

Interface Assembly Synthesis of Inorganic Composite Hollow Spheres

Jin-Song Hu,[†] Yu-Guo Guo,[†] Han-Pu Liang,[†] Li-Jun Wan,^{*} Chun-Li Bai,^{*} and Yan-Guo Wang[‡]

Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100080, China

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A facile method with interface assembly was developed to prepare TiO₂/CdS composite hollow microspheres. By changing reactant concentration, stirring rate, and temperature, the hollow microspheres could be controlled in diameter, shell thickness, and composition. The morphology, structure, composition, and photoluminescence (PL) property of the hollow spheres were investigated with SEM, TEM, X-ray diffraction, and spectroscopic techniques. In photoluminescence (PL) spectra, a strong PL band appeared in the bluish violet wavelength range.

Introduction

Nanomaterials have received considerable attention due to their potential applications in chemistry, physics, electronics, biotechnology, and materials science. Recently, various nanomaterials with different morphologies such as particle, wire, and tube have been prepared.¹ Owing to peculiar and fascinating properties superior to their bulk counterparts, these nanomaterials are widely employed in nanoscale electronic, optoelectronic, electrochemical, and electromechanical devices. Among various nanomaterials, inorganic semiconductor composite materials have increasingly attracted interest because of their improvable optical limiting, photoluminescence photosensitization, and photocatalysis properties.^{2–8} Especially, micro- or nanometer scale hollow spheres with controllable structure, composition, and properties have shown a promising perspective in many fields such as controllable release capsule, drug delivery, photonic crystal, light filler, shape-selective absorbant, and catalyst.^{9–21} So far, the common method to fabricate hollow sphere nanomaterials is sacrificial templates including the templates of colloid particles (e.g., polymer microspheres and monodispersed silica),^{11–15} liquid droplets,^{16,17} microemulsion droplets,^{18,19} and micelles.^{20,21} An important procedure in this method is the removal of the template or the usage of two immiscible liquid phases, which results in the complication of the preparation and limits their application. Although several new techniques with sonochemical and solvothermal methods have been reported for synthesizing hollow microspheres such as CdSe or ZnSe,^{22,23} it is still highly desirable to develop an efficient, template-free, and surfactant-free method to prepare hollow spherical nanomaterials, especially in miscible solvents. Herein, we report a new facile approach to fabricate the semiconductor composite hollow spheres such as TiO₂/CdS on a large scale. The so-prepared hollow spheres are easily tuned in average diameter, shell thickness, and composition by controlling preparation conditions, and exhibit a strong photoluminescence (PL) band in the bluish violet wavelength range.

Experimental Section

Material Preparation. In a typical procedure, two solutions were first mixed together. One contained cadmium acetate dihydrate (CAD), thiourea (Tu), and 1-thioglycerol (TG) in 20 mL of *N,N*-dimethylformamide (DMF)/water (3:1, in volume) solvent. Another was Ti(OBu)₄ (TOB) and acetylacetone (Acac) in 40 mL of butanol. The mixed solution was in a milk-white turbid state. Then the mixture was stirred for 20 min and refluxed at 140 °C for about 3 h. The produced ivory white precipitates were collected and repeatedly washed with ethanol and distilled water. Finally, the product was dried in a vacuum chamber (~ -0.1 MPa) at 85 °C for 6 h.

The calcination procedure was carried out at 500 °C (heating rate 10 K min⁻¹) under N₂ environment for 5 h. In the present experiment, five samples are prepared. The concentrations of reactants in samples A, B, C, and D are gradually increased. The content of TOB in sample E is higher than that in sample B, while that of cadmium complex is the same in two samples. The detailed preparation conditions for all samples in this study are shown in Table 1.

TABLE 1: Preparation Conditions, Average Diameters, and Shell Thickness

sample	preparation conditions					average diameter (nm)	shell thickness (nm)
	CAD (g)	Tu (g)	TG (mL)	TOB (mL)	Acac (mL)		
A	0.23	0.095	0.095	0.25	0.15	245 ± 20	35 ± 4
B	0.46	0.190	0.190	0.50	0.30	300 ± 27	52 ± 5
C	0.69	0.285	0.285	0.75	0.45	460 ± 40	100 ± 12
D	0.92	0.380	0.380	1.00	0.60	550 ± 60	
E	0.46	0.190	0.190	0.75	0.45	360 ± 40	70 ± 8

Characterization. For TEM observation, the samples were ultrasonically treated and dispersed on copper grids. Transmission electron microscopic images were collected by using a Philips TECNAI-20 working at 120 kV, equipped with an energy-dispersive X-ray analyzer (Phoenix). High-resolution TEM (HRTEM) images were recorded on a Philips F20 working at 200 kV. A Hitachi S-4300F scanning electron microscope was used to investigate the morphology of the hollow spheres.

