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Hydrophobic Properties of Calcium Carbonate Nanoparticles/ Chitosan Composite Membrane†

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Calcium carbonate nanoparticles/chitosan composite membranes were prepared *in situ* on chitosan films