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Short communication

Porous Al_2O_3 microspheres prepared by a novel ice-templated spray drying technique

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Abstract

A novel ice-templated spray drying technique was developed for producing uniform Al_2O_3 microspheres with controlled pore structures. Surface morphologies of microspheres demonstrated a higher sphericity degree with the increase of solid loading from 1 to 10 vol%. The pore structure of microspheres transformed from randomly distributed pores to aligned macropores, when the spray-height more than doubled using 10 vol% solid loading suspension. The thickness of the aligned pore structure was also influenced by the liquid nitrogen volume in the apparatus.

Keywords: A. Suspensions; D. Al_2O_3; Microspheres; Pore structure

1. Introduction

Porous microparticles play a pivotal role in numerous fields of electronics [1], pharmaceuticals [2], and bioengineering [3], due to their special features of low density and high surface area. Some physical properties of porous microspheres are essential for the potential applications in drug delivery, such as pore shape, pore size, particle size, and morphology of the particle [4]. Microspheres loaded with cells have been proved to be easily implanted at the target site and aligned pore structures may have the potential to direct stem cell differentiation or cell growth as 3D scaffolds [5].

Various technologies have been designed universally to produce porous microparticles with required properties and structures, including spray freezing [2], electro-spraying [6], ultrasonic spray pyrolysis [7] and spray-drying [8]. Among those methods, the spray-drying technique has a wide application in the food industry and the pharmaceutical and biochemical industry, because it is simple and suitable to produce spherical powders [9]. Spray freeze drying (SFD) has attracted much interest for the fabrication of porous microparticles, owing to these characteristics as follows: (1) Microparticles with controlled size and a high sphericity degree can be easily prepared by the spraying procedure [10]. (2) Pore structures can be obtained through the removal of the solvent in the frozen microspheres. However, this technique normally produces microparticles with random pore structures and irregular surface morphology [2,11]. Spray freezing into liquid nitrogen (SFL) has been applied to fabricate nanostructured microparticles, while the droplets froze directly in the liquid nitrogen rather than the cold vapor in the SFD technique [12]. The complex freeze-photocuring-casting (FPC) has been recently proposed to generate large Al_2O_3 microspheres (diameter > 50–$70\ \mu m$) with ordered pore network, but small microspheres were obtained at the same time and showed cellular or random pore structures [13].

Aligned pore structures in porous ceramics have been obtained from the removal of directional ice crystals which grows in a controlled directional temperature gradient, by the ice-templating method [14,15].Therefore, in order to produce microspheres with aligned pore structures in a controlled manner, a novel method which combines spray drying with ice-template is proposed to produce aligned pore structures in microspheres in this research. The present approach for fabricating porous Al_2O_3 microspheres is similar to the SFD technique, however, there is a notable difference: the present work provided a sufficient temperature gradient for the droplets during the freezing process, whereas SFD only provided a cold

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vapor environment. Here, this new method was termed as the ice-templated spray drying (ITSD). The objectives of this study were to investigate the influences of the spray height, solid loading and temperature gradient on the morphology and pore structure of the microsphere obtained by the ITSD method, using Al_2O_3 as the model material system.

2. Experimental procedure

Alumina suspensions were prepared by the addition of deionized water, 1 wt% binder (PVA, Kuraray Co. Ltd. Japan), dispersant (ammonium polyacrylate, HydroDisper A160), as well as α-Al_2O_3 powders with an average particle size of 300 nm (Yixin ceramic material Co. Ltd., PR China). Suspensions with three kinds of solid loadings of 1 vol %, 5 vol% and 10 vol% were prepared and followed by ball milling for 24 h. The schematic set-up of the ice-templated spray drying technique is shown in the Fig. 1. The suspension was sprayed directly into the cryogenic steel vessel through a circular nozzle of ∅ 300 μm at a flow rate of 12 ml/min by a pipeline pumping system. Two types of the distance between the tip of nozzle and the surface of liquid nitrogen were altered elaborately as 260 mm (H_1) and 570 mm (H_2). Meanwhile, the liquid nitrogen volume in the vessel was adjusted using $V_1=1120$ ml and $V_2=1792$ ml. The temperature distributions over the vertical height of the spray freezing zone were measured by a digital thermometer with a T-type thermocouple (HE801, HUATO, China) according to different volumes of liquid nitrogen, as shown in Fig. 1B. Inside the vessel containing the liquid nitrogen, i.e. H of 0–100 mm, the temperatures at the same height above the liquid nitrogen surface became lower for larger volume of V_2, as shown in the inset of Fig. 1B. Subsequently, the ice in the Al_2O_3 microspheres was removed in a freeze-drier device (FD-1A-50, Beijing Boyikang Medical Equipment Co., PR China) at −60 °C. The dried Al_2O_3 microspheres were heated at 600 °C for 2 h, and sintered at 1550 °C for 2 h.

