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Original article

A facile one-step route to synthesize titania hollow microspheres with incontinuous multicavities

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ABSTRACT

The titania hollow microspheres with incontinuous multicavities were successfully fabricated *via* an oil/water (O/W) emulsion process accompanied by sol–gel reaction in the presence of polyvinylpyrrolidone (PVP). In the one-step route, the addition of PVP to the tetrabutyl titanate (TBT) 1-octanol solution as the oil phase of the O/W emulsion clearly expands the size of the cavities inside the microspheres. The *n*-propanol and atoleine alters the polarity of the oil phase to affect the interior structure significantly. The Span 80 is used as a stabilizer to preserve spherical shape. A preliminary mechanism based on phase-separation for the structural evolution of titania hollow microspheres with multicavities is suggested. Zirconia and alumina hollow microspheres with incontinuous multicavities can also be prepared by this one-step route successfully.

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1. Introduction

Hollow microspheres have attracted much attention because of their special characteristics, such as low density, low thermal conductivity, high specific surface and good flow ability [1]. So far, various porous microspheres with unique characteristics such as hollow spheres with a single cavity [2–4], hollow spheres with multiple shells [5,6], and hollow sphere with multicavities [7], have been fabricated by the templating method, emulsion processing, high temperature smelting, layer-by-layer self-assembly techniques, etc. Wherein, hollow spheres with multicavities as an important class of hollow sphere have gained growing attention for their potential applications such as delivery systems, adsorption and catalysis [8–10]. Although organic spheres with multicavities consisting of diverse polymers have been prepared [11–13], manipulation of inorganic spherical particles with multicavities is still a challenging task. So far, cage-like SiO_2 hollow spheres have been prepared by templating methods and template-free methods in emulsion route [14–16]. However, we notice that the preparation of metal oxide hollow spheres with multicativies including titania (TiO_2), zirconia (ZrO_2) and alumina (Al_2O_3) hollow spheres have rarely been mentioned in the literature. To the best of our knowledge, there is only one paper concerning the transition-metal oxide microspheres with multicavities, which were prepared by using template in aerosol-assisted self-assembly method [17]. However, the reported method to prepare transition-metal oxide microspheres with multicavities needs heat treatment to remove the latex template.

In the present work, we demonstrate a facile one-step synthesis of cage-like porous titania microspheres *via* oil/water (O/W) emulsion accompanied by a sol–gel reaction without any templates. The presence of polyvinylpyrrolidone (PVP) played an important role in forming porous structure of titania hollow microspheres with multicavities, while Span 80 had great effects on preserving spherical structure of both macrocavities and TiO_2 particles. Moreover, zirconia and alumina hollow spheres with multicavities were also fabricated *via* the same method mentioned. It is anticipated that the method presented in this work will offer an approach to fabricate metal oxides hollow spheres with multicavities, including their composites.

2. Experimental

2.1. Materials

1-Octanol, ethyl acetoacetate (EAA, AR), zirconium propoxide (70 wt.% of popanol solution) and aluminum tri-*sec*-butoxide (97%) were purchased from Aladdin Reagent Co., Ltd. Other chemicals, *i.e.*, tetrabutyl titanate (TBT, AR), Span 80 (CP), sodium dodecyl sulfate (SDS, CP), alkylphenol ethoxylates (OP-10, CP) and polyvinylpyrrolidone (PVP, K30, CP) were purchased from Sinopharm Chemical Reagent Co. Ltd. All the chemicals were used as received.

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2.2. Synthesis

The detailed preparation of the gel microspheres was as follows. First, an external water phase was prepared by adding 4.0 g of SDS and 8.0 g of OP-10 in 300 g of deionized water under strong stirring at 1000 rpm. Second, 2.377 g of EAA and 6.217 g of TBT were added to 10.450 g of 1-octanol with constant stirring for 1 h to prepare the oil phase. Then, a certain amount (0.190, 0.571, 1.142 and 1.903 g) of PVP and 0.571 g of Span 80 were added to the oil phase under stirring for 1 h as an additive. Third, the mentioned oil phase was added to the external water phase once under strong stirring at 1000 rpm. After stirring for 24 h, the samples were collected by centrifuge and dried at 40 °C for 24 h.

The fabrication of zirconia and alumina microspheres followed the same process, except with zirconium propoxide and aluminum tri-*sec*-butoxide as the precursors, respectively.

2.3. Characterization

The microstructures including average cavity sizes and size distributions of the TiO_2 microspheres were performed using scanning electronic microscope (SEM, FEI Siron). Thermal analysis for the TiO_2 gel microspheres was carried out using a DTA analyzer (German Netzsch Co. STA449C) from room temperature to 700 °C in air at a heating rate of 10 °C/min.

3. Results and discussion

It was found that the initial oil phase was a yellow transparent solution. When the oil phase was mixed with water phase and broken into small droplets by high-speed shearing, water molecules around the oil droplets diffused through oil–water interface and reacted with TBT to initiate the sol–gel process. The sol–gel transition of oil droplets, which built the solid spheres, is caused by two kinds of reaction, *i.e.*, hydrolysis and polycondensation [18]. The effects of PVP will be discussed and a preliminary mechanism will be suggested accordingly.