X-ray photoelectron spectra (XPS) were collected on a VG-ESCALAB 220I-XL photoelectron spectrometer using Al K α as the exciting source. Thermogravimetric analysis (TGA) of

* Authors to whom correspondence should be addressed. E-mail (Wan): wanlijun@iccas.ac.cn.

[†] Also in Graduate School of CAS, Beijing 100064, China.

[‡] Beijing Laboratory of Electron Microscopy, CAS, Beijing 100080, P.R. China.

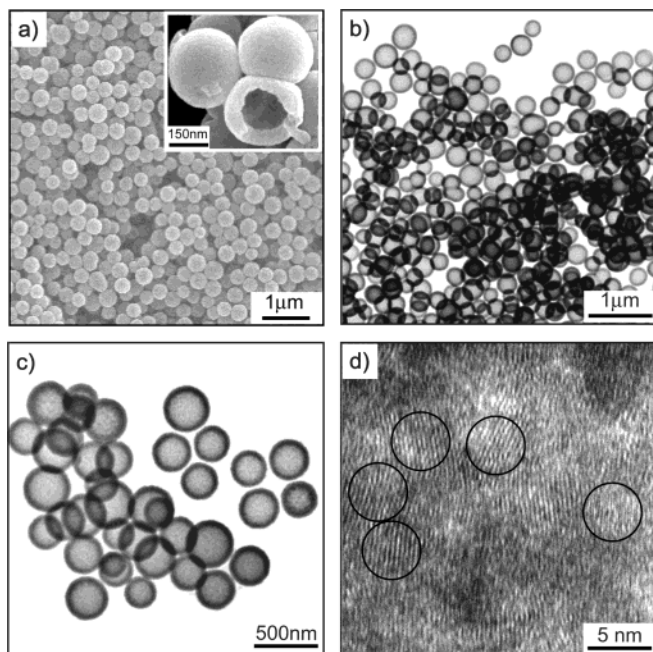


Figure 1. SEM and TEM images of sample B. (a) SEM image. The inset shows the high magnification image indicating hollow structures. (b) TEM image. (c) and (d) TEM and HRTEM images after calcination of the microspheres.

the sample was performed on Perkin-Elmer thermal analysis equipment. X-ray powder diffractions (XRD) were carried out with a Rigaku D/max-2500 using filtered Cu K α radiation.

UV-vis spectroscopy (UV-1601PC, SHIMADZU) was used to characterize the optical absorbance of the hollow microspheres. Photoluminescence (PL) spectra were measured in a HITACHI F-4500 fluorescence spectrophotometer under excitation at 347 nm at room temperature.

Results and Discussion

The structure and morphology of samples were first investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 1a is a typical SEM image recorded in sample B. From the image it is clear that large-scale well-dispersed spherical materials have been prepared. The average diameter of the hollow spheres is 300 ± 27 nm. The hollow structure of the spheres is clearly revealed from the inset micrograph in Figure 1a showing a mechanically fractured particle. Further evidence for the hollow structure can also be found from the TEM image shown in Figure 1b. It is seen that there is a strong contrast difference in all of the spheres with dark edge and bright center, confirming their hollow structure.

The chemical composition of sample B was determined by X-ray photoelectron spectroscopy. In XPS spectra shown in Figure 2, Cd, S, Ti, and O are detected. All peaks were calibrated by using C(1s) (284.6 eV) as a reference. The two peaks located at 405.1 and 412.3 eV are assigned to Cd (3d) and those at 161.7, 458.4, and 530.5 eV correspond to S (2p), Ti (2p), and O (1s). The ratio of Cd to S and that of Ti to O are approximately 1:1.1 and 1:2.3, respectively. The rich sulfur and oxygen possibly originate from remaining organic groups or molecules. The TGA results demonstrate a 20.0% weight loss at 550 °C due to the removal of the remaining groups or molecules.

