

New Synthetic Route for Preparing CdS-Nanoparticle/Polystyrene Polymer Shells Hybrid Materials

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ABSTRACT: In this article we describe the combined use of γ -irradiation initiated micro-emulsion polymerization and redox interfacial-initiated micro-emulsion polymerization to prepare hollow polystyrene micro-spheres with movable CdS nanoparticles inside (CdS@PSt) hybrid materials under room temperature and ambient pressure. First, mono-dispersed CdS nanoparticles with diameters 50 nm were synthesized in inversed micro-emulsion under γ -irradiation. Then, CdS nanoparticles were coated with PSt via interfacial-initiated micro-emulsion polymerization with

cumene hydroperoxide/ferrous sulfate (CHPO-Fe²⁺) as the redox initiation pair. The resulted CdS@PSt hybrid materials were identified by transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), dynamic light scattering (DLS) and X-ray powder diffraction (XRD). © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3204–3209, 2008

Key words: composites; core-shell polymers; dynamic light scattering; interfacial-initiated; polystyrene

INTRODUCTION

Recently, polymeric hollow micro-spheres have attracted considerable research attention due to their large variety of applications in chemistry, biotechnology, and materials science.^{1–6} The advantages of polymeric hollow microspheres include its encapsulation property, controllable permeability, and surface functionality. Many methods^{7–10} have been developed to prepare these hollow nanostructures.

An important aspect about hollow microspheres with movable inorganic cores is that their functionalization could be achieved by encapsulating guest species, which would endow them with diverse properties. Hollow microspheres functionalized with movable inorganic nanoparticle cores have been explored as novel nanostructures by several groups.^{11–14} Nanoparticles such as tin, gold, or silica could be incorporated into the interior of hollow nanospheres. Novel properties can be introduced to the hollow nanospheres by this method. Lee et al.¹¹ prepared Tin-encapsulated hollow carbon spheres as an anode material in lithium secondary batteries. The encapsulation of Sn nanoparticles with hollow

carbon spheres improved the cycle performance of metal Sn as an anode material. Kamata et al.¹² reported that the incorporation of Au nanoparticle as a movable core into a polymeric hollow sphere could provide an optical probe for monitoring the diffusion of chemical reagent into and out of the shell. Skirtach et al.¹⁵ showed that, under laser illumination, the capsules containing Ag nanoparticles could be deformed or cut, thus providing avenue for remote release of encapsulated materials.

The usual method for the preparation of hollow microspheres with movable cores is based on a template-assisted approach.^{12,13} First, the core (e.g., Au nanoparticle) particle is prepared and then it is coated with a polymeric shell. The shell is further functionalized with certain reactive groups to grow another polymer layer. With removal of the middle polymer layer using a solvent or calcination, hollow spheres with movable cores are formed. This method often needs a complicated organic synthetic technique to grow another polymer layer. It is also not convenient to control the size of the core nanoparticle.

In this article, we describe an easy redox interfacial-initiated microemulsion polymerization for producing a novel core-shell nanostructure: CdS-PSt hollow microspheres containing movable CdS nanoparticles (CdS@PSt). Compared with the usual approach, this method does not require any template-assisted and just under room temperature and ambient pressure. In this method, hollow microspheres were prepared by one-step via interfacial initiated microemulsion polymerization. We have

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taken advantage of this interfacial-initiated (micro-) emulsion polymerization to synthesize different polymer particles.^{16–19} This novel approach has two essential features: (1) CdS nanoparticles were synthesized in inversed micro-emulsion under γ -irradiation, (2) The synthesis of PSt submicrometer hollow spheres coated around CdS nanoparticles by one-step via (CHPO/Fe²⁺) as the redox initiation pair of the interfacial-initiated polymerization in reverse microemulsion. This method affords a convenient platform for building novel core-shell nanostructures with controllable properties.

EXPERIMENTAL

Chemicals

Styrene (St) was distilled under vacuum and kept in a refrigerator before use. Na₂S₂O₃ · 5H₂O, 3CdSO₄ · 8H₂O, isopropanol, Cumyl hydroperoxide (CHPO), ferrous sulfate hydrate (FeSO₄·7H₂O), and sodium dioctyl sulfosuccinate (AOT) are all analytical reagents and used as received.

