Microwave-assisted Fabrication of PS@CdS Core–Shell Nanostructures and CdS Hollow Spheres

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PS@CdS core–shell nanostructures were fabricated by microwave irradiation at 70 °C from the aqueous solution of $CdCl_2$, TAA, and PVP with PS microspheres without surface modification. The products were investigated by XRD, FE-SEM, TEM, IR, and Raman. CdS hollow spheres were easily obtained by removing the PS cores in toluene solution. The method presented here can be used for the preparation of other PS@II–VI semiconductor core–shell nanostructures and hollow spheres.

Inorganic-coated polymer (core–shell) capsules and hollow spheres have been increasingly attracted interest because of their potential applications in catalysis, controlled delivery, artificial cells, light fillers, and low dielectric constant materials.[1] Among them, semiconductor-coated polymer capsules and hollow spheres have attracted many researchers.[1–5] To achieve this aim, colloidal monodisperse particles are always used as templates. And there are two main approaches as multicycle coating or direct chemical deposition onto the modified colloidal surface to obtain a complete covering or multilayered capsules.[3,4,6,7] The layer thickness can be controlled by the coating material concentration or the cycling times. However, these processes to obtain the desired layer thickness are limited by slow process, multisteps and surface modification.[6,7] Therefore, finding a facile and controllable preparation method in core–shell structures is still a challenge in materials science.

Microwave synthesis is a rapidly developing technique. In this system, an understanding of the microwave interaction with materials has been based on the concept of dielectric heating and the resonance absorption due to rotational excitation. In contrast to the conventional methods, it has been extensively employed because this technique can make some reactions completed in very shorter durations.[8–12] Here, we report the fabrication of polystyrene@CdS (PS@CdS) core–shell nanostructures by microwave irradiation from the aqueous solution of $CdCl_2$, thioacetamide (TAA), and polyvinylpyrrolidone (PVP) with PS microspheres. To our knowledge, this is the first successful attempt to form monodisperse PS@CdS nanostructures from aqueous solution in one step. The PS microspheres are free of surface modification. Also CdS hollow spheres are easily obtained by removing the PS cores in toluene solution.

In a typical procedure, PS@CdS nanostructures were prepared as following: 5 mmol (1.14 g) of $CdCl_2 \cdot 2.5H_2O$, 7 mmol (0.53 g) of TAA (≥99%), and 0.1 g of PVP (K30) was dissolved into 50-mL deionized water (TAA to $CdCl_2 \cdot 2.5H_2O$ molar ratio equal to 1.4). The above solution was added to the colloid solution of 0.05 g of PS microspheres dispersed in 10-mL alcohol (PS microspheres prepared as described elsewhere[13]). Then, the obtained mixed solution was transferred into a 100-mL flask, which was maintained at 70 °C for 1.5 h during microwave irradiation (MAS-II, 2450 MHz, 100–1000 W, Sineo Microwave Chem. Sci. & Tech. Co., Ltd., Shanghai) and cooled to room temperature. The as-prepared products were washed several times with deionized water and dried in a vacuum oven at 60 °C for 8 h. In order to prepare CdS hollow spheres, the PS@CdS particles were dissolved in toluene, and a centrifugation–redispersion cycle was repeated several times to ensure PS cores completely removed.

The as-synthesized samples were characterized by X-ray diffraction (XRD, Philips X'pert PRO), field emission scanning electron microscopy (FE-SEM, Sirion 200 FEG), transmission electron microscopy (TEM, JEOL 2010, 200 kV), and Fourier-infrared (Nicolet Magna-IR750) and Raman spectroscopy (LABRAM-HR Raman spectrophotometer).

Figure 1 shows TEM images of the as-prepared products. Figures 1a and 1b show the CdS-coated PS nanostructures, from which one can see the coating layer of CdS particles. The strong contrast between the dark edge and darkish center provides convictive proofs for the core–shell structure. It reveals that CdS particles generated by microwave irradiation are almost uniformly deposited on the PS microspheres. The CdS shell thickness is about 20 and 40 nm as it can be seen clearly in Figures 1a and 1b, respectively. When the PS@CdS particles of 1.5 h were treated with toluene, the hollow CdS spheres were obtained as shown in Figure 1c. Compared with Figures 1b, PS cores were removed completely and CdS hollow spheres retained the same size and morphologies as PS@CdS core–shell nanostructures.

Figures 2a and 2b show the XRD patterns of PS@CdS core–shell nanostructures and CdS hollow spheres, respectively. All the peaks in CdS particles coated on PS and the hollow shells obtained by dissolving PS in organic solvent exhibit the pattern of hexagonal wurtzite structure CdS bulk crystals (JCPDS Card

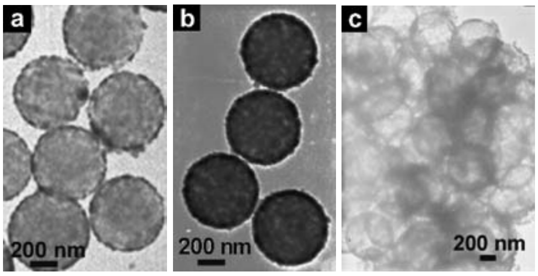

Figure 1. Typical TEM images of PS@CdS core–shell nanostructures prepared with 5 mmol of $CdCl_2$ for (a) 1 h, (b) 1.5 h and the corresponding CdS hollow spheres in (c).

