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Synthesis of shape-controlled hollow silica nanostructures with a simple soft-templating method and their application as superhydrophobic antireflective coatings with ultralow refractive indices

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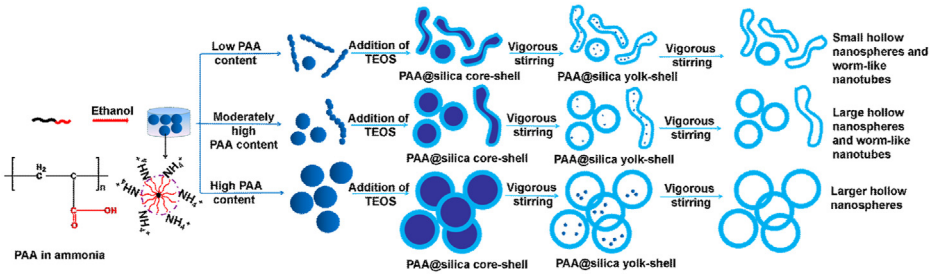
HIGHLIGHTS

- Shape-controlled hollow silica nanoparticles were synthesized by changing the contents of the template.
- This method can be scaled up for synthesis of other inorganic materials with hollow structures.
- A water contact angle as high as 153° was achieved on the coating after hydrophobic modification.
- The highest transmittance of a coated K9 glass was much higher than that of a blank K9 glass.
- The refractive indices of the coatings ranged from 1.10 to 1.12 after calcination at 300–450 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

A soft-templating method for synthesizing shape-controlled hollow silica nanoparticles (HSNs), including worm-like hollow silica nanotubes (HSNTs), hollow silica nanospheres (HSNSs) was developed by simply changing the contents of the template, Poly(acrylic acid) (PAA). The possible formation mechanism of HSNs was investigated. Multi-functional coatings were prepared using HSNs as follows: HSNs sols were dip-coated on K9 glass, followed by chemical vapor deposition with 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (POTS). Results showed that a water contact angle as high as 153° was achieved on the coating after hydrophobic modification. The refractive indices of corresponding films ranged from 1.10 to 1.12 after calcination at 300–450 °C. The highest transmittance of coated K9 glass was much higher than that of blank K9 glass. The multi-functional coatings have potential applications in opto- and microelectronic fields due to their high transmittance, ultralow refractive indices and superhydrophobicity.

1. Introduction

Synthesis of inorganic hollow materials with novel morphologies has attracted worldwide attention due to their potential

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applications *e.g.* white light emitting diode [1], controlled drug release [2], catalytic applications [3] and AR coatings [4]. Silica is well-known as one of the promising candidates owing to its chemical stability, high corrosion resistance, excellent mechanical and thermal properties *etc*. Many efforts have been devoted in the fabrication of hollow silica-based materials with varying sizes and shapes to satisfy the different requirements of the aforementioned applications [1–4]. Template and template-free methods are most commonly used for synthesizing hollow silica nanoparticles (HSNs). The template-free formation of HSNs is generally based on some novel mechanisms such as the nucleation and growth of pores [5]. The template method has been well known for its versatility in fabricating HSNs with narrow-size distribution and a wide range of well-defined shapes. The widely employed templates include emulsion droplets [3,6,7], inorganic nanoparticles [8,9], polymers [10],and micelles of surfactants [11,12]. This method mainly involved two steps: firstly, the silica shells are fabricated via the fast hydrolysis and condensation of the silica precursor, typically Tetraethoxysilicate (TEOS) under basic conditions [13,14], onto the core templates to form core-shell-like particles; Then the core templates are removed by high-temperature calcinations [8,15,16], washing or chemical etching with acid [9,17] to form HSNs.

Normally, the sizes of the obtained HSNs can be carefully controlled through precise manipulation of the template dimensions. However, the HSNs obtained by the template method were mostly spherical because it is difficult to obtain uniform nonspherical sacrificial templates. Moreover, available methods for the controlled synthesis of nonspherical mono-dispersing HSNs were complicated. Zhou et al. [2] used polymer nanorods as templates for the deposition of silica to fabricate hollow silica nanotubes (HSNTs). Dahlberg and Schwank [3] synthesized HSNTs containing Ni nanoparticles in a template nonionic surfactant water-in-oil microemulsion. It is highly demanded to develop facile methods to prepare HSNs with different shapes. Du [10] realized the morphologies changing from HSNTs, large hollow silica nanospheres (HSNSs) to small HSNSs using polystyrene-block-poly(vinylpyridine) block copolymer micelle templates by controlling the intermolecular interactions with the corona chains. Mandal and Kruk [11] reported a family of hollow organosilica nanospheres and nanotubes synthesized at appropriately low organosilica-precursor/block-copolymer-surfactant ratios. However, these multistep processes involving high-temperature calcination or chemical etching with environmentally hazardous solvents are expensive, time-consuming and raising environmental and energy concerns [10]. Thus, there is a big challenge to develop a simple, efficient and environmental friendly method for synthesis of shape-controlled HSNs.