Preparation of the CdS nanoparticles by γ -irradiation

To prepare CdS nanoparticles, Na₂S₂O₃·5H₂O (0.602 g), 3CdSO₄·8H₂O (0.206 g), isopropyl alcohol (0.025 mol) were dissolved in distilled water (4.0 mL) and the solution obtained was added into 0.15 mol/L AOT/hexane solution (40 mL) to form inversed micro-emulsion by the aid of a supersonic cleaner. After the microemulsion was transferred into a 50 mL container and was bubbled with N₂ for 40 min to eliminate oxygen, it was sealed and irradiated under γ -ray with 110 Gy/min for 24 h. The resulted micro-emulsion was named as emulsion A.

Preparation of CdS@PSt hybrid materials via redox interfacial-initiated microemulsion polymerization

To introduce the reducing reagent of Fe²⁺ into the dispersion phase of emulsion A, FeSO₄·7H₂O (60 mg) was dissolved in distilled water (4.0 mL). The resulted solution was added into 0.15 mol/L AOT/hexane solution (40 mL) to form inversed emulsion B. The mixed microemulsion of emulsions A and B was heated to 35°C while being purged with nitrogen for 2 h. The oil-soluble solution of St (1.5 g) and CHPO (100 mg) in hexane (10 mL) was added into in batch or continuously with a Sp1001 syringe pump in 5 h. The water-soluble Fe²⁺ of the initiation system should react with the oil-soluble CHPO of the initiation system at the oil-water interface to form the radicals initiating the polymerization. The reaction continued for another 12 h to ascertain the

limiting monomer conversion. Then the micro-emulsion was destabilized with ethanol. The precipitate was separated by centrifugation and washed repeatedly with hexane and ethanol to remove the surfactants. The morphology was observed under TEM and FESEM.

