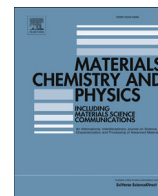




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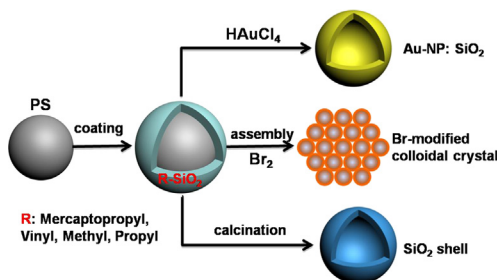
A one-step method to coat polystyrene particles with an organo-silica shell and their functionalization

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HIGHLIGHTS

- Demonstrated a one-step controllable coating method of organo-SiO₂ on polystyrene.
- The Br-modified PS@vinyl-SiO₂ colloidal crystal has tunable photonic band gaps.
- PS@mercaptopropyl-SiO₂ particles allow the encapsulation of small Au nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile method of coating polystyrene (PS) particles with organo-silica and their functionalization was presented. By adding the organo-silane precursor into PS aqueous solution in presence of ammonia, an organo-silica shell could be coated on PS particles directly. This method has several characteristics. First, only one process, one precursor and one solvent were used. Second, the organic groups could be varied from methyl, propyl, vinyl, to mercaptopropyl. The third is the tunable shell thickness with a high monodispersity. The organo-silica shells are further functionalized. The PS@vinyl-SiO₂ particles were used to assemble colloidal crystals, and further modified with bromine, resulting in tunable photonic band gaps. PS@mercaptopropyl-SiO₂ particles allow the encapsulation of Au nanoparticles. The resulting 2.2 nm Au particles were stable at 550 °C and well-distributed in the whole SiO₂ shell with a loading up to 20 wt%.

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1. Introduction

Core-shell particles have attracted considerable attention in physics, chemistry, and medicine, due to their application potential in photonic crystals, catalysis, and drug delivery [1–6].

Extrapolating these interesting works, one may envisage tunable optical systems usable as breadboards of photonic integrated circuits or geometrically designed catalysts for consecutive chemical reactions. In the developments, PS@SiO₂ is a popular basic core-shell system [7–11]. The PS core can have a highly uniform spherical shape, a high monodispersity, and a possible inner core-shell structure as well. Also the PS can easily be removed via chemical leaching or calcination, and then hollow particles [10,11] or yolk-shell systems can be obtained. The SiO₂ shell is usually fabricated by a Stöber-like method [12] delivering a controllable homogeneous thickness and a tunable porosity [1–3]. In addition,

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owing to the negative charge, SiO₂ can prevent the aggregation of the colloidal particles. However, commonly used PS particles are also negatively charged [13]. Therefore, it's hard to get smooth and homogeneous coating of SiO₂ directly on the negatively charged PS particles. Many groups have developed different ways to modify the surface of PS particles, e.g. SiOH-functionalized surfaces [8], PVP-stabilized surfaces [9], and polyelectrolyte deposited (positively charged) surfaces [13]. It takes two or even more steps, which are very time-consuming in reaction and cleaning process.

One application of core–shell systems is photonic band gap materials. Such materials require a high monodispersity of the building blocks and a usable chemical flexibility to tune the system towards applications such as photonic waveguides or resonators. Monodispersity and tuning abilities were achieved in several works, e.g. PNIPAM-based thermo-responsive colloidal crystals [14,15]. However, temperature and most chemical tunings lead to lattice constant changes, which can be acceptable for sensor applications but not for application in many other photonic devices. They destroy the device or induce defects. Therefore, constant-lattice tuning possibilities are required. The refractive index of the building blocks has to be changed, but the geometry should stay constant. The functionalization of core–shell systems is now an important way to connect them with optically active ligands in a flexible manner.

Another interesting application could be catalysis. Noble metals grafted on inorganic matrices are widely investigated. Especially gold nanoparticles (Au-NPs) are often used for the catalytic applications [16–24]. Different ways have been applied to graft Au-NPs on or in SiO₂ matrix particles. One way is to infiltrate Au ions into mesoporous SiO₂ spheres being the host for the formation of Au-NPs inside the pores [16–18]. Another way is the use thiol groups [20,22,24]. For example, a series of organically functionalized core–shell spheres was synthesized [22] which fixed the Au-NPs on the core surface by the binding between thiol and Au. However, two problems have been recognized for such systems. First, the migration of Au-NPs leads to aggregation and to a loss of catalytic activity at elevated temperatures (about 200 °C) [16–18]. Also Au-NPs protected by a shell of SiO₂ cannot endure much higher temperatures [22]. The second problem is the low loading with Au-NPs especially for low-surface area materials [24]. High and temperature-stable loading is therefore a challenge for many Au-NP containing catalysts.

