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Synthesis and characterization of hollow glass–ceramics microspheres

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Abstract

Hollow glass–ceramics microspheres (HGCM), with the diameter from 10 μm to 60 μm and the shell thickness less than 2 μm, were successfully fabricated by a simple technique using polyacrylamide microspheres (PAM) as template. The corresponding HGCM were obtained by a thermal treatment of the core–shell microspheres, which were synthesized with organic template method. The size, morphology and phase composition of synthesized products were determined via XRD, SEM, TGA. The effects of the amount of glass powder, the Hydrophile–Lipophile Balance (HLB) value, the sintering temperature, and the ratios of pre-adsorbed water and the water in the slurry on the morphologies of HGCM have been investigated. The results showed that the agglomeration of HGCM can be reduced by adjusting the HLB value. In addition, the amount of solid beads decreases obviously by reducing ratios and adjusting the HLB value. As the sintering temperature increases, the surface of the HGCM becomes smooth and compact.
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1. Introduction

Hollow inorganic microspheres of micrometer to nanometer have been used in widespread areas such as catalysis, drug delivery, waste removal, artificial cells, and buoyancy materials [1–4], due to their promising applications and functions. Hollow glass microspheres (HGM) with low density and high mechanical strength [5,6] have been used to prepare light-weight, high strength buoyancy materials in the field of deep-sea exploration [7]. The mechanical behaviors of these composites are intrinsically determined by the properties of matrix material (e.g., chemical composition) and the unit cell structure (e.g., geometry of HGM and their distribution) [8]. To improve the mechanical properties of composites above, HGCM in the system $MgO–Al_2O_3–SiO_2$ was prepared to replace the hollow glass microspheres, due to the excellent mechanical properties of glass–ceramics of higher mechanical strength up to 450 MPa, a hardness up to 13 GPa, and Young's moduli up to 140 GPa [9].

Among known preparative methods, template method has more advantages in tailoring the hollow structure compared with conventional methods [10]. Through the method, the size and the shell structure of the HGCM can be controlled, via employing templates of different size and varying the concentration of inorganic oxide powder.

Herein, we first report the synthesis of HGCM with spherical morphology, diameter of ca. 10–60 μm and shell thickness less than ca. 2 μm through template method. In our experiments, PAM were used as template and glass–ceramics in the system $MgO–Al_2O_3–SiO_2$ was prepared as shell material.

2. Experimental

2.1. Synthesis of PAM

PAM were synthesized through inverse suspension polymerization [11]. In a typical synthesis procedure, an aqueous solution was prepared by dissolving 10 g acrylamide (AM), 0.09 g N,N′-methylene bisacrylamide, and 0.5 g ammonium-persulfate (APS) in 15 mL deionized water. The resulting solution was then transferred into a 250 mL three-necked round-bottomed flask containing 70 mL cyclohexane in the presence of 1.3 g sorbitan monooleate (Span-80) and stirred at 55 °C for 3.5 h. The products were filtrated, rinsed, and dried at 50 °C.

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Table 1
Composition of the base glass (wt%).

MgO	Al_2O_3	SiO_2	B_2O_3	ZrO_2	TiO_2	SeO_2
20	21	49	4	2	3	1

2.2. Synthesis of HGCM

In this synthesis, an aqueous solution was prepared in a beaker by dissolving appropriate amount of AM, N,N′-methylene bisacrylamide and ammonium citrate in 6 mL deionized water and the pH value of the solution above was adjusted to 10 using ammonia. Aqueous slurry was obtained by dispersing the glass powder in above solution with stirring at room temperature for 2 h. Powder mixtures (Table 1) were melted at 1600 °C for 2 h and treated by water quench process, followed by ball-milling for 72 h. The resulting product was the glass powder above. Then 0.4 mol/L APS solution was added with stirring for 30 min. The slurry above was dropped into the three-necked round-bottomed flask, in which 1.5 g PAM had been dispersed into 70 mL cyclohexane in the presence of appropriate amount of Span-80 and Tween-80 (polyoxyethylenesorbitan monooleate). Through varying the amount of Span-80 and Tween-80, the HLB value of surfactant can be controlled and calculated by the following equations:

$$\mathrm{HLB} = \frac{\sum m_i \mathrm{HLB}_i}{\sum m_i}$$

where m_i is the weight of surfactant and HLB_i is the corresponding HLB value. The solution was continuously stirring for 3 h at 55 °C. The products were filtrated, rinsed, and dried at room temperature. HGCM were obtained through a thermal treatment of the precursors by keeping the temperature at 600 °C for 1 h and at sintering temperature for 3 h with a heating rate of 2 °C min^{-1}, respectively. The synthesized HGCM were denoted as H − x, x being equal to 1, 2, 3, 4, 5 or 6 (see Table 2 for details).