The microspheres shown in Figure 1a were then calcined under N₂ gas atmosphere at 500 °C for 5 h. Figure 3a and 3b show X-ray diffraction pattern of sample B before and after

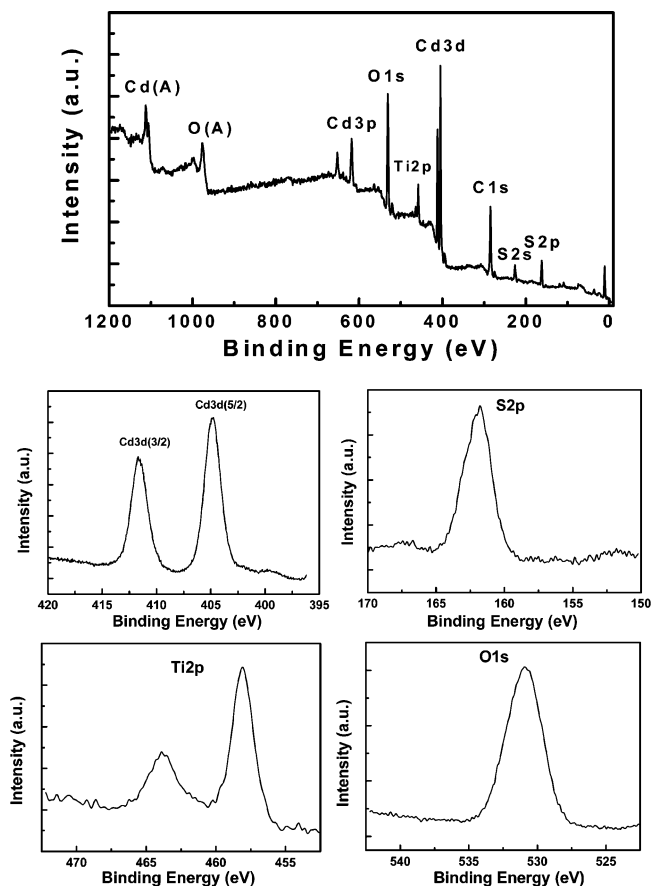


Figure 2. XPS spectra of TiO₂/CdS hollow spheres.

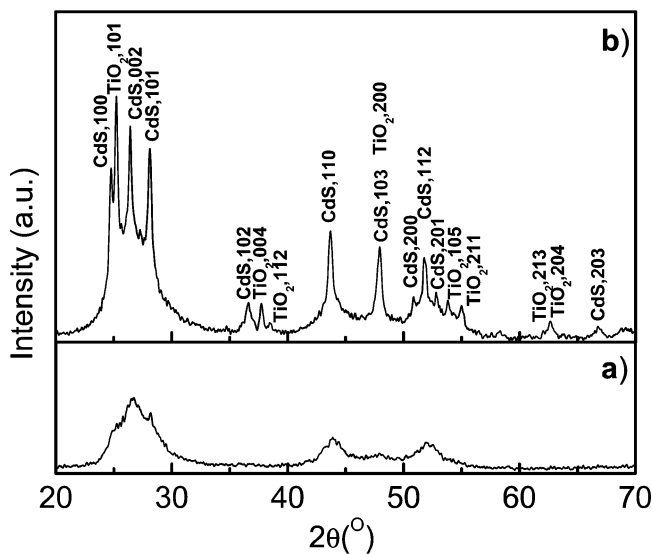


Figure 3. XRD patterns of sample B (a) before calcination, and (b) after calcination. The results confirm the existence of the anatase phase of TiO₂ and hexagonal phase of CdS in the sample.

calcinations, respectively. The diffraction peaks of TiO₂ and CdS in the sample before calcination is not very clear and not well-separated. However, the calcined microspheres display clear crystalline reflection peaks that are characteristic to the anatase TiO₂ and hexagonal phase CdS,²⁴ due to the removal of organic component and the improvement of crystallization. The structures of the calcined microspheres are investigated by TEM and HRTEM. Figure 1c and 1d are the typical images obtained from the sample B after calcination. It can be seen from Figure 1c that the hollow spherical structure is well maintained after