Recently, we reported a method to synthesize monodisperse PS@v-SiO₂ core–shell particles, by using PS particles as template and vinyltrimethoxysilane (VTMS) as the precursor [25]. The procedure involved the pre-hydrolysis of VTMS precursor in water and then directly coating vinyl-SiO₂ on the PS surface at room

temperature. In this paper, we develop a one-step method to coat PS particles with organo-SiO₂ (Scheme 1). By elevating the reaction temperature, pre-hydrolysis of the precursor is not necessary. The reduction of this two-step procedure to one-step makes it easier to generalize this approach to flexible organic ligands. In addition, the enhanced temperature enables the use for several organo-silanes, which are strongly hydrophobic and hard to be dispersed in cold water. Subsequent modifications demonstrate the accessibility of the functional groups and the efficient tunability of these building blocks. For example, PS@v-SiO₂ core–shell systems were modified with bromine leading to efficiently tunable colloidal crystals with stable lattices. Furthermore, Mercaptopropyl-SiO₂ shells were impregnated with HAuCl₄ forming a high loading of well-distributed Au-NPs inside the SiO₂ shell.

2. Experimental section

2.1. Materials

Methyltrimethoxysilane (MTES, 99%), n-Propyltriethoxysilane (n-PrTES, 97%), vinyltrimethoxysilane (VTMS, 98%), 3-Mercaptopropyl trimethoxysilane (MPTMS, 95%), and bromine (≥99.5%) were purchased from Sigma–Aldrich. Ammonia solution (NH₃·H₂O, 28–30%) and Ethanol (99.9%) were purchased from Merck. PS particles (284 nm in diameter, terminated with sulfate groups, negatively charged) were purchased from Microparticles GmbH (Berlin). All chemicals were used as received. Ultrapure water was used directly from a Milli-Q water system.

2.2. PS@Organo-SiO₂ core–shell particles

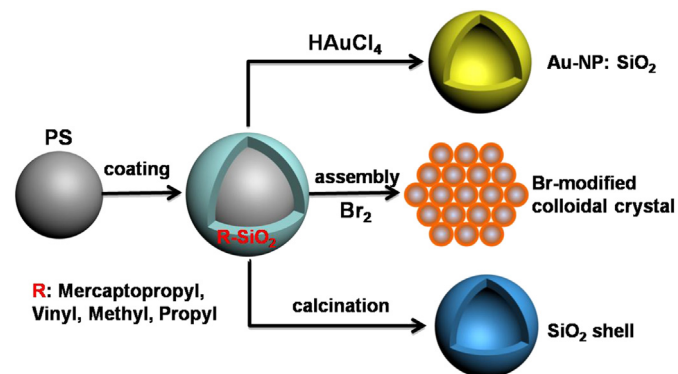
Core-shell particles were prepared by coating an organo-SiO₂ shell on the surface of PS core via a modified Stöber process that involved hydrolysis and condensation of the organo-silane in aqueous solution. For the PS@methyl-SiO₂ particles, 15 mL 0.5 wt% of PS aqueous suspension was heated to 60 °C under stirring, and then 10 mL ammonia solution was added. After 5 min, 0.5 mL MTES was dropped into the PS/NH₃/H₂O system. The reaction was allowed to proceed for 5 h at 60 °C. The resulting particles were washed three times with ethanol. For the n-PrTES/MPTMS precursor, 30 mL 0.25 wt% PS was used. The processes were the same as the MTES synthesis. The details are listed in Table 1.

2.3. Hollow SiO₂ shells

The hollow SiO₂ shells were obtained after removing the PS core. The core–shell particles were heated to 550 °C with a rate of 2 °C/min in air, kept for 6 h, and then cooled to room temperature. The obtained hollow SiO₂ shells were dispersed in ethanol for further use.

2.4. Br-modified colloidal crystals

The colloidal crystals were fabricated by using the capillary deposition method [6]. A suspension of 0.5 wt% PS@v-SiO₂ particles (sample DNT-DA-071-01, shell thickness 104 nm) in ethanol was used. The planar capillary cell was consisted of two glass slides separated by two polymer spacers (15 μm). A capillary tube was connected the colloidal suspension and the lower glass plate. The suspension was dragged up into the cell due to the capillary force. The colloidal crystal film was formed after evaporation of the solvent at the open edges of the capillary cell. For the bromine modification, a 2% (v/v) bromine solution in ethanol was infiltrated into the crystal via the capillary tube instead of the suspension. The infiltration was allowed to process 24 h. After infiltration, the cell



Scheme 1. One-step R-SiO₂ coating on PS and their functionalization to form Au-NP: SiO₂, Br-modified colloidal crystal, and hollow SiO₂ shell.

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