2.3. Characterization

The morphologies of PAM and HGCM were observed with scanning electron microscopy (SEM, Model JSM-6700F, Japan). The phase composition and purity of HGCM was characterized by X-ray diffraction (XRD, Model D8 Advance, Bruker, Germany) using Cu Kα radiation. Thermogravimetric analysis (DTA-TG, ZRY-2P, Shanghai) was used to probe the thickness of HGCM.

3. Results and discussion

Core–shell microspheres were prepared via organic template method using PAM in Fig. 1a as template. As the polymerization continues, all monomers and cross-linkers are reacted and a cross-linked PAM network is formed on the interface with the glass powder tightly adhered to template. After thermal treatment, the HGCM were obtained with the sintering of the glass powder. The HLB value, the ratios of pre-adsorbed water and the water in the slurry, the sintering temperature, and the amount of glass powder will largely influence the morphologies of HGCM. The as-prepared HGCM are summarized in Table 2, in which the morphologies were also listed.

The morphologies of as-prepared products have been studied with SEM, as shown in Fig. 1b–f. Fig. 1b–d illustrates the influences of the HLB value on the morphologies. As the HLB value is reduced to 6, HGCM began to agglomerate. After thermal treatment, the hole on the products can be observed in Fig. 1b. It has been well-known that the HLB value at 6 was the range of forming W/O solution and the aqueous phase has the tendency of agglomeration in the organic phase. In Fig. 1c, intact HGCM with fine spherical morphology were obtained with the HLB value at 7.5 and the surface is not smooth. In addition, the amount of solid beads increases with HLB value up to 12.5 with seldom intact HGCM formed (Fig. 1d), which is the range of forming O/W solution. In this range, the aqueous slurry cannot be well dispersed in the organic phase and the glass powder has the tendency of aggregation to form solid beads. Thus, the HLB value at 7.5 is appropriate, at which the organic phase can wet the surface of glass powder and the glass powder is well dispersed, and the coating process is only depending on hydrophilicity of PAM.

In addition to HLB value, the influences of the pre-adsorbed water on the morphologies of HGCM were also investigated. The products were prepared by controlling the pre-water and water in the slurry at the ratios 7:2, 1:2 and 0:9 (see details in Table 2). The solid beads are formed at the ratios of 7:2 and 1:2 with 0.6 g glass powder. Further reducing the ratio to 0:9 led to

Table 2
Morphologies of as-prepared HGCM.

Sample code	Pre-water (g)	Water (g)	Glass powder (g)	HLB	Surface morphology
H-1	3	6	0.6	6	A, S
H-2	3	6	0.6	7.5	S
H-3	3	6	0.6	12.5	S
H-4	7	2	0.6	7.5	S
H-5	0	9	0.6	7.5	
H-6	3	6	0.3	7.5	

Pre-water: the amount of pre-adsorbed water in the PAM; water: the amount of water in the slurry; HLB: Hydrophile–Lipophile Balance; A: agglomeration; S: solid beads.