In this article, the synthesis of shape-controlled nanosized hollow silica from HSNTs to HSNSs using PAA polymer micelles as templates was reported. The complicated template removal steps were eliminated. The effects of operation parameters on the microstructure were studied systematically. The possible mechanism of morphological change of HSNs was proposed. The potential applications of the prepared HSNs were investigated by fabricating thin films on K9 glass to study their hydrophobic and anti reflective (AR) properties.

2. Experimental

2.1. Materials

Tetraethoxysilicate (TEOS, 98 + %), ethanol (99.5%), and 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (POTS, 97%) were obtained from Alfa Aesar (U.S.A.). Poly(acrylic acid) (PAA, M.W. ~3000) was purchased from Aladdin Chemistry (China). Deionized water was used through all of the processes.

2.2. Synthesis of HSNs

HSNs were prepared by the modified Stöber method [18,19]. Though this method is well-known, few researchers have paid attention to the shape change of PAA aggregates in ethanol solution, which will be discussed in detail later. Typically, PAA (0.04 g, 0.08 g, 0.15 g) was dissolved in 7 mL ammonia hydroxide at an ambient temperature, mixed with 180 mL of ethanol in a 250 mL glass conical flask. 1 mL TEOS was injected within 5 h at a time interval of 1 h under vigorous magnetic stirring. Finally, the corresponding PAA concentration was 0.213 g/L, 0.426 g/L, 0.798 g/L. A 90 mL aliquot of a synthetic solution was collected when the reaction had proceeded for 15 h and 48 h, which were denoted as sol A and sol B, respectively.

2.3. Monitoring of the formation process of the HSNs with different reaction times

PAA aggregates (0.213 g/L, 0.798 g/L) without the addition of TEOS, and the intermediates of the HSNs were collected at different times (0 d, 10 d for PAA aggregates; 15 h, 48 h for HSNs) to study their formation process.

2.4. Film preparation

K9 substrates were cleaned by ultrasonication in deionized water and ethanol and wiped carefully before dip-coating. The cleaned substrates were dipped into the sols for 5 min, then withdrawal at a desired rate of 1000 mm/min. The obtained films were then calcined at 300–450 °C for 60 min to remove the residual PAA [4].

2.5. Hydrophobic modification of coatings

Hydrophobic modification of HSN coatings on K9 substrates was carried out by the chemical vapor deposition of POTS [20]. Typically, the K9 glasses with coatings were placed in a Teflon container, and sealed by stainless steel autoclave, at the bottom of which was dispersed a few droplets (10–20 μL) of POTS. There was no direct contact between the substrates and the POTS droplets. The autoclave was then put in an oven at 120 °C for 2 h to volatilize POTS to react with the hydroxyl groups on the coating surface. Finally, the autoclave was opened and placed in an oven at 150 °C for additional 1.5 h to remove unreacted POTS molecules on the coating.

2.6. Characterization

For transmission electron microscopy (TEM) observations, the samples were dropped on carbon-coated copper grids. After drying at 60 °C overnight, they were observed on a JEM-1200EX transmission electron microscope at an acceleration voltage of 120 kV. The surface morphologies of silica coatings were investigated using a Zeiss Supra55 field-emission scanning electron microscope (FESEM). The visible light transmittance spectra of the AR coatings were measured by an UV-vis-NIR (Mapada, UV-3100PC, transmittance error ≤0.2%, wavelength ≤0.1 nm). The values reported are averages of at least five measurements made on different areas of the sample. Atomic force microscopy (AFM) investigation (contact mode) of the films was performed using a SPA-300HV Scanning Probe Microscope under ambient conditions. AFM was operated in the tapping mode with an optical readout using Si Cantilevers. Water contact angles (WCAs) of surfaces were measured