

Synthesis of hollow silica nanosphere with high accessible surface area and their hybridization with carbon matrix for drastic enhancement of electrochemical property



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ARTICLE INFO

Article history:

Received 7 April 2014

Received in revised form 13 June 2014

Accepted 7 July 2014

Available online 12 July 2014

Keywords:

Hollow silica

Carbon

ABC polymer

Sol-gel reaction

Carbon/silica composite

ABSTRACT

Hollow silica nanospheres with high accessible surface area have been synthesized by using core-shell-corona polymeric micelle of poly (styrene-*b*-2-vinylpyridine-*b*-ethylene oxide) (PS45k-PVP26k-PEO82k) as a template. The size of the template polymeric micelle depends on the pH of the solution, *i.e.* ≈ 100 nm at pH 7 whereas ≈ 300 nm at pH 4. The enlarged size of the micelle is possibly due to the protonation of the PVP block, which also serves as reaction sites for silica precursor. The size of the obtained silica nanosphere measured with transmission electron microscope (TEM) is around ≈ 70 nm and shell thickness is ≈ 20 nm. Fourier transformed infrared spectroscopy (FTIR) data confirms that the polymer template is completely removed during calcination. Conductive carbon is doped into the silica nanosphere through glucose solution followed by hydrothermal treatment and pyrolysis. It is found that the electrochemical performance and stability of the silica nanosphere is dramatically enhanced after carbon doping. The combined strategy of the core-shell-corona micelle as template and carbon doping could represent a new platform for the researchers to develop functional nanomaterials.

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1. Introduction

Due to the well-controlled kinetics for hydrolysis and condensation of silicon alkoxides in aqueous solutions, silica is the most popular inorganic materials. Particularly, fabrication of hollow silica nanospheres with porous shells has been attracted much attention due to their non-toxicity, biocompatibility, low density, high surface area, high pore volume and a permeable porous matrix wall, which expands the application area to energy storage, controlled drug-delivery, chemical conversion, and catalysis [1–7]. There are number of methods available in the literature to prepare hollow silica nanosphere, *e.g.*, sonochemical [8], hard templates [9,10], surfactant/vesicle templates [11–14] and emulsion templates.

Polymeric micelles with *core-corona* or *core-shell* structure have been using for preparation of hollow particles with controlled morphology and structure. The polymeric micelles so far employed have AB diblock or ABA triblock copolymers [15–18]. In the case of core-corona micellar system, the inorganic precursors are selectively adsorbed over the corona and form the shell of relevant hollow particles (not only polymerization but also precipitation reactions are used for shell formation). The core-forming polymer is removed either by calcination or solvent extraction to get a void space inside the inorganic shell. However, a problem is always raised due to the secondary aggregation because there is no option to prevent.

Nakashima *et al.* recently reported a facile template using ABC triblock copolymer which forms *core-shell-corona* micellar architecture to prepare various types of inorganic hollow nanospheres [19,20]. The advantages of the ABC triblock copolymer over AB diblock copolymer are that the corona of the triblock copolymer prevents the secondary aggregation. Moreover, the size of the void space and shell thickness of the nanosphere can be controlled by

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considering the molecular weight (M_w) of each block of the template polymer and the precursor amount [21].

Till now the reported nanospheres contains the void space of 15–20 nm and the shell thickness of 8–12 nm which means that the space in the core of the particle is not enough to load drugs, chemicals and so on. Moreover, the shell thickness of the nanospheres is thin, which cause breaking easily [21–23]. Liu *et al.* [21] described that the void space diameter of the hollow silica can be increased (from 20 to 28 nm) by the addition of homo polystyrene polymer. However the procedure to adjust the homo polystyrene and PS-PVP-PEO polymer is complicated. It is still a challenge to fabricate hollow silica nanospheres with large void space and thick shell for loading enough and preventing rupture during processing.

In this article, we have shown a facile way to synthesize hollow silica nanospheres, which have wide void space (≈ 30 nm) and thick shell (≈ 20 nm) by using a long chain ABC tri block polymer. We have used poly (styrene-*b*-2-vinyle pyridine-*b*-ethylene oxide) (PS-PVP-PEO) polymer with long PS block as a soft template and tetramethoxysilane (TMOS) and octadecyltriethoxysilane (ODTES) as silica precursors. The carbon was introduced by adding glucose solution followed by hydrothermal process to enhance the electrochemical activity of the silica nanosphere. The resultant hollow nanospheres were thoroughly characterized by TEM, XRD, FTIR, N_2 adsorption/desorption analyses. Electrochemical analysis was performed by using CR2032 type coin cells. We believe that the present materials will satisfy the requirements in a robust application condition.

