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Journal of Colloid and Interface Science 315 (2007) 434–438
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

# Preparation of $SiO_2$@polystyrene@polypyrrole sandwich composites and hollow polypyrrole capsules with movable $SiO_2$ spheres inside

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Received 6 February 2007; accepted 28 June 2007

Available online 13 August 2007

**Abstract**

In this paper, we describe a flexible method for preparing conducting building blocks: $SiO_2$@polystyrene@polypyrrole sandwich multilayer composites and hollow polypyrrole (PPy) capsules with movable $SiO_2$ spheres inside. First, $SiO_2$@polystyrene (PS) core/shell composites were synthesized, and then $SiO_2$@PS@PPy sandwich multilayer composites were prepared by chemical polymerization of pyrrole monomer on the surface of $SiO_2$@PS composites. Furthermore, hollow polypyrrole capsules with movable $SiO_2$ spheres inside were obtained after removal of the middle PS layer. The diameter of sandwich multilayer composites could easily be controlled by adjusting the dosage of pyrrole monomer. The conductivities of composites increased with the increase of PPy content. After the insulating PS layer was selectively etched, the conductivities of hollow capsules with movable $SiO_2$ spheres inside were much higher than those of the corresponding sandwich multilayer composites.


*Keywords:* Polypyrrole (PPy); Sandwich multilayer composite; $SiO_2$; Polystyrene (PS); Building block

## 1. Introduction

Self-assembled colloid crystals stand out as ideal templates for creating highly ordered three-dimensional (3D) or two-dimensional (2D) structures. They have remarkable potential applications in the fields of microelectronics, chemical sensors, engineering, and biomedicine due to their special periodical dielectric structures and unique optical properties [1–6]. Various methods have been successfully established to create colloidal crystals with lattice constants of micrometers or nanometers, and many perfect structures have been fabricated [7–14]. As is well known, building blocks play an important role in self-assembly methods. 3D or 2D structures with different building blocks display different properties. For example, packed magnetic nanoparticles with regular arrays can be used in data storage [15,16]. The incorporation of metal nanoparticles into ordered structures may find applications in catalysis and photonic crystals [17–20]. Although many functional materials have been used as building blocks, little attention has been paid to conducting polymers. Once conducting polymers are used as building blocks to form ordered structures, it will enlarge their applications in electronic devices, light-emitting diodes, electrochromic devices, and transparent electrode materials [21–24].

It is well known that polypyrrole (PPy) is an outstanding conducting polymer. It can easily be synthesized by various approaches—for example, oxidative polymerization and electrochemical polymerization. In addition, PPy presents several advantages such as environmental stability, good redox properties, and the ability to give high electrical conductivities [25–28]. One of the most widely studied and applied techniques in this respect is to form core/shell composites using conducting polymers as the shells and organic or inorganic particles as the cores [29–36]. In this paper, we synthesized $SiO_2$@polystyrene@polypyrrole sandwich multilayer composites and hollow PPy capsules with movable $SiO_2$ spheres inside. First, $SiO_2$ nanoparticles grafted with 3-(trimethoxysilyl)propyl methacrylate (MPS) were employed as cores in styrene emulsion polymerization to synthesize $SiO_2$@polystyrene (PS) core/shell composites. Then steric

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0021-9797/$ – see front matter 
doi:10.1016/j.jcis.2007.06.072

agent poly(*N*-vinylpyrrolidone) (PVP) was adsorbed onto the surface of $SiO_2$@PS by ultrasound as an anchor molecule and the polymerization of pyrrole monomers was performed around $SiO_2$@PS composites to form $SiO_2$@PS@PPy sandwich multilayer composites. Finally, the middle PS layer was selectively etched by tetrahydrofuran (THF) and hollow PPy capsules with movable $SiO_2$ spheres inside were obtained.

## 2. Experimental

### 2.1. Materials

Pyrrole and divinylbenzene (DVB) were purchased from Fluka. PVP with molecular weight of $3.6 \times 10^5$ was obtained from Sigma and used without further purification. 3-(Trimethoxysilyl)propyl methacrylate (MPS), styrene, and pyrrole were distilled under reduced pressure before being used. Tetraethyl orthosilicate (TEOS), absolute ethanol, ammonium hydroxide, sodium dodecyl benzene sulfonate (SDBS), potassium persulfate (KPS), $FeCl_3 \cdot 6H_2O$, and THF were analytical grade and used as received.