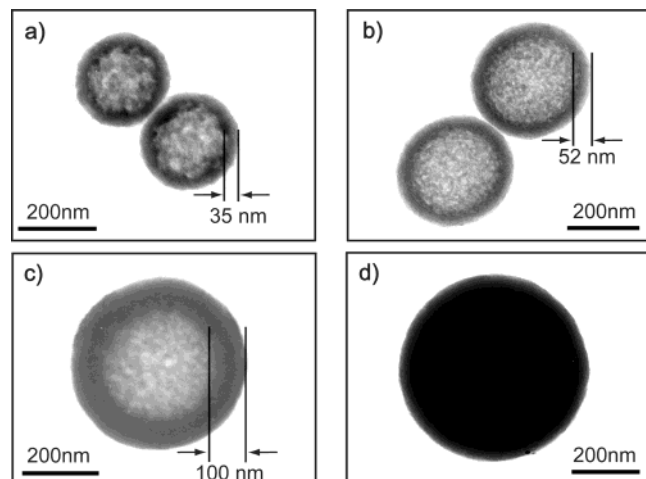


Figure 4. From (a) to (d): TEM images corresponding to the samples A, B, C, and D.

calcination. The HRTEM image in Figure 1d clearly shows the lattice fringes of nanocrystals, although it is not easy to distinguish TiO_2 nanocrystals from CdS nanocrystals.

In further studies, the effects of experiment conditions on the shape and size of the hollow spheres are investigated. It is found that the diameter and shell thickness of the spheres are dependent on the concentration of reactants. Figure 4, parts a–d, show high magnification TEM images of samples A, B, C, and D, respectively. The low magnification TEM images of these samples are presented in Supporting Information (Figure S1). In Figure 4a, b, and c, the thickness of TiO_2/CdS shells is varied from 35 ± 4 and 52 ± 5 to 100 ± 12 nm, corresponding to the spheres in the diameters of 245 ± 20 nm, 300 ± 27 nm, and 460 ± 40 nm. In Figure 4d, however, there is no strong contrast between the edge and the center of the microspheres with diameter of 550 ± 60 nm in sample D, which indicates they have solid structures. Additionally, we had viewed the sample D by using SEM. No fractured hollow sphere was found, which further confirmed that the spheres have solid structures. In the experiment, the concentrations of the reactants are increased from sample A to D. Compared with these TEM images, it can be concluded that the shell thickness will increase with the increasing of reactant concentration. In addition, the composition ratio of TiO_2 and CdS in hollow spheres can also be tunable by changing relative contents of their precursors. Energy-dispersed X-ray (EDX) analysis (Figure S2) of samples B and E reveals that the relative peak intensity of Ti in sample E is remarkably higher than that in sample B, which demonstrates the increased amount of precursor can lead to the increased content of the corresponding component in product.

Moreover, the stirring rate and temperature of the reaction solutions are two other critical factors that determine the morphology of TiO_2/CdS hollow spheres. In the experiments, cadmium-source solution was poured into titanium-source solution under different stirring rates. Figure 5 shows SEM images of sample B prepared at the stirring rates of 200 and 600 rpm, respectively. It can be seen that irregular hollow spheres were formed in the case of stirring rate at 200 rpm, whereas regular spherical structures were generated in the case of stirring rate at 600 rpm. On the other hand, to investigate the influence of reaction temperature on the shape and size of hollow spheres, the two solutions to be mixed were kept and mixed at the predetermined temperature. There is a tendency that the average diameters of the hollow spheres decrease with the elevation of reaction temperatures: average diameter 360

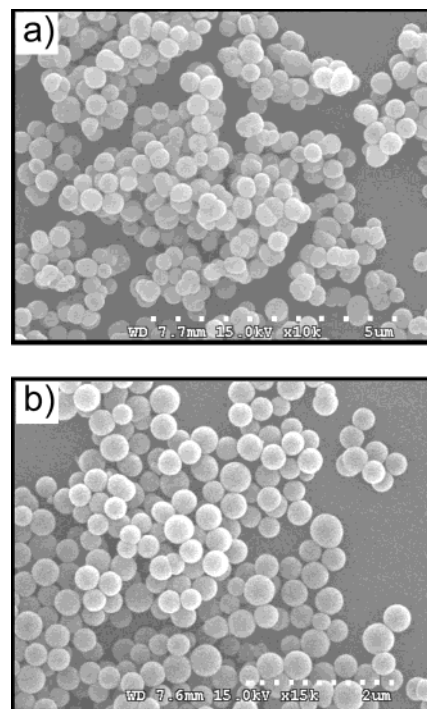


Figure 5. SEM images of sample B prepared at different stirring rates: (a) 200 rpm and (b) 600 rpm.

