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Encapsulation of multiple large spherical silica nanoparticles in hollow spherical silica shells

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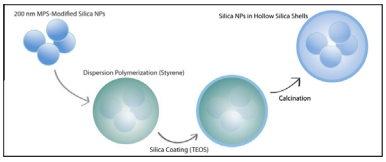
GRAPHICAL ABSTRACT



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ABSTRACT

Here we present the results of a stepwise synthesis of multiple large silica nanoparticles encapsulated in hollow, micron sized silica shells for future display applications. In the first step, 200-nm diameter silica nanoparticles were modified with 3-(trimethoxysilyl) propylmethacrylate (MPS) coupling agent. These nanoparticles were then embedded in micron-sized polystyrene particles synthesized through dispersion polymerization. To form silica shells on the polymer composite particles, tetraethylorthosilicate (TEOS) was added with cetyltrimethylammonium bromide (CTAB) surfactant. These three steps resulted in the formation of silica shell-covered solid polystyrene particles, each containing multiple silica nanoparticles. In the last step, polystyrene content was removed via calcination to achieve a multiple-silica-core-in-hollow-silica-shell composite structure. Dynamic light scattering (DLS) analysis and transmission electron microscopy (TEM) confirmed the core/shell morphology of the composite structure.

1. Introduction

Encapsulation offers benefits to many medicinal applications by providing controlled-release of cargos while facilitating storage, transport and stability of the encapsulated content. On the other hand, display applications may require relatively large nanoparticles be trapped inside isolated environments such as hollow spherical shells. For example, photonic displays may be possible if large, free to move around nanoparticles are ordered inside transparent hollow shells. Each of these assemblies can be considered as a single pixel. For this purpose, the size of the shells may be of the order of microns in size. These large hollow spheres can also be used as drug carriers or building blocks for photonic crystals. The nanoparticles inside should be of the order of tens to hundreds of nanometers so that they can be easily and quickly manipulated externally, e.g., using a magnetic field.

To entrap large nanoparticles in hollow shells, two general methodologies are possible. The first and more practical approach is to trap the desired nanoparticles in larger nanoparticles such as polymer particles, grow a shell around the larger nanoparticles and then etch or calcinate away the media between the original nanoparticles and the shells to create the final encapsulation product in hollow shells. Efforts have been devoted to some part or steps of this first synthetic method. A few groups have embedded smaller nanoparticles in larger solid particles, without the outer shell. For example, Sondi et al. successfully coated MPS modified multiple 8–11 nm silica particles with tert-butyl acrylate polymer in 2-propanol [1]. Bourgeat-Lami and Lang prepared polystyrene with multiple silica nanoparticles inside [2]. 50–120 nm silica particles were directly synthesized through the Stöber process and grafted with

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MPS (hydrophobic character) [3]. The dispersion polymerization of styrene was conducted in aqueous ethanol medium with polyvinylpyrrolidone (PVP) as stabilizer. Qi et al. also fabricated acrylate polymer/silica nanocomposite solid particles through miniemulsion polymerization [4]. Silica nanoparticles were initially grafted with MPS. They found that the coupling treatment of silica improved the encapsulation efficiency. Ding et al. encapsulated oleic acid modified 30–50 nm silica nanoparticles in polystyrene by *in situ* emulsion polymerization [5]. They proved that adjusting styrene concentration can alter polystyrene thickness, and adjusting silica concentration can control the diameter of composite particles. The diameter of composite particles varies from rom 180 to 250 nm. Lee et al. trapped fluorescent polymer (PDDF) and Fe_3O_4 nanoparticles inside silica spheres [6]. The composite particles PDDF/Fe_3O_4@SiO_2 possess both fluorescent and magnetic properties. Liz-Marzán et al. synthesized monodisperse silica-coated amorphous cobalt nanoparticles [7]. They demonstrated that controlling synthetic conditions could change the core size and the silica shell thickness. Ohnuma et al. trapped single Au or Ag nanoparticles in polymer particles [8,9]. In addition, Fayen et al. produced so-called mushroom nanostructures by trapping single Fe_2O_3 nanoparticles in silica shells [10]. Xing et al. trapped Ag/Au alloy nanostructures in polymer as well [11]. Other groups have also put a single large nanoparticle inside a hollow shell. For example, Okada et al. prepared two micron-sized silica rattle particles with single 920-nm silica core and proved the mobility of the inner silica core in the micron silica shell [12]. They obtained rattle structures in two steps: synthesizing silica core/polystyrene/silica shell composite structures and removing polystyrene component. Chen et al. also reported a selective-etching method to synthesize silica nanorattles [13]. They started with pure silica framework hydrolyzed from tetraethylorthosilane (TEOS), then coated the framework with TEOS and N-(3-(trimethoxysilyl) propyl) ethylenediamine (TSD) as the middle layer, and finally used HF to etch away this middle layer. The growth of shells outside large particles have been shown, although not with multiple nanoparticles embedded inside.