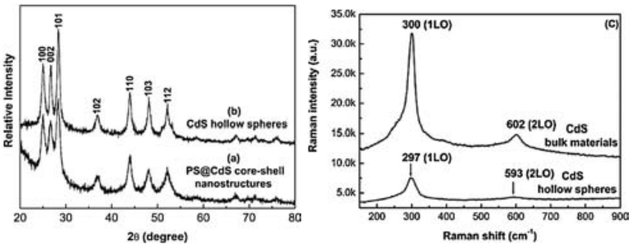

Figure 2. XRD patterns of (a) PS@CdS core–shell nanostructures and (b) CdS hollow spheres. (c) Raman spectra of CdS hollow spheres and bulk materials.

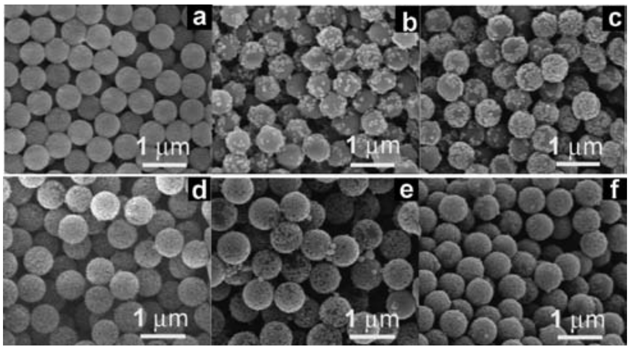

Figure 3. SEM images of (a) PS spheres and (b)–(f) PS@CdS core–shell nanostructures prepared by microwave irradiation at 70 °C with (b)–(d) different $CdCl_2$ concentration for 1.5 h: (b) 3 mmol, (c) 4 mmol, (d) 5 mmol, and with (e)–(f) 5 mmol of $CdCl_2$ concentration for different reaction time: (e) 1 h and (f) 2 h.

File, No. 41-1049). The broadening of the peaks indicated that CdS particles were of nanometer scale. The red shift and broadening of peaks in Raman spectrum of CdS hollow spheres compared to bulk materials (Figure 2c) further revealed the quantum confinement and also showed that the shell was composed of CdS nanoparticles.[14]

The IR spectra of PS microspheres, PS@CdS core–shell nanostructures, and CdS hollow spheres further reveals that PS cores could be successfully removed from PS@CdS core–shell nanostructures to form CdS hollow spheres.

The growth process of the PS@CdS core–shell nanostructures could be controlled by the precursor concentration and different microwave irradiation time (shown in Figure 3). SEM image of PS spheres (diameter about 580 nm) is shown in Figure 3a. At 70 °C for 1.5 h using 3 mmol of $CdCl_2$, CdS nanoparticles formed on the surface of PS spheres, and a large area of uncoated PS surface was left (Figure 3b). Increasing the $CdCl_2$ concentration to 4 mmol, more CdS nanoparticles on PS spheres (Figure 3c) were formed, while partially uncoated PS surface was observed. Increasing the $CdCl_2$ concentration (5 mmol) also resulted in the formation of CdS nanoparticles smoothly formed on the whole PS spheres as shown in Figure 3d, and TEM image indicated the shell thickness of about 40 nm. The shell thickness could be controlled by reaction time. At 70 °C with a $CdCl_2$ concentration of 5 mmol, PS@CdS core–shell nanostructures with a limited bare area (Figure 3e) were achieved after 1 h; the shell thickness was about 20 nm. When the reaction time was extended to 2 h, perfect PS@CdS core–shell nanostructures (Figure 3f) were formed similar to the products obtained at 1.5 h (Figure 3d), and the shell thickness increased to 50 nm. Comparing to other methods,[3,4] the whole process takes only 1.5 h owing to the effect of microwave irradiation. When the temperature or concentration was higher than 70 °C or 5 mmol, there were separated CdS particles formed in the bulk solution. When the temperature was below 60 °C, there were no CdS particles formed because of TAA decomposition temperature higher than 60 °C. We also found the rotating speed of stirring bar affecting the formation of CdS particles. The detailed works are in the progress.

On the basis of the above observations, the possible mechanism for the formation of PS@CdS core–shell nanostructures is proposed as following. Cd^{2+} ions can be absorbed on the surface of PS microspheres,[12] and TAA decomposes in water to form H_2S under microwave irradiation. This property is exploited to give the formation of CdS in the surface region of PS microspheres as S^{2-} reacts with Cd^{2+}. Once CdS nanoparticle is formed on the surface, it could act as a nucleating site for the further adhesion of CdS formed in the bulk solution. Whereafter, the formed CdS nanoparticles assemble compact CdS layer on the surface of PS microspheres under the ripeness.

In summary, we found a facile microwave-assisted method to fabricate complete and smooth PS@CdS core–shell nanostructures quickly and without modifying the colloidal surface. The thickness of CdS shells could be easily controlled by varying reaction time. This method offers the possibility of a generalized approach to prepare other core–shell nanostructures in a shorter duration.

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