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A new approach of fabricating monodisperse micrometer hollow zirconia spheres

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Abstract

The monodisperse micrometer hollow zirconia sphere was prepared in mixed solvents. It was fabricated by using the preformed poly(styrene-acrylic acid) (PSA) as template spheres which was mixed with zirconyl chloride octahydrate in ethanol solvent under steam treatment. The hollow zirconia spheres obtained by the calcination of PSA/ZrO_2 composite spheres had a narrow particle size distribution and commendable surface topography characterized by SEM. The calcined hollow zirconia spheres displayed monoclinic crystalline reflection peaks characterized by XRD. Besides, the micro-morphology, composition and molecular composition of sample were analyzed by FESEM, TG–DSC and FTIR, respectively.

Keywords: Monodisperse; Steam treatment; Zirconia; Calcining process

1. Introduction

Zirconia was an important material which had tolerance to high temperature, strong mechanical property and high refractive index. It was also well known for its practical applications in solid oxide fuel cells, high-performance ceramics, acid–base catalyst, strong anion exchange material for HPLC, and bioanalysis for amino acids, peptides and proteins [1–4]. However, it was difficult to obtain monodisperse micrometer hollow zirconia spheres because the zirconia would aggregate during preparation.

Recently, there had been intense interest in fabrication of zirconia spheres and hollow zirconia spheres in micrometer. Many chemical and physicochemical methods have been used to synthesize zirconium spheres, such as sol–gel process [5,6], spray pyrolysis technique [7,8], layer-by-layer self-assemble technique [9], and so on. However, these methods had a lot of disadvantages such as the formation of irregular coatings, aggregation of the coated particles, and low efficiency of controlling over the coating thickness. The main reason is that the hydrolysis rate of these zriconia precursors is too fast to allow the sequential nucleation and growth. Therefore, it was necessary to control the hydrolysis rate and the diffusion rate of zirconia precursors in the reaction system.

In this study, we proposed a new approach to fabricate hollow zirconia spheres based on templating method. In this procedure, the preformed monodisperse micrometer anionic poly(styrene-acrylic acid) (PSA) was used as template spheres, which could be simply synthesized in previous study. Then the zirconia precursor was catalyzed by the ammonia vapor generated from the water bath, and the forming zirconia nanoparticle was adsorbed on the PSA spheres by electrostatic attraction. Finally, the obtained monodisperse micrometer PSA/ZrO_2 composite sphere was calcined to generate hollow structure. As far as we know, this method was for the first time to fabricate hollow zirconia with regular spherical morphology and controllable diameter. In addition, this method could also be used widely for the preparation of other hollow inorganic spheres.

2. Experimental section

2.1. Materials

Styrene (St), polyvinylpyrrolidone (PVP), anhydrous ethanol, α-methylacrylic acid (AA), 2,2′-azobisisobutyronitrile (AIBN),

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zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) and aqueous ammonia solution (28 wt%) were all purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium Methyl Allyl Sulfonate (SMAS) was purchased from Zibo Wanduofu Chemical Reagent Co., Ltd and used as the cationic monomer. EGDMA was prepared in our laboratory and used as the crosslinking agent. It was stored at 4 °C before use. Deionized water was prepared in our laboratory and applied in all polymerization and treatment processes.

2.2. Preparation of anionic poly(styrene-acrylic acid) (PSA) spheres

St, PVP, AA, AIBN, EGDMA, anhydrous ethanol, and water were charged into a 250 mL three-neck round-bottomed flask which was equipped with a mechanical stirrer, a thermometer, a N_2 inlet, a Graham condenser, and a heating mantle. The reaction system was deoxygenated by bubbling nitrogen gas and then heated to 72 °C under stirred condition. After 5 h, SMAS was dispersed in anhydrous ethanol and then added into the reaction system. The reaction lasted for 6 h at 72 °C. The latex emulsion was separated centrifugally and washed twice with ethanol. The obtained white precipitate was air-dried to use as follows.

