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Hollow spheres of silver synthesized using polyelectrolyte capsules as microreactors

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Abstract

Ag/polyelectrolyte (PE) hollow spheres were prepared using PE capsules as microreactors and electroless deposition of Ag. The external layer of the PE capsule was found to have a great effect on the morphology and permeability of the Ag shell. A positive surface charge will form compact and continuous Ag shells whereas a negative surface charge will form expanded and discontinuous shells. After removing the PE, hollow spheres of Ag with different morphologies were obtained.

Keywords: Ag hollow sphere; Microreactor; Polyelectrolyte capsule; Electroless deposition

1. Introduction

In recent years, layer-by-layer (LBL) assembly (SA) has been used widely to construct multilayer films and composite particles with delicate structures [1,2]. Both the composition and structure of LBL film can be controlled efficiently by adjusting SA condition. Hollow spheres with SA film as shell also attract more and more attention for their promising applications on delivery, transportation and catalysis [3]. In addition hollow polyelectrolyte (PE) capsules have also been used as a carrier or microreactor to prepare organic/inorganic hollow materials [4].

The composite particles or hollow spheres with metallic shell possess various applications, for example, using as surface optical enhancement, photonic crystals, catalysts, etc. [5a–c]. The synthetic methods based on chemical reductions, vacuum evaporation, sol–gel approaches have been used to introduce a metallic shell on colloid surface [6a,b] or to prepare metallic composite spheres with tunable shell thickness [7,8].

The procedures introducing a metallic shell on colloid surface, however, are rather complex to build up a relative thick shell. Rubner et al. developed a method to prepare metal films based on SA technique [9]. This method was also used to make metallic composite spheres having thick shell [10,11]. Antipov and co-workers reported the preparation of Ag hollow spheres using the solid colloid spheres as core [12].

The hollow PE capsules comprising polyelectrolytes (PEs), biomolecules, lipid and multivalent small molecules have been used as building block to construct delicate hollow structure [13]. The wall thickness, permeability, stability, biocompatibility, and affinity of the hollow capsules can be accurately designed and conveniently adjusted. Compared to solid templates, the hollow capsule has an infiltrative shell with controllable permeability [13,14]. The different composition of a capsule shell will exhibit different permeable properties towards special functional molecules or ions whereas the solid templates do not have this penetration ability. That is to say the hollow PE capsules using as microreactor can afford more varieties and choices for microreactions than using solid template as microreactor. Shchukin et al. reported that the Ni hollow spheres were prepared using PE capsule as microreactor in different crystallization conditions [15].

Herein we report an approach to prepare Ag hollow spheres with different morphologies using PE capsule as microreactor and Ag electroless deposition. Our method is much easier to control the morphology of Ag shell as compared with Shchukins' method in which the crystallization condition must be elaborately adjusted. The morphology of Ag shell, in this article, was controlled effectively by the external layer charge of shell, i.e., a positive charge layer will produce a compact and continuous Ag

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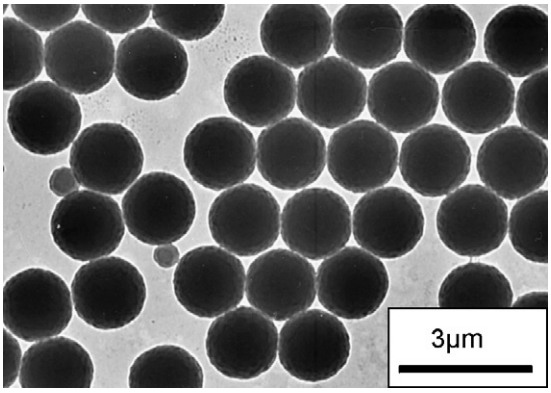


Fig. 1. TEM image of the PS beads prepared with dispersion polymerization.

shell whereas a negative charge layer prefer to form an expanded and discontinuous shells.

2. Experimental

2.1. Materials and instruments

Styrene was distilled under vacuum before used. Polyvinyl pyrrolidone (PVP) ($Mw = 4 \times 10^4$ g/mol) and polydiallyldimethyl ammonium chloride (PDDA) ($Mw = 2 \times 10^5$ g/mol) were purchased from Aldrich. Polystyrene sulfonate (PSS) ($Mw = 1 \times 10^5$ g/mol) was purchased from Acros. Other chemicals are analytical grade and were used without further purification.