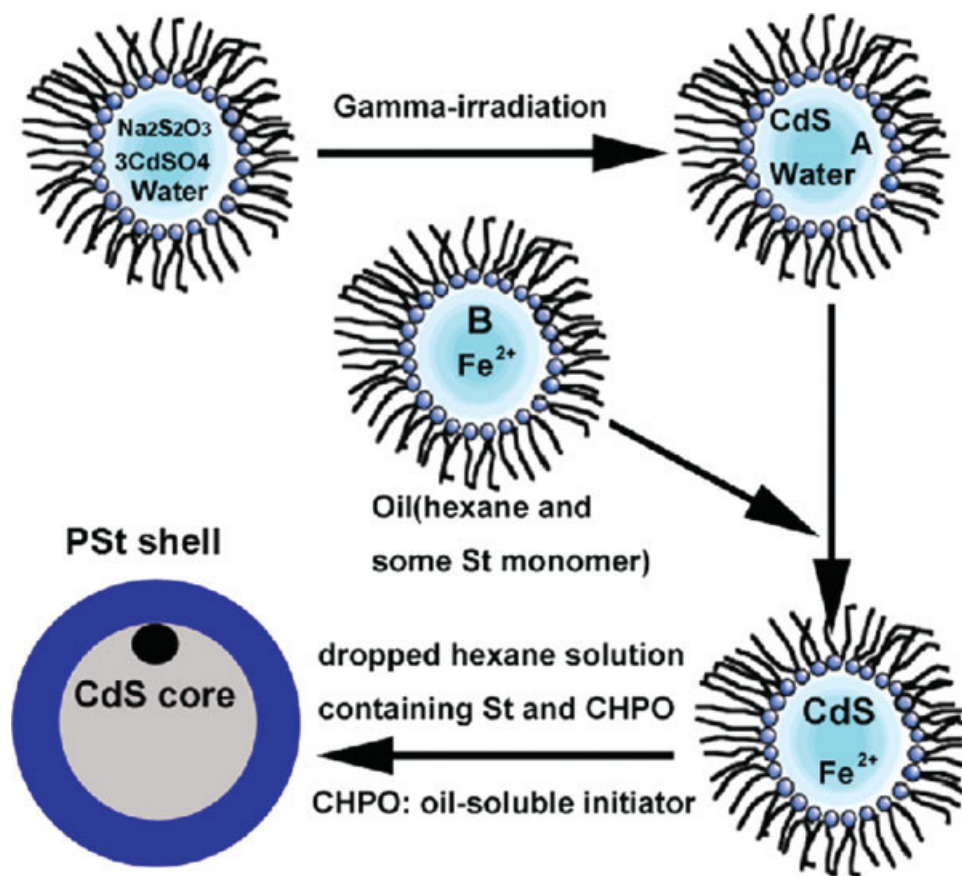
Characterization

Diffraction pattern of CdS nanoparticles and CdS@PSt hybrid materials were recorded on X-ray diffractometer (Rigaku D/max γ A) equipped with graphite monochromatic Cu Ka radiation ($\lambda = 0.154178$ nm), at a scanning rate of 0.02°/s with 2 θ in the range of 10–70°. The transmission electron microscopy (TEM) and electron diffraction (ED) images were performed on a Hitachi model H-800 transmission electron microscope with an accelerating voltage of 200 kV. As for the morphology observation under Field-emission Scanning Electron Microscopy (FESEM, JEOL JSM-6700) with the acceleration voltage of 5 kV, the solid particles were attached to adhesive tape and coated with gold under vacuum. The particle size and its distribution were determined on Dynamic laser light scattering (DLS). Dynamic laser light scattering was performed on a modified commercial LLS spectrometer (ALV/SP-125) equipped with an ALV-5000 multi- τ digital time correlation and a He-Ne laser (output power = 10 mW at 632 nm) at 25°C to get the size of PSt/PNVP latex particles. Before DLS measurement, the latex was diluted with distilled water to a given concentration and a filter (0.45 μ m) was used to eliminate any dust. Laplace inversion of the intensity-intensity time correlation function G(2) (t, q) in the self-beating mode resulted in a line-width distribution G(Γ). G(Γ) was directly converted to the hydrodynamic radius distribution f(Rh) by using the Stokes-Einstein equation: Rh = kBT/(6 π η D) with kB, T, η and the translational diffusion coefficient being Boltzman constant, absolute temperature, the solvent viscosity and translational diffusion coefficient, respectively. Polydispersity index (PDI) of Rh was defined as eq. (1).

$$PDI = \mu_2 / \Gamma^2 \quad \mu_2 = \int (\Gamma - \Gamma)^2 G(\Gamma) d\Gamma \quad (1)$$

RESULTS AND DISCUSSION

CdS@PSt hybrid materials were prepared by a novel method as shown in Scheme 1. This novel approach has two essential features: (1) The synthesis of CdS nanoparticles by γ -irradiation via inversed micro-emulsion; (2) in-situ preparing PSt encapsulation around CdS nanoparticles to form CdS@PSt hybrid



Scheme 1 Schematic synthesis of CdS@PSt hybrid materials. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

materials through redox interfacial-initiated micro-emulsion polymerization of styrene at the water-oil interface.

A typical TEM image of CdS nanoparticles synthesized by γ -irradiation is shown in Figure 1(a), its diameter be about 50 nm, while the electron diffraction

pattern of the same specimen is shown in Figure 1(b). During the irradiation of the emulsion under γ -ray, the radiolysis of water produces many active species such as e_{aq}^- , H, and OH.²⁰ Then, the e_{aq}^- could reduce sulfur source to S^{2-} , which reacted with Cd^{2+} to generate CdS. Meanwhile, the scav-