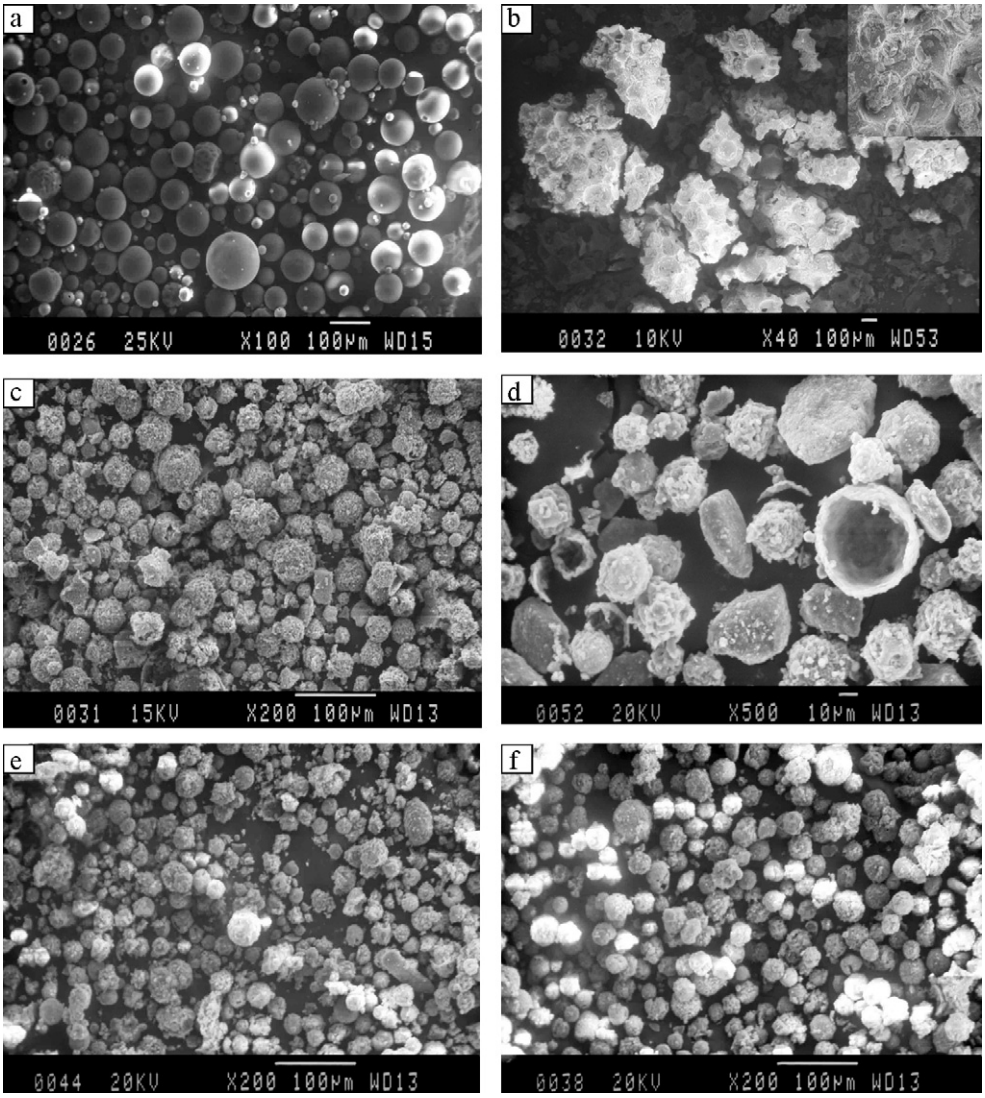

Fig. 1. SEM images of (a) PAM, (b) H-1, (c) H-2, (d) H-3, (e) H-4, and (f) H-5.

no solid beads formed (Fig. 1f). It has been known that PAM has the maximum water holding capacity, which determined the maximum amount of powder adsorbed and the thickness of shell. Thus, the amount of powder adsorbed in the slurry tends to increase with decreasing the pre-adsorbed water in the template, due to approaching the maximum water holding capacity. It can also be demonstrated in Fig. 3a. For this reason, the glass powder cannot be adsorbed on the template surface and has the tendency of aggregation (Fig. 1c and e). Meanwhile, the solid beads decreased obviously due to reducing the amount of glass powder to 0.3 g in Fig. 2a. In summary, the amount of maximum adsorbable powder can be controlled by the ratios and the maximum water holding capacity.

Fig. 2 shows the typical SEM images of as-prepared products. HGCM with spherical morphology and diameter ranging from ca. 10 μm to 60 μm, are prepared. Fig. 2b shows the crushed HGCM for further study on the surface morphology of HGCM. It shows that the microspheres were hollow-structured with shell thickness less than 2 μm. Increasing the sintering temperature led to smooth and compact surface (Fig. 2c and d).

Fig. 3a presents the thermogravimetric curves of PAM and HGCM. In order to probe the thickness of the shell and to remove the template inside, thermogravimetric analysis was performed. It shows that the amount of powder adsorbed in the slurry tends to increase with decreasing the pre-adsorbed water in the template. We can control the thickness of the shell by the amount of the glass powder and the ratios of pre-adsorbed water and the water in the slurry. Thermal decomposition of template within the core–shell microspheres starts at approximately 200 °C (Fig. 3). Compared to the thermogram of pure PAM, decomposition of template begins at slightly higher temperatures, which can be explained by the blocking effect of the glass coating. Decomposition of template is completed at approximately 580 °C. SEM images of HGCM revealed that the products are not destroyed by heating. Even with great shrinkage, HGCM remain intact and spherical morphology.

Fig. 3b shows the X-ray diffraction patterns of sample H-6 thermally treated at different temperature for 3 h. Fig. 3b, curve a, attributes to the sample crystallized at 905 °C, shows the main reflection at $2\theta = 26.4^\circ$, 20.4° and 49.8°, which might be