The rheological properties of the suspensions was tested by a rheometer (AR2000,TA Instruments, USA) at 20 °C. In addition, the morphology and particle size distribution of microspheres were observed using a scanning electron microscope (SEM, Nova NanoSEM230, USA) and a laser diffraction scattering particle sizer (Malvern Mastersizer, China), respectively. The pore size distribution in microspheres was measured by the mercury intrusion porosimetry (AutoPore IV 9500, Micromeritics, USA).

3. Results and discussions

Fig. 2 shows the relationship between the viscosity of Al_2O_3 suspensions and the shear rate, with solid loadings increasing from 1 to 10 vol%. 1 vol% and 5 vol% suspensions were the Newtonian fluids, remaining the same values of 0.7 mPa s and 0.4 mPa s in the shear rate range of 10–500 s^{-1} respectively.

Fig. 3 shows the micrographs of Al_2O_3 microspheres synthesized from the suspension with 10 vol% solid loading, using the liquid nitrogen volume of V_1 at different spray heights. The pore structure of Al_2O_3 microspheres transformed from a random distribution (Fig. 3A) into an aligned layer structure (Fig. 3C), with the spray height increasing from H_1 to H_2. The sintered microspheres maintained the pore structures with little distortion, as shown in Fig. 3B and D. Higher spray height provided more time for the droplets falling through the temperature gradient atmosphere, leading to more opportunities for the formation of aligned structure in the Al_2O_3 microspheres.

Fig. 4 shows the typical morphology and pore structure of dried porous Al_2O_3 microspheres fabricated using the liquid nitrogen volume of V_1 and V_2 at the spray height of H_2. Microspheres prepared at V_1 condition show an increase of the sphericity degree and alignment of pore structure with the increase of solid loadings, as shown in Fig. 4A, B and C. Microspheres produced from 1 vol% suspensions had no alignment, as shown in Fig. 4E. Microspheres produced from

