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Self-assembly of silica nanoparticles into hollow spheres *via* a microwave-assisted aerosol process

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ABSTRACT

In this work, a simple and efficient strategy for fabrication of silica hollow spheres (SHSs) has been successfully introduced with a one-step microwave-assisted aerosol process using silica nanoparticles (SiO_2, 12–50 nm) and NH_4HCO_3 as precursor materials. This approach combines the merits of microwave radiation and the aerosol technique. And the formation of SHSs is ascribed to solvent evaporation and the as-generated gas from NH_4HCO_3 decomposition in the microwave reactor. The morphology of the SHSs can be easily tuned by varying the residence time, amount of NH_4HCO_3 and silica sources. The formation mechanism of SHSs was also investigated by structure analysis. In addition, the hollow spheres exhibited remarkable sustained release of potassium persulfate, by loading it into the porous structures. The results provide new sights into the fabrication of inorganic hollow spheres *via* a one-step process.

1. Introduction

Hollow spheres in the dimension of nanometer to micrometer are an appealing structure design due to their large specific surface areas, low density and high activity. Such unique structures have many promising applications including photocatalysis [1,2], photonic crystals [3], encapsulation [4,5], gene delivery [6], drug storage, delivery and sustained release [7–9], and etc. Procedures to prepare hollow spheres mainly involve hydrothermal method [10,11], interfacial synthesis [12] and aerosol spraying [2,4]. And the sacrificial template strategy is by far the most used in these procedures [13–18], in which the templates are coated with suitable precursors by surface precipitation or layer-by-layer self-assembly of polyelectrolyte or inorganic nanoparticles [19], following removal of the core by acid dissolution or high temperature calcination to generate the hollow interior. The approach is simple and feasible, and however, it is labor-intensive and time-consuming, requiring multiple steps to be done in a sequential manner.

An aerosol-based process is a simple and efficient approach for synthesis of spherical silica structures. The as-prepared silica particles present a well-defined spherical shape and highly ordered structures. This approach has been combined with solvent evaporation to create mesoporous or hollow materials. For example, Zheng et al. [5] have synthesized hollow silica microspheres encapsulated with Fe_3O_4 nanoparticles by a surfactant-aided aerosol process and subsequent treatment, using cetyltrimethyl ammonium bromide (CTAB) as structure-directing agent in the process. Jiang et al. [4] have prepared hollow mesoporous silica nanoparticles by evaporation-induced self-assembly (EISA) using CTAB as the mesoporous template and ammonium salt ($(NH_4)_2SO_4$) as templates for larger pores. Wu et al. [20] have reported solid or hollow mesospheres fabricated by aerosol-based self-assembly of nanoparticles and pointed out that the structure of the mesospheres can be controlled by the rate of solvent evaporation and the size of primary particles. Although silica hollow spheres (SHSs) can be obtained by the aerosol-based processes mentioned above, these procedures require high temperature heating or calcination, resulting in the increase of complexity and difficulty of the process. However, microwave heating is a unique intramolecular heating method and has been extensively used in many chemical syntheses for its high reaction efficiency, short processing time, low energy consumption and etc [21,22]. Therefore, we suggest that the efficiency of the aerosol-based process can be increased greatly by incorporating with microwave radiation.

Herein, we successfully present a method to fabricate SHSs *via* a one-step microwave-assisted aerosol process, based on silica sol and ammonium bicarbonate (NH_4HCO_3) as the starting materials. NH_4HCO_3 and H_2O (used as the solvent), with high dielectric constant, can efficiently absorb the energy of microwave radiation. Meanwhile, NH_4HCO_3 begins to decompose significantly at the

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temperature higher than 30 °C. Therefore, the self-assembly of silica primaries into hollow spheres can be dramatically improved by the as-decomposed gas. Furthermore, the effects of the residence time in the microwave reactor, amount of NH_4HCO_3, and silica sources on the morphology of the SHSs were explored in detail. Finally, potassium persulfate ($K_2S_2O_8$), a common initiator widely applied in solution polymerization, is used as a model substance to be encapsulated into the as-prepared hollow spheres, and the release process of the encapsulated sample was investigated.

2. Experimental

2.1. Materials

Silica sol LS50C40 (SiO_2, ~50 nm, 40 wt%) was purchased from Shangdong Peak-tech New Material Co., Ltd., China. Ludox® AS-30 (SiO_2, ~12 nm, 30 wt%) and Ludox® AS-40 (SiO_2, ~22 nm, 40 wt%) were purchased from Sigma–Aldrich. Anhydrous ethanol, potassium persulfate ($K_2S_2O_8$) and NH_4HCO_3 were obtained from Sinopharm Chemical Reagent Co., Ltd., China. All chemicals were used as supplied. Distilled water was used throughout the experiments.