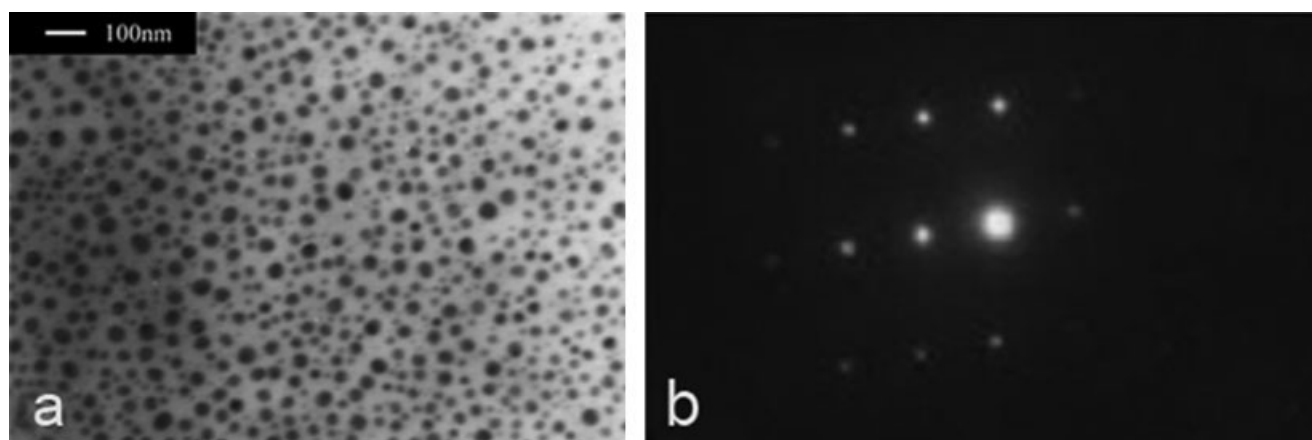


Figure 1 (a) TEM image of CdS nanoparticles (b) the selected area electron diffraction (ED) pattern of the CdS nanoparticles.

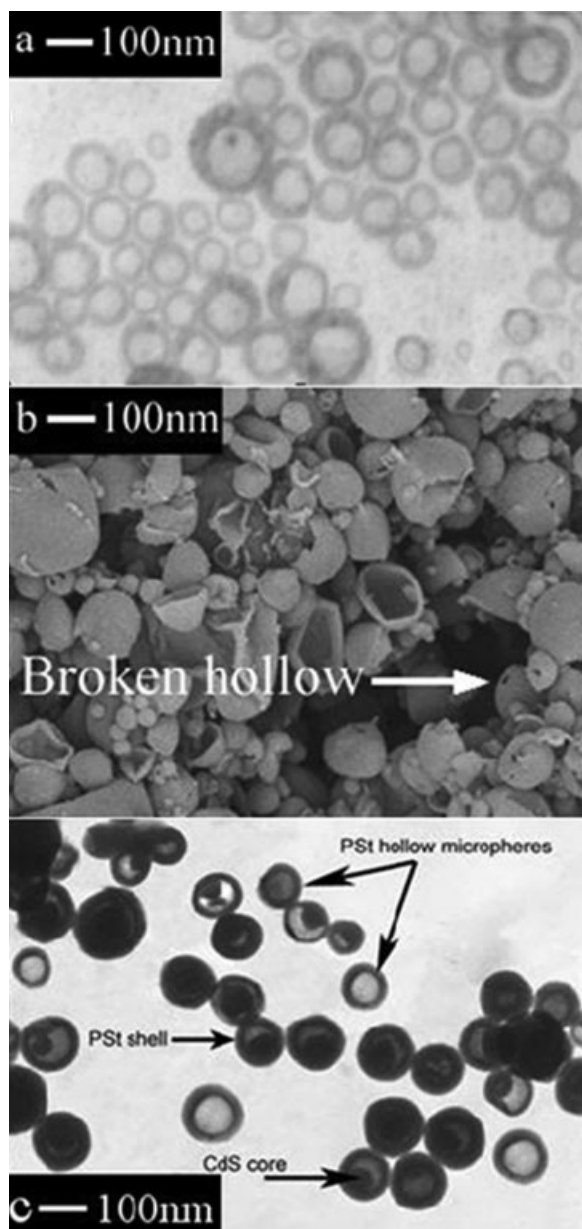


Figure 2 TEM image (a) and FESEM image (b) of PSt hollow microspheres; TEM image (c) of CdS@Pst hybrid materials.

enger of oxidative radicals, isopropyl alcohol could eliminate the influence of oxidative radicals on the formation of S^{2-} anion. The possible reactions are described as follows:

- Radiolysis of water: $H_2O + \gamma \rightarrow e_{aq}^-, H\cdot, \cdot OH, H_3O^+$ etc
- Reduction of $Na_2S_2O_3$: $e_{aq}^- + S_2O_3^{2-} \rightarrow S^- + \cdot SO_3^{2-}$ and $e_{aq}^- + S^- \rightarrow S^{2-}$
- Combination: $S^{2-} + Cd^{2+} \rightarrow CdS$
- CdS aggregation: $n CdS \rightarrow (CdS)_n$
- Some oxidative radicals such as OH were scavenged by isopropyl alcohol.
- $OH + CH_3CH(OH)CH_3 \rightarrow H_2O + (CH_3)_2(OH)C\cdot$

- The inversed micro-emulsion can act as a nano-reactor to form nanoparticles.