± 35 nm at 0 °C, 300 ± 27 nm at 25 °C, and 190 ± 30 nm at 60 °C (Figure 6).

We have also tried other organic solvents such as ethanol, 1-propanol, dimethyl sulfoxide, and acetonitrile to replace 1-butanol and dimethylformamide. The almost similar hollow spheres to those shown in Figures 1 and 4 can be formed. However, we found that the acetylacetone and 1-thioglycerol play important roles in the formation of the hollow structures. The hollow spheres cannot be formed without acetylacetone or 1-thioglycerol.

On the basis of the mentioned results, an interface complex assembly mechanism to form TiO_2/CdS hollow spheres is proposed in Figure 7. Briefly, the complex of cadmium ions with thiourea is combined with 1-thioglycerol in the solution of DMF/ H_2O ,²⁵ which is insoluble in butanol. TOB is partly complexed by Acac in butanol.^{26,27} When the two solutions are mixed together, the acetylacetone complexed with titanium butoxide attacks the thiourea–cadmium–1-thioglycerol complex due to its strong coordinating ability to cadmium, thus leads to the formation of an intermediate complex consisting of acetylacetone, titanium butoxide, cadmium, and thiourea. The yielded intermediate product immediately separates and assembles at interfaces, forming an initial skeleton of the hollow spheres. Meanwhile, TOB in the initial skeleton is attacked by water molecules and partly hydrolyzes into titanium oxides, which consequently strengthens the hollow structure. During the refluxing procedure, the hydrolysis of TOB into TiO_2 and the decomposition of cadmium complex into CdS are completed, finally resulting in the formation of TiO_2/CdS hollow spheres. According to the above proposed mechanism, the increasing reactant concentration results in the thicker shell and larger size of spheres. The stirring will produce regular spherical liquid droplets with a narrow size distribution so as to form regular hollow spheres. The increasing temperature will accelerate the movement of molecules in solution, with the result that initial liquid droplets tend to be smaller. Even before the spherical liquid droplets are completely formed, interfacial reaction could take place. Therefore, we could observe the structures that

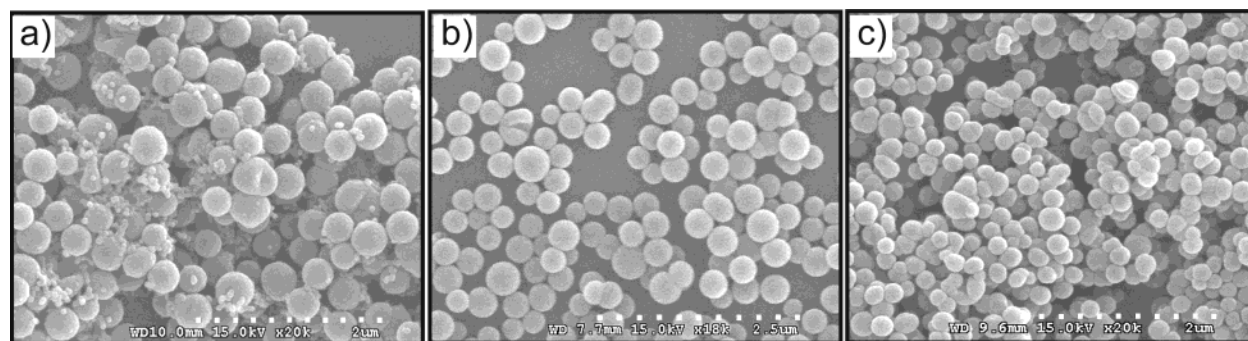


Figure 6. SEM images of TiO_2/CdS hollow spheres synthesized at different reaction temperatures: (a) 0 °C, (b) 25 °C, and (c) 60 °C.