Transmission electron microscopy (TEM, JEM200CX) and scan electron microscopy (SEM AMERT1900) were used to observe the size and morphology of Ag hollow spheres. X-ray photoelectron spectroscopy (XPS) was used to identify the composition of the Ag hollow spheres.

2.2. Preparation of PS beads

Polystyrene (PS) beads were prepared with dispersion polymerization. Typically the distilled styrene (2 g), deionized water (5 g) and ethanol (25 g) were mixed in a three-necked flask. PVP (1 g) as stabilizer, azobisisobutyronitrile (AIBN, 0.2 g) as initiator were added. The mixture then was polymerized under N_2 protection at 70 °C for 24 h. The beads with yield of ~80% and the size of ~1.52 μm (in diameter) were obtained. The TEM image of the beads is shown in Fig. 1.

2.3. Preparation of polyelectrolyte (PE) capsules

The sulfonated PS (SPS) beads were prepared in a mixture composed of PS beads (1 g) and concentrated sulfuric acid (100 mL) under stirring at 40 °C for 2 h. On the surface of SPS beads PDDA and PSS were assembled layer-by-layer to form a core–shell composite particle. The PE capsule with (PDDA/PSS)*n* multilayer film as shell were obtained after dissolving out the SPS core with tetrahydrofuran (THF).

2.4. Preparation of Ag/PE hollow spheres

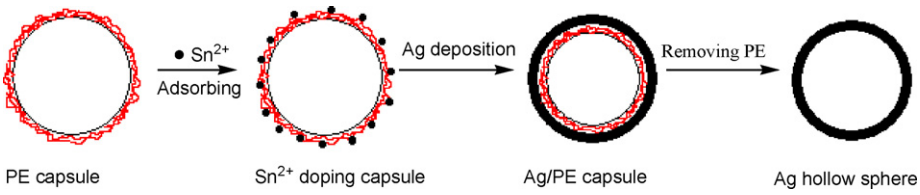
Ag hollow spheres were prepared as follows: 2 mL of PE capsule aqueous dispersion (1 mg/mL) was mixed with 2 mL of $SnCl_2$ aqueous solution (5 mg/mL, 0.1 M HCl) and stirred for 30 min to obtain Sn^{2+} modified capsules. After centrifugation and washing, 2 mL of Sn^{2+} modified capsule dispersion (1 mg/mL in water) was added into a mixture composed of 2 mL of $[Ag(NH_3)_2]^+OH$ (5 mg/mL) and 2 mL of sodium–potassium tartrate (SPT) (10 mg/mL) aqueous solution. The $[Ag(NH_3)_2]^+$ ions were reduced to Ag atoms by Sn^{2+} and SPT in the PE capsule, which plays a role of the microreactor to form Ag/PE capsule. The Ag/PE capsules then were immersed into a saturated sodium dodecyl sulfate (SDS) aqueous solution (~0.4 M) for 24 h at ~25 °C, in which the PE component can be dissolved [16], or sintered at 500 °C for 3 h under Ar in a quartz tube for removing the PE [17] to achieve Ag hollow spheres.

The full preparation of Ag hollow spheres can be schematically illustrated in Scheme 1.

3. Results and discussion

The SA film of $(PDDA/PSS)_3/PDDA$ or $(PDDA/PSS)_4$ was used as the shell of PE capsule in this article. In former the external layer is PDDA and in latter it is PSS. Fig. 2 shows the TEM (a) and SEM (b) images of the PE capsules with $(PDDA/PSS)_4$ films as shell. From it we can see that the PE capsules are spherical with a little fold originated from the core-removing process [3]. The PE capsules with $(PDDA/PSS)_3/PDDA$ as shell have a similar appearance.

Fig. 3a and b show the SEM images of Ag/PE hollow spheres after Ag electroless deposition. Here we use Ag/PSS and Ag/PDDA to represent the relevant hollow spheres made from $(PDDA/PSS)_4$ and $(PDDA/PSS)_3/PDDA$ as shell, respectively. We can see that the Ag/PE hollow spheres made from different shell exhibit very different appearances. The Ag/PSS (Fig. 3a) hollow spheres have a very rough surface composed of many small Ag granules whereas the Ag/PDDA (Fig. 3b) spheres show a smooth appearance with compact Ag shell. The above result indicates that the external layer of the PE capsules will affect obviously the morphology of Ag/PE hollow spheres. It is considered that the negative PSS layer is favorable to adsorb Sn^{2+}



Scheme 1. Schematic representation of the synthesis of hollow Ag spheres.