### 2.2. Preparation of $SiO_2$@PS@PPy sandwich multilayer composites

$SiO_2$@PS core/shell composites with different sizes were synthesized according to the references [37,38].

PVP was dissolved in ethanol by ultrasound in the presence of $SiO_2$@PS composites for 1 h; then the suspension was stirred for 24 h to ensure that the surface of the composites was adequately covered by PVP. Unadsorbed PVP was removed by centrifugation. Subsequently, the composites were redispersed into deionized water, which was directly used for the pyrrole-coating step.

A quantity of 1.0 g $FeCl_3 \cdot 6H_2O$ was added into 30 ml of the above solution (containing 0.24 g $SiO_2$@PS composites covered by PVP) under magnetic stirring at ambient temperature. After half an hour, the pyrrole monomer was added into the system using a syringe. The suspension color turned from yellow to dark green; at last it became black. After stirring for 16 h, black $SiO_2$@PS@PPy sandwich composites were obtained.

### 2.3. Preparation of hollow PPy capsules with movable $SiO_2$ spheres inside

$SiO_2$@PS@PPy composites were soaked in THF solution under magnetic stirring for 12 h; the PS layer between the PPy shell and the $SiO_2$ core was selectively etched. After being washed with deionized water and ethanol several times, the black sediments were dried in vacuum overnight. Hollow PPy capsules with movable $SiO_2$ spheres inside were obtained.

### 2.4. Characterization

A JEOL JSM-6700F scanning electron microscope (SEM) was employed to observe the surface morphologies. The mean diameter of composites was estimated by counting all particles in SEM images. The structure and shell thickness of the composites were determined by a JEOL-2010 transmission electron microscope (TEM). The FT-IR spectrum was measured at wavenumbers ranging from 500 to 4000 $cm^{-1}$ using a Nicolet Avatar 360 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) was conducted with a Netzschsta 449C thermogravimetric analyzer at a heating rate of 10 °C per min in $N_2$ from room temperature up to 700 °C. (The temperature of $SiO_2$@PS composites was up to 480 °C.)

## 3. Results and discussion

### 3.1. Morphology and structure

The overall procedure for forming $SiO_2$@PS@PPy composites and hollow PPy capsules with movable $SiO_2$ spheres inside is illustrated in Fig. 1.

MPS was critical during the preparation of $SiO_2$@PS composites. Only pure $SiO_2$ nanoparticles and pure PS nanoparticles were obtained in the reactor when the surface of the $SiO_2$ spheres was not grafted with MPS. Fig. 2 shows SEM and TEM images of the $SiO_2$@PS composites, which display good dispersity. The mean diameters of the $SiO_2$ cores and the composites are 80 and 230 nm, respectively. It is seen that most of the core/shell composites contain only one $SiO_2$ core, but in

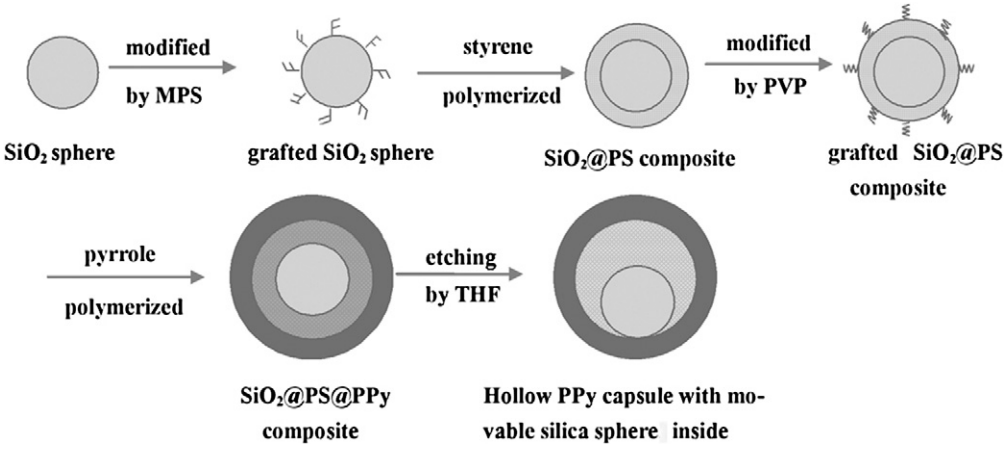


Fig. 1. The synthesis scheme for $SiO_2$@PS@PPy composites and hollow PPy capsules with movable $SiO_2$ spheres inside.