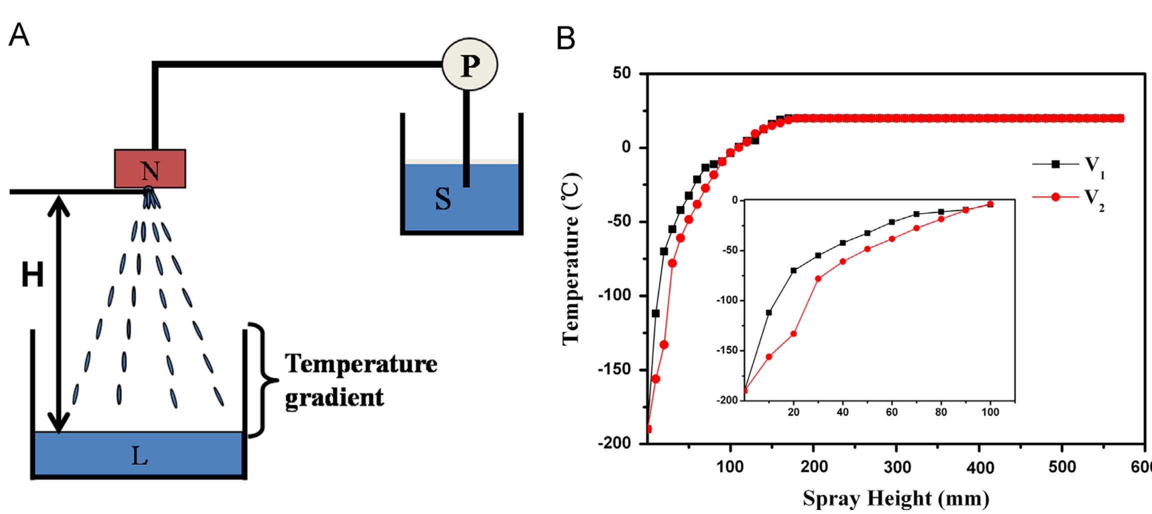

Fig. 1. (A) Schematic diagram of the spray freezing. Key: N: nozzle, S: slurry, P: pump, and L: liquid nitrogen. (B) The temperature distribution over the vertical height in the vessel containing V_1 and V_2 liquid nitrogen. The inset showed the temperature gradients in the region of 0–100 mm above the liquid nitrogen surface.

5 vol% and 10 vol% suspensions exhibited little difference in the sphericity, but obvious difference in the pore alignment, as shown in Fig. 4F and G. Higher viscosity of suspensions due to higher solid loadings resulted in a more spherical surface. Only a portion of Al_2O_3 microspheres (Fig. 4C) produced at V_1 condition showed aligned pore structures. In the contrast, all microspheres (Fig. 4D) produced at V_2 condition demonstrated aligned pore structures. As shown in Fig. 4 G and H, the aligned pore width was about 1 μm and the thickness of aligned pore structures increased from 1 to 2 μm, with the liquid nitrogen volume increasing from V_1 to V_2.

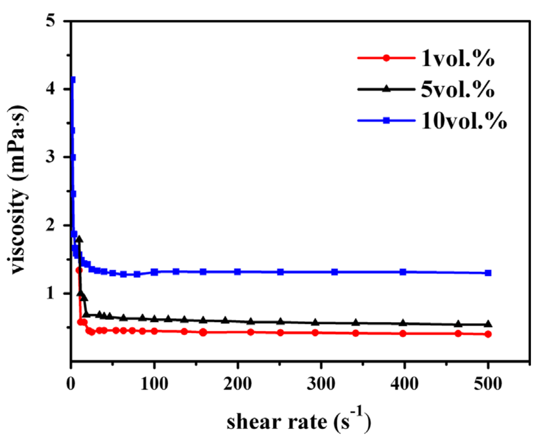

Fig. 2. Viscosity vs. solid loading of the Al_2O_3 suspensions.

Fig. 5 shows the pore size distribution and particle size distributions of microspheres produced using the liquid nitrogen volume of V_1, at the spray height of H_2. As shown in Fig. 5A, the average pore size in Al_2O_3 microspheres produced using 10 vol% suspension was about 1.8 μm, which was in good agreement with SEM micrographs in Fig. 3C and Fig. 4G. Porous Al_2O_3 microspheres prepared from the suspensions with 5 and 10 vol% solid loadings displayed a relatively narrower particle size distribution than that of the 1 vol% suspension, as shown in Fig. 5B. The average particle sizes of microspheres prepared by 5 and 10 vol% solutions were about 50 μm. The 1 vol% suspension can be used for fabricating microspheres with a bit smaller average particle size of about 40 μm. The suspensions with low viscosities were more likely to form small Al_2O_3 droplets during the spraying process, leading to a small particle size.

4. Conclusions

A novel ice-template spray drying technique was demonstrated to be feasible for producing porous Al_2O_3 microspheres with controlled pore structures and the average particle size of 40–50 μm. The sphericity degree increased