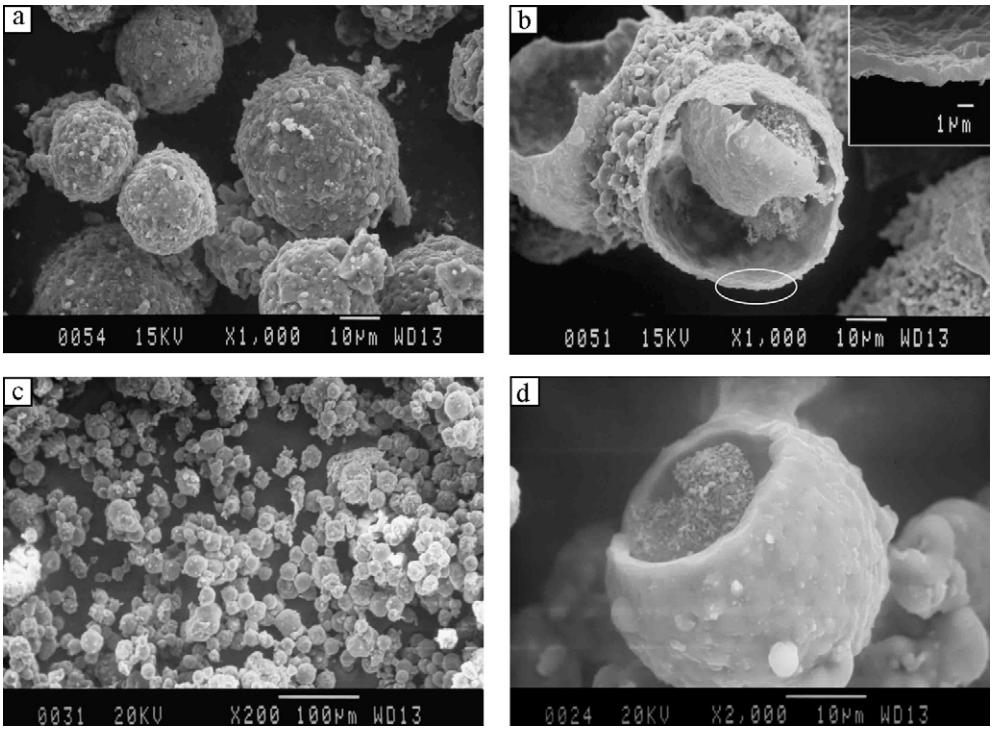

Fig. 2. SEM images of HGCM: (a and b) H-6 with sintering temperature of 905 °C for 3 h and (c and d) H-6 with sintering temperature of 950 °C for 3 h at different magnifications.

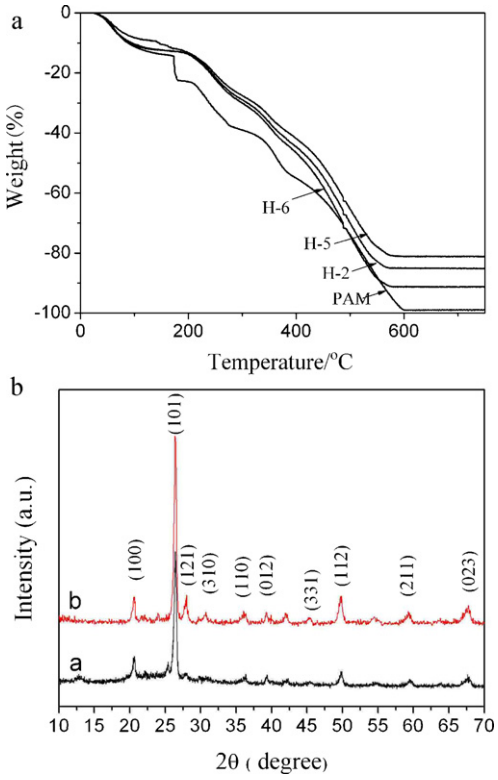

Fig. 3. (a) Thermogravimetric curves, (b) XRD patterns of H-6 with different sintering temperature for 3 h (a: 905 °C and b: 950 °C).

attributed to low-quartz (SiO_2, solid solution, JCPDS 65-0466). Additional reflections attributable to protoenstatite ($MgSiO_3$, JCPDS 11-0273) also occur at 28.1 and 30.7. A notable quantity of glass matrix is evident from the high background level and the low intensity of the reflections. Curve b, recorded from a sample crystallized at 950 °C, exhibits reflections at approximately the same 2θ positions; however, the lines are significantly sharper than those of curve a. It indicates that glass shell turned into low-quartz solid solution from amorphous phase.

4. Conclusions

In summary, intact hollow glass–ceramics microspheres with spherical morphology were successfully prepared using organic template method with PAM as template. The size, morphologies, and the shell thickness of HGCM can be controlled by the reaction conditions, that is, the template size, the ratios of pre-adsorbed water and the water in the slurry, the HLB value, the sintering temperature, and the amount of glass powder. The agglomeration can be reduced by adjusting the HLB value around 7.5. In addition, the amount of solid beads decreases obviously by decreasing the ratios above and adjusting the HLB value. Increasing the sintering temperature led to smooth and compact surface.

The hollow glass–ceramics microspheres produced by this process could be used to synthesize lightweight and high strength buoyancy materials in the field of deep-sea exploration. Meanwhile, hollow microspheres, made of different kinds of inorganic oxide powder, can also be synthesized through this method.

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