2.2. Preparation of SHSs

The microwave-assisted aerosol process is depicted in Fig. 1. In a typical process, 2.2 g of silica sol LS50C40 and 1.0 g of NH_4HCO_3 were dissolved in 40.0 g of distilled water. Then, the mixture was sonicated for 10 min. The final concentration of SiO_2 in the precursor solution was 2.0 wt%. An aerosol was generated from the precursor solution using a TSI 9302A atomizer and 20 psi N_2 as the carrier gas. Next, the aerosol droplets were carried into a 2450 MHz microwave reactor with a power of 700 W and followed by passing through a heating zone maintained at 400 °C to remove any residual water from the surface of the samples. Finally, the particles were collected on a filter paper maintained at 80 °C to prevent recondensation of solvent vapor. The residence time in the microwave reactor and the heating zone were ~50 s and ~2 s, respectively. In order to investigate the influence of experimental conditions on the morphology of samples, experimental parameters, such as the residence time in the microwave reactor, amount of NH_4HCO_3 and silica sources, were adjusted. The SHSs obtained from Ludox® AS-30, AS-40, and silica sol LS50C40, were denoted as SHS-30, SHS-40, and SHS-50, respectively.

2.3. Encapsulation of potassium persulfate into SHSs

The encapsulation process was conducted according to the established procedure reported in the previous literature [4] with a slight modification. In details, 0.15 g of $K_2S_2O_8$ and 0.10 g of SHS-50 were added into 10 mL of anhydrous ethanol in a glass vial. The mixture was stirred at 600 rpm at room temperature for 1.5 h and kept at −18 °C overnight. After crystallization, white $K_2S_2O_8$ precipitate was observed on the glass wall and the surface of the particles. To make $K_2S_2O_8$ crystallize predominately inside the cavity of silica spheres, the mixture was stirred at 600 rpm for 15–20 min at room temperature to dissolve the precipitated crystals on glass beaker and particle surface before storage in −18 °C refrigerator. The process was repeated ~10 times. The final obtained samples were washed with anhydrous ethanol several times and dried at room temperature for 24 h before the analysis of sustained release.

2.4. Characterization

Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 microscope operating at an accelerating voltage of 200 kV. The as-synthesized particles were diluted with anhydrous ethanol and sonicated at room temperature for 5 min and then dried onto carbon-coated copper grids before examination. Scanning electron microscopy (SEM) measurements were carried out with a JEOL JSM-6360LA microscope. Optical microscopies were performed on a B204LED microscope purchased from Chongqing Optec Instrument Co., Ltd., China. X-ray diffraction (XRD) patterns were recorded on a D/MAX 2500PC diffractometer with Cu Kα radiation (λ = 1.541 Å). Nitrogen absorption-desorption isotherm measurements were conducted on a Micromeritics Tristar II 3020 pore size analyzer at 77 K under a continuous adsorption condition. Prior to the measurements, samples were degassed at 150 °C for 12 h. The analyses of Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) were used to determine the specific surface area, pore volume and pore size, respectively.

The sustained release of $K_2S_2O_8$ encapsulated inside the SHSs was characterized using a Mettler Toledo seveneasy S30 K conductivity meter. 0.01 g of the encapsulated sample was added to 20 mL of mixing solution consisting of deionized water (a resistance of 18.2 Ω cm^{-1}) and anhydrous ethanol with a volume ratio of 1:1. The conductivity of sample was automatically recorded by the conductivity meter once a second at 25 °C while stirring the mixture at 400 rpm. For control experiment, the release process of $K_2S_2O_8$ (0.01 g) was also conducted by the same procedure.

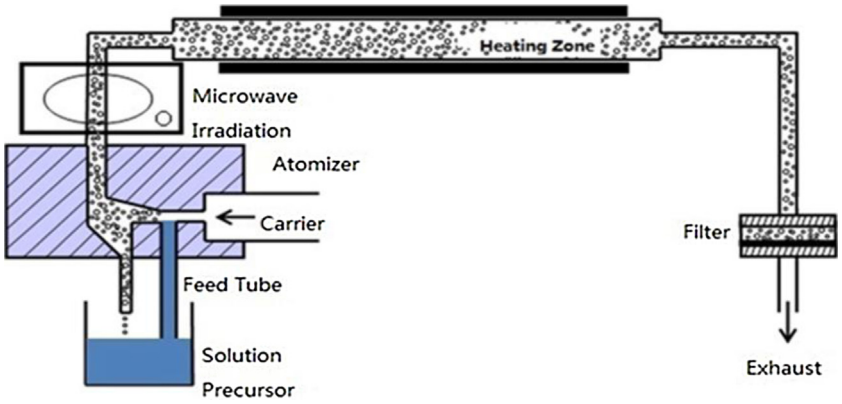

Fig. 1. Schematic of experimental setup of the microwave-assisted aerosol process.