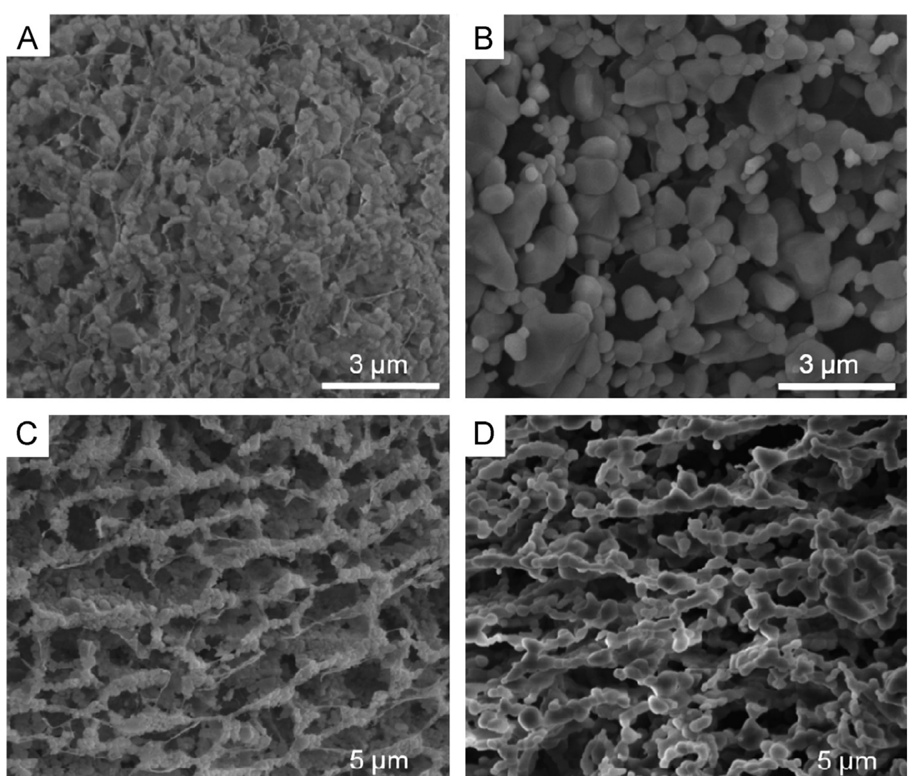

Fig. 3. SEM micrographs of freeze-dried Al_2O_3 microspheres produced at (A) H_1 spray height and (C) H_2 spray height; (B) and (D) were micrographs of sintered microspheres corresponding to (A) and (C), respectively.