2. Experimental

2.1. Materials

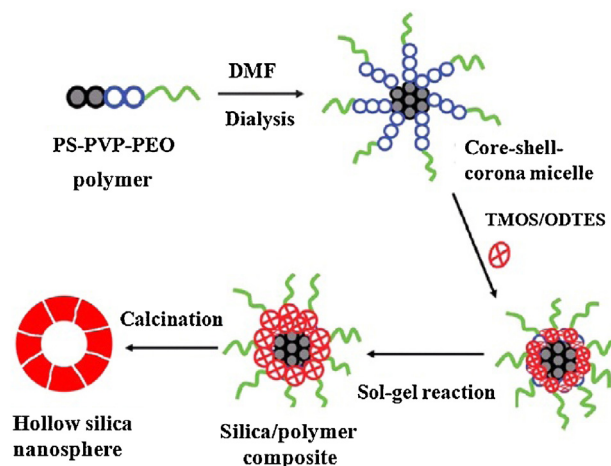
Triblock copolymer PS(45k)-PVP(26k)-PEO(82k) was purchased from Polymer Source Inc. The numbers in the parentheses are the molecular weights of the block chains (45k, for example, denotes 45,000). TMOS (>98%) and ODTES (>98%) were obtained from Shin Etsu Chemical Co. Dimethylformamide (DMF, 99.8%, Aldrich), hydrochloric acid (HCl) were obtained from Wako Chemicals and were used without further purification. D-Glucose was purchased from Sigma Aldrich.

2.2. Preparation of PS-PVP-PEO micelles

To prepare polymeric micelles of PS-PVP-PEO, the desired amount of the polymer was solubilized in DMF and then 5 wt% water was added by stirring with a magnetic stirrer. The solution was then dialyzed against water to obtain the polymeric micelles. The micelle solution was transferred to 100 mL volumetric flask and diluted with water to a polymer concentration of 1 g L^{-1} . The micelle solution was adjusted to pH 4 with dilute HCl solution.

2.3. Fabrication of hollow silica nanospheres

Scheme 1 shows a general procedure for fabrication of hollow silica nanospheres through sol-gel reaction under PS-PVP-PEO micelles, which was developed by us [19]. In a typical synthesis, 10 mL of micelle solution (polymer concentration: 1 g L^{-1}) was taken in a conical flask and the pH was adjusted to about 4 using dilute HCl. Then, the desired amount of silica precursors was added by keeping the molar ratio of total silica precursors to pyridine unit at 15. Fabrication of hollow silica nanospheres was carried out by co-condensation of TMOS with ODTES. The molar ratio of TMOS to ODTES was fixed at 3:1. After addition of silica precursors to the polymeric micelle solution, the mixture was stirred for 24 h at 50°C and further aged for 1 more day under static condition for extensive



Scheme 1. Fabrication route of hollow silica nanospheres with high surface area.

condensation of various silica species. The silica/polymer composite were separated from the aqueous suspension by centrifugation (12,000 rpm). The solid product was repeatedly washed with distilled water and ethanol followed by drying at 50°C . The polymeric template was removed by calcination at 500°C for 4 h in a muffle furnace in air atmosphere. Finally, hollow silica nanospheres were obtained, as shown in **Scheme 1**.

2.4. Characterization

Dynamic light scattering (DLS) measurements were carried out with an Otsuka ELS-Z electrophoretic light scattering spectrophotometer at a fixed 165° scattering angle. The correlation functions were analyzed by the cumulant method to determine the diffusion coefficient (D) of the micelles. Low-angle X-ray diffraction (XRD) were measured on a Rigaku Rint-ultima diffractometer with $\text{Cu K}\alpha$ radiation (40 kV, 20 mA) with 0.02° step and 2 s step time in 2θ range from 0.7° to 6.0° . The morphology of the samples was observed with JEOL JEM-2100 transmission electron microscope (with acceleration voltage of 200 kV) and scanning electron microscope (SEM) using a Hitachi SU-1500 an accelerating voltage of 25 kV. In the case of hollow silica nanospheres, the TEM samples were prepared by casting a drop of water suspension on a copper grid. The samples were finally dried at room temperature. Fourier transform infrared (FTIR) spectra were recorded on a Jasco FTIR 7300 spectrometer using KBr pellet technique. Total pore volume and surface area were obtained using nitrogen adsorption/desorption isotherms with a Quantochrome Autosorb 1C. The Raman spectra were measured by SpectraPro 2300i imaging spectrograph (Princeton Instruments, New Jersey) equipped with a liquid nitrogen cooled charge-coupled device (Spec-10:256E, Roper Scientific). All samples were excited with the 532 nm light available from a diode-pumped solid-state laser (Ventus532, Laser Quantum, Cheshire, UK), and a back scattered light was collected by collection optics. A long wave path edge filter (LP03-532RS-25, Semrock) was used to eliminate the intense Rayleigh light. All the spectra were taken at room temperature and homemade software eliminated the noise spikes in the spectra caused by cosmic rays. Electrochemical analysis was performed by using CR2032 type coin cells. Lithium foil was used as the anode and polypropylene as separator (GA-100, ADVANEC). For the fabrication of working electrodes, 5 mg active material and 4 mg conducting binder (Teflon:acetylene black = 1:2) were mixed and pressed on the stainless steel mesh under a pressure of 500 kg cm^{-2} . Then, the electrodes were dehydrated at 180°C for 6 h under vacuum condition. The electrolyte used was 1 M lithium phosphorus hexafluoride (LiPF_6) in a mixture

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