There are several reports describing the synthesis of hollow shells, and most approaches for fabrication of hollow structures rely on template-assisted synthesis, using hard (polymer particles) or soft (emulsion or vesicles) templates to form shell structures. By removing the middle polymer or emulsion layer with chemical dissolution or thermal calcination, a hollow structure is created. For example, Sandberg et al. prepared 180–190 nm polystyrene particles as sacrificial templates for hollow silica shells [14]. They proved that silica-coating process affects surface roughness of silica shells. Yin et al. described a "surface-protected etching" strategy to prepare permeable silica shells [15]. They first prepared solid silica nanoparticles. PVP was then covered the surface to serve as the protecting agent on silica surface through forming strong hydrogen bonds. Selective etching was conducted at room temperature with sodium hydroxide solution as etchant. Strong base diffused into the silica surface and eventually etched away the interior of solid silica nanoparticles. Xia et al. synthesized hybrid core–shell particles using monodispersed polystyrene beads as templates [16]. The polystyrene particles of diameter from 0.1 to 1.0 μm were coated with a uniform silica shell, which is controlled in the 50–150 nm ranges. They reported that functional groups on the surface of polymer, the pH value of the medium, and TEOS deposition time are important factors in affecting the silica shell formation. Mashimo et al. presented a strategy for preparation of nanoporous hollow silica shells (<100 nm) using polystyrene beads as hierarchic cores and polyethyleneimine (PEI) as shell template [17]. Carboxylate (COOH) functionalized polystyrene beads can facilitate the silica formation. Ge et al. prepared polystyrene–methyl acrylic acid latex as template for porous hollow silica spheres [18]. CTAB served as a wall structure-directing agent and Stöber method for silica coating. The soft template-route to prepare hollow shell structures utilized the liquid–liquid interface for nanoshell formation without removing core. The formation of micelle is extreme important for subsequent silica shell deposition. Song et al. prepared hollow silica spheres using water in oil (W/O) emulsion system with surfactant CTAB [19]. TEOS served as silica precursor. Fujiwara et al. synthesized hollow silica microcapsules with a water/oil/water (W/O/W) emulsion without core material [20]. Silica shell was formed on the micelles using sodium silicate as silica source. Only a few reports exist on producing nanoparticles inside shells using pre-made shells. Xu et al. reported three-step chemical procedure for preparing polystyrene/silica/maghemite composite particles with superhydrophobic and superparamagnetic properties [21]. It is evident that although it is possible to merge all these steps together to complete the synthesis of hollow shells containing multiple, large cores, it is still challenging to experimentally combine all these steps, and trapping large nanoparticles in hollow shells have not been reported.

The second general approach is to impregnate an existing shell with reactants and grow nanoparticles within the shells. In this approach, shells such as those discussed above are made first. Chemicals are then delivered into the shells to synthesize a particle or particles inside the shells. Koo et al. prepared rattle-type silica particles with copper cores [22]. Copper core was obtained via chemical reduction of copper ion inside the silica shell. Nann et al. prepared Au@SiO_2 composite particles [23]. Gold core was formed by chemical reduction of $HAuCl_4$ inside hollow silica shells. Because this approach could not produce encapsulation of multiple, large nanoparticles in hollow shells due to the limited supplies of chemicals available in the shells, this method is not viable to easily produce the desired products.

Here we wish to show a systematic approach through which we can trap multiple large nanoparticles in hollow shells. We selected silica to make nanoparticles and shells. Silica is chemically inert, nontoxic, highly biocompatible and optically translucent, hence it is considered as a model material for the encapsulation process. In the experiments shown below, the dispersion polymerization of styrene in an aqueous medium was carried out in the presence of nanosized silica particles made by the Stöber method in the hydroalcoholic medium. Silica particles were functionalized by grafting 3-(trimethoxysilyl) propyl methacrylate (MPS) on their surfaces. Mesoporous silica shell was synthesized with hexadecyl trimethyl ammonium bromide (CTAB) as a structure-directing agent. Polystyrene was removed by calcination to obtain the shell structure. The resulting composite material is characterized by DLS and TEM. The core can be replaced with magnetic nanoparticles, gold nanoparticles and fluorescent nanoparticles for other applications.

2. Experimental section

Tetraethoxysilane (TEOS), cetyltrimethylammonium bromide (CTAB), ammonia solution (25%), styrene (contain 4-tert-butylcatechol inhibitor), potassium persulfate (KPS, ⩾99.0%), 3-(trimethoxysilyl) propyl methacrylate (MPS, 98%), chloroform, sodium hydroxide (analytical grade), concentrated hydrochloric acid (12 M), acrylic acid (99%), polyvinylpyrrolidone (PVP, MW 30 kDa) and tetrahydrofuran (THF) were purchased from Sigma Aldrich.

Monodisperse 200-nm silica particles in aqueous alcohol were prepared according to the Stöber method. 3.08 ml TEOS was quickly added to the vigorously stirred mixture of 2.38 ml water, 3.88 ml ammonia (25%) and 80 ml ethanol. The reaction mixture was stirred at room temperature for 24 h. For purification, 200 nm monodisperse silica particles were collected after centrifuged (6000 rpm, 15 min) and washed three times with ethanol. To modify the surface of the 200-nm silica particles, 700 μl of