Fig. 1 shows the SEM images of TiO_2 microspheres fabricated with different amounts of PVP. Spherical structures are obtained for all five particles, and the surfaces of the microspheres fabricated with different amounts of PVP are generally smooth. However, different interior structures are observed for the five samples. The microspheres fabricated without PVP are solid as shown in Fig. 1b, while the addition of PVP led to cage-like porous structures as shown in Fig. 1b, d, f, i, k. The average cavity diameters calculated from the SEM images are ~500 nm, ~750 nm, ~1.2 μm, and ~1.3 μm, respectively. In addition, the microspheres obtained with 1.903 g of PVP show generally broken structures, which can be attributed to the fragility caused by the decrease in wall thickness of cavities. As shown in Fig. 2, the cavity size distributions also become wider with the increase of PVP content generally.

To clarify the role of PVP in fabricating the cage-like porous structure, DTA measurements were performed for the TiO_2 microspheres (Fig. 3a) and the supernatant phases obtained by centrifuge (Fig. 3b), respectively. For the supernatant phase, two exothermic peaks at around 430 and 500 °C are observed, which are attributed to the decomposition of PVP. For the TiO_2 microspheres, only an exothermic peak at 270 °C is observed for all five samples, which can be associated with the decomposition of butoxy and residual 1-octanol [19]. As shown by the DTA measurement, PVP is preferentially distributed into the water phase, rather than the titania oligomers rich phase. It indicates that the interaction between polymerizing titania oligomers and PVP is less attractive, although the reported literature mentioned that there is a strong interaction between PVP and Ti atom [20,21]. The

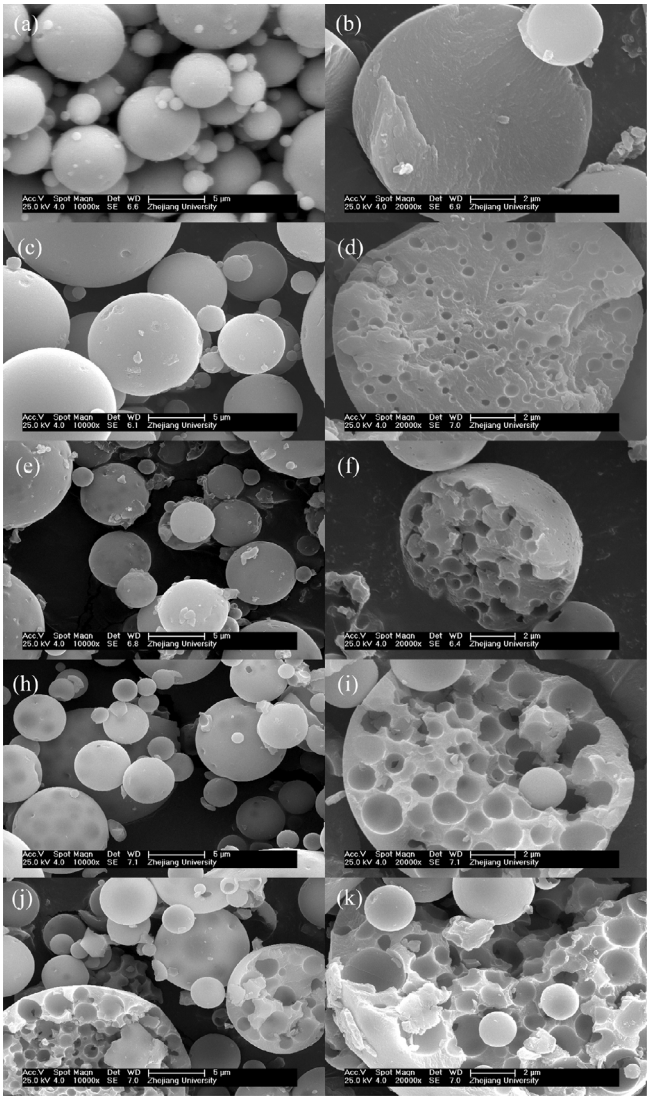

Fig. 1. SEM images of the titania microsphere synthesized with 0 (a and b), 0.190 (c and d), 0.571 (e and f), 1.142 (h and i), and 1.903 g (j and k) PVP.

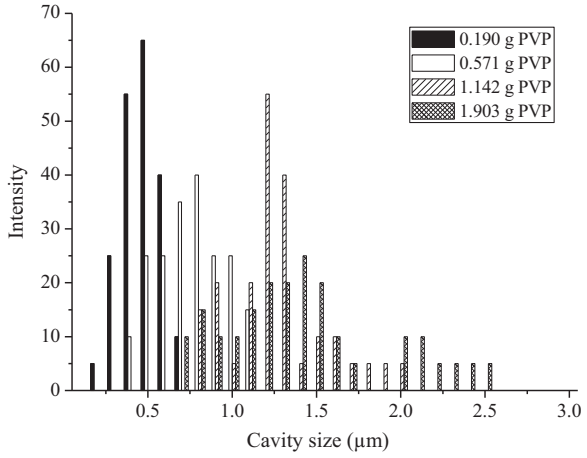

Fig. 2. Cavity size distribution of the microspheres fabricated with different PVP contents.

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