We have synthesized PSt hollow micro-spheres through this one-step redox interfacial-initiated emulsion polymerization in the absence of CdS nanoparticles. Figure 2(a) shows TEM image of PSt hollow microspheres obtained by this method, with the diameter of hollow spheres being 80–150 nm and the shell thickness about 10–20 nm. The hollow microspheres were also recorded on FESEM, Figure 2(b) shows FESEM image of PSt hollow microspheres and hollow structure with broken shell can be identified. In this article, CdS@Pst hybrid materials with the diameter of about 120 nm and the thickness of polymer shell about 25 nm were prepared through the same route in the presence of CdS nanoparticles and their TEM image were shown in Figure 2(c), demonstrating clearly the hollow structure with CdS interior (black core) and PSt outer loop. There have some pure PSt hollow micro-spheres in Figure 2(c) because redox interfacial initiated St micro-emulsion polymerization in the absence of CdS nanoparticles. Compared with PSt hollow particles

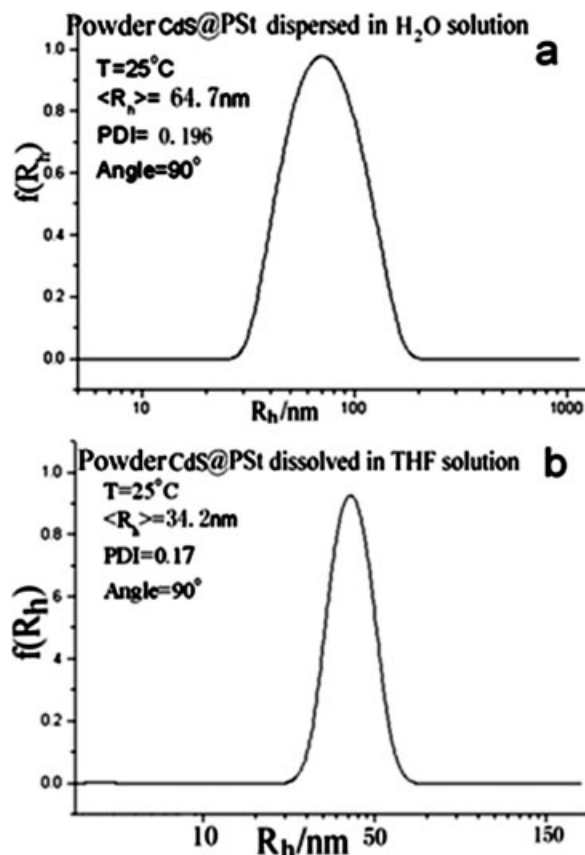


Figure 3 Hydrodynamic radius distribution ($f(R_h)$) of (a) CdS@Pst (b) CdS@Pst core/shell hybrid materials dissolved in THF.

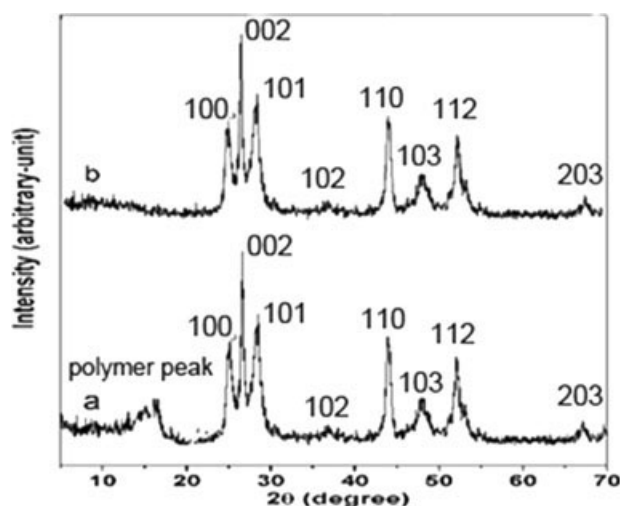


Figure 4 XRD pattern of (a) CdS@PSt hybrid materials (b) CdS nanoparticles.

and CdS@PSt hybrid materials, the PSt hollow microspheres are much more uniform.

