol–TiO_2 nanospheres but using C_{60}@2β-CD solution in DMF instead of the fullerenol solution in methanol in T2. After the ageing step, the resulting sol–gel was kept still for one week. The gel was discarded, and the solvent was removed from the sol to obtain a sample for TEM and XRD characterization.

XRD patterns were recorded using a powder diffractometer (Philips PW1830) operating in the reflection mode with CuKα radiation and equipped with a graphite back monochromator. X-Ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. Transmission electron microscopy (TEM) measurements were carried out on a Hitachi H-800 instrument with a tungsten filament at an accelerating voltage of 200 kV.

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