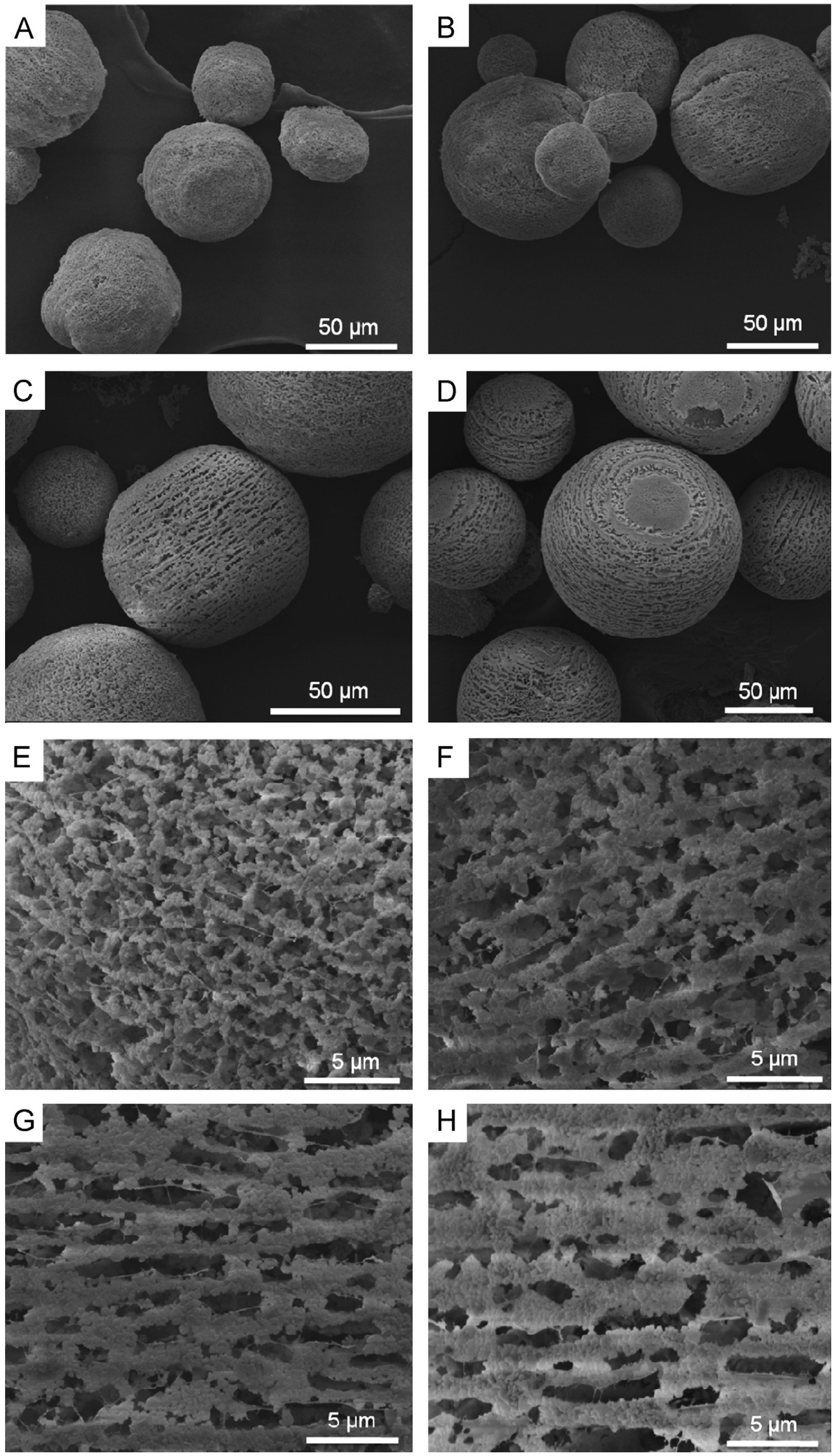

Fig. 4. SEM micrographs of dried porous Al_2O_3 microspheres prepared under different conditions. (A), (B) and (C) fabricated using the liquid nitrogen volume of V_1 and from the suspensions with different solid loadings of 1 vol%, 2 vol% and 10 vol%, respectively; (D) fabricated using the liquid nitrogen volume of V_2 and from 10 vol% solid loading; (E), (F),(G) and (H) are the surface morphologies of microspheres in (A), (B), (C) and (D) at higher magnification, respectively.

with the increase of solid loadings from 1 to 10 vol%. The pore structures transformed from randomly distributed pores to aligned macropores with an average pore width of 1 μm when the spray height increased from H_1 to H_2. The thickness of the aligned pores increased from 1 to 2 μm with the liquid nitrogen volume increasing from V_1 to V_2.

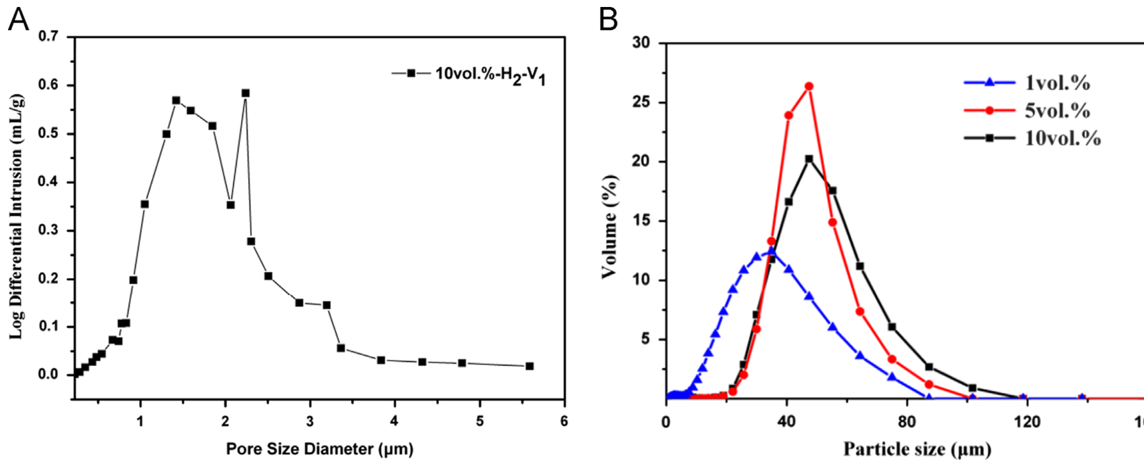

Fig. 5. (A) The pore size distribution for the porous microspheres and (B) particle size distribution of sintered porous Al_2O_3 microspheres.

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