DLS data also can give us evidence to illuminate the CdS@PSt core/shell hybrid materials with hollow interiors. Before DLS measurement, the CdS@PSt hybrid materials sample powder was re-dispersed with distilled water and the same sample was re-dispersed in THF (The PSt shell layer will be dissolved in THF), respectively, a filter was used to eliminate any dust (0.45 μm). The Hydrodynamic radius $f(R_h)$ and its distribution (PDI) are demonstrated in Figure 3. The $f(R_h)$ and PDI of CdS@PSt core/shell hybrid materials are 62.4 and 0.196 nm, respectively, The $f(R_h)$ and PDI of CdS nanoparticles are 34.2 and 0.17 nm, respectively, which is in good agreement of TEM result as shown in Figures 1 and 2.

The sample was identified by XRD, Figure 4 is the XRD pattern of the sample as-prepared CdS and CdS@PSt hybrid materials, all the main broad peaks at 2θ are very close to the reported data (JCPDS Card File no. 41-1049), Which indicates that the CdS nanoparticles is hexagonal phase. The broaden part at $2\theta = 16$ should be attributed to the amorphous polymer PSt.

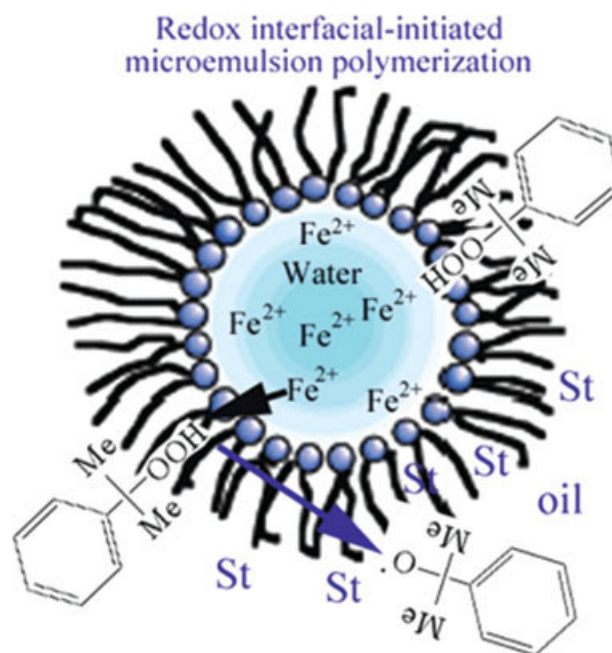
MECHANISM FOR THE FORMATION OF HOLLOW MICROSPHERES

Hollow PSt microspheres were prepared through one-stage interfacial-initiated polymerization in inversed microemulsion and the probable mechanism was suggested as follows. In this polymerization initiated by the redox couple, the oil-soluble oxidant component of CHPO stayed in the media of inversed emulsion while the reductive water-soluble component of Fe^{2+} existed in the water phase. Pri-

mary radicals would be produced only at the oil-water interface where both of them met. The primary radicals initiated the polymerization of St monomers near the interface to form PSt propagating chains. PSt propagating chains might be anchored to the surfactant monolayer or escape to the media bulk. In our case, the anchoring could be caused by the interaction between the chains and the octyl group of AOT. Feng et al.²¹ reported tertiary amine and peroxide that composed the redox initiation couple and the radicals derived from tertiary amine were produced. In the appropriate polymerization conditions, the anchoring of PSt chains would form a PSt enriched layer at the oil-water interface and absorb the coming monomer. Because of the feature of primary radical formation, the polymerization would occur mainly at the interface. Propagating radicals seldom had the chance of escaping from the interface to initiate the monomers in the oil media. In this way, hollow spheres with PSt as the corona and water as the core would be produced, as demonstrated in Scheme 2.

CONCLUSIONS

In conclusion, we present a simple but efficient redox interfacial-initiated microemulsion method for the synthesis of a novel nanostructure: CdS@PSt core-shell nanoparticle with movable CdS core. This method has the following two characteristics: (i) core



Scheme 2 Schematic preparation of PSt hollow spheres through interfacial-initiated microemulsion polymerization. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nanoparticles are fabricated via γ -irradiation before the formation of the hollow spheres and (ii) formation of PSt shell encapsulation around CdS nanoparticles is a simple one-stop interfacial-initiated microemulsion process. No additional reduction reagent is needed and just under room temperature and ambient pressure. Although only CdS is demonstrated in this work, other inorganic materials (e.g., Au, Ag, or ZnO) can also be incorporated into the interior of the hollow nanospheres. This novel core-shell nanostructure with movable inorganic core may find many applications in the future.

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