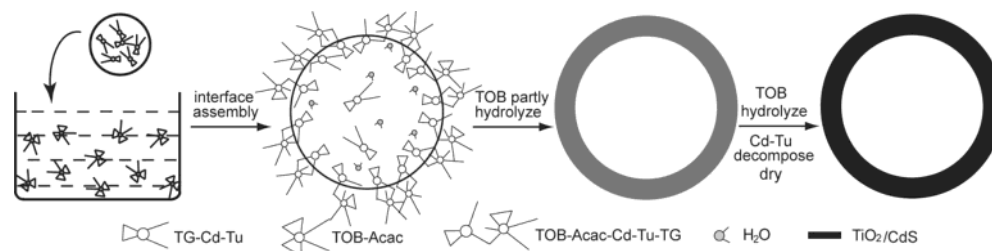


Figure 7. Schematic illustration of the formation mechanism of TiO_2/CdS hollow spheres.

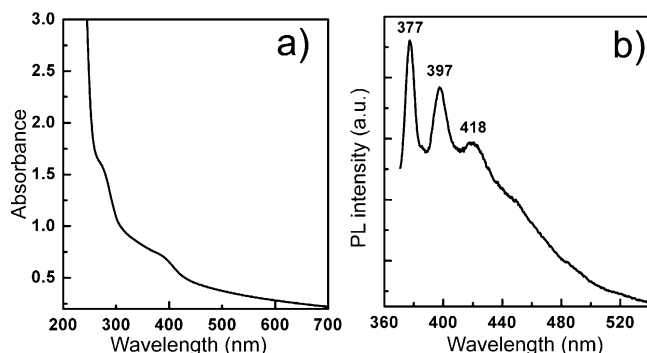


Figure 8. (a) UV-vis absorption spectrum of TiO_2/CdS hollow spheres. (b) PL spectrum of TiO_2/CdS hollow spheres under excitation at 347 nm.

coupled by two, three, or several spheres in the SEM images as shown in Figure 6a. The existence of these coupled structures showed that the skeleton of spherical hollow structures was formed at the moment when the solutions were mixed. On the other hand, we characterized the samples before and after refluxing by using SEM and TEM. The results are shown in Figure S3. It was found that the two samples appear in very similar morphologies, also suggesting that the hollow structures of the microspheres had formed just after the two solutions were mixed. The result is consistent with the proposed formation mechanism.

Figure 8a and 8b show the UV-vis absorption spectrum and PL spectrum of the typical hollow spheres (sample B), respectively. In Figure 8a, TiO_2/CdS hollow spheres exhibit typical absorption features near 390 and 300 nm, corresponding to the optical absorptions of CdS and TiO_2 , respectively.^{28,29} The obvious blue shifts of absorption peaks may be attributed to the small dimension of CdS and TiO_2 nanoparticles in the sphere walls. The PL spectrum of TiO_2/CdS hollow spheres (Figure 8b) was recorded under the excitation wavelength of 347 nm. Intriguingly, two strong and sharp bluish violet light-emitting peaks, situated at 377 and 397 nm, can be observed. The PL peak at 377 nm may be attributed to higher level transition in CdS nanocrystals. It has been reported that this kind of band-edge luminescence arises from the recombination

of excitons and/or shallowly trapped electron-hole pairs.^{30,31} The striking PL peak at 397 nm can be ascribed to another type of band-to-band transition observed in nanosized TiO_2 colloids.³² The weak shoulder peak at 418 nm should originate from photon repetitions of the free-exciton of TiO_2 nanocrystallines.³³

Conclusions

To summarize, we have developed a new synthetic procedure for the preparation of composite TiO_2/CdS hollow spheres on a large scale with interface assembly route. The diameter, shell thickness, and composition of hollow spheres can be conveniently controlled through experiment conditions such as the reactant concentration, stirring rate, and reaction temperature. The TiO_2/CdS hollow spheres exhibit a strong PL band in the bluish violet wavelength range, which is important in optical and electronic applications. Furthermore, the present one-pot method should be extended to fabricate other inorganic composite hollow structures by optimizing suitable reactants. Additionally, since the hollow spheres are formed at the moment that two miscible solvents are mixed, and could be dissolved in certain conditions, the reported technique might provide a practical approach to in-situ loading and transporting nanoparticles, functional molecules, drugs, and nucleic acid.^{34,35}

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Supporting Information Available: SEM and TEM images of TiO_2/CdS hollow spheres and EDX analysis patterns of hollow spheres with different composition ratio (PDF). These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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