2.3. Preparation of hollow zirconia spheres

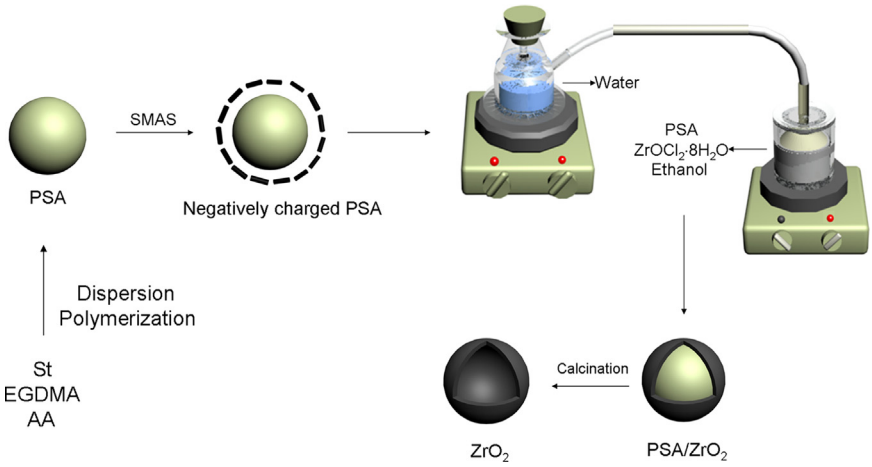
The fabrication of hollow zirconia spheres was shown in Scheme 1. The prepared PSA powder was redispersed into anhydrous ethanol under gentle stirring. In the subsequent coating process, $ZrOCl_2 \cdot 8H_2O$ was added to the PSA suspension for the sol–gel reaction. Under this condition, the ammonia (14%) was heated to 50 °C, and then ammonia vapor which was evaporated from the water bath reacted with $ZrOCl_2 \cdot 8H_2O$, continuously generating white precipitate to deposit on the prepared PSA spheres slowly. The mixture was stirred at ambient condition until the solvent was fully evaporated. The white precipitate obtained was washed three times with anhydrous ethanol and heated in a vacuum oven at 90 °C for 12 h. Finally, the powders were calcined in a muffle furnace to generate hollow structure.

2.4. Characterization

The morphology of the products was characterized by SEM (JSM-6380LV). Before the examination, the products were sputtered with gold. TGA–DSC was performed using a STA 449C Instruments. The composite spheres were heated from the ambient temperature to 800 °C at a rate of 5 °C/min under oxygen purge. The infrared spectra was recorded with FTIR (Nicolet IR100) in the range of 400–4000 cm^{-1}. The sample was prepared by the usual KBr pellet method. The purity and composition of the products were characterized by powder XRD with D8 Advance X-ray diffractometer (Cu *K*a, $\lambda = 0.02$ nm, (10)30 mA, 40 kV).

3. Results and discussion

In this study, we fabricated hollow zirconia spheres based on templating method. In the making process of hollow zirconia spheres, the preparation of monodisperse PSA template sphere was the key to the self-assembly of zirconia spheres with large domain size. Previously, we have developed a facile method to fabricate monodisperse micrometer PSA template spheres in dispersion polymerization. In this method, the diameter of PSA spheres was controlled by altering the initial water volume and the crosslinking agent ethylene glycol dimethacrylate (EGDMA) concentration. The PSA spheres had well-defined surface topography. In the current study, hollow zirconia spheres were fabricated with a complex approach which combined the dispersion polymerization with a sol–gel process (Scheme 1). In dispersion polymerization, the PSA spheres were fabricated by the method mentioned above. In sol–gel process, the negatively charged PSA colloids were obtained by depositing the functional groups in SMAS onto the PSA colloids. PSA/ZrO_2 core–shell spheres were obtained by the interaction between negatively charged polyelectrolyte chains and positively charged zirconia groups of $ZrOCl_2 \cdot 8H_2O$ under the ammonia catalysis. Finally,



Scheme 1. Diagram of the formation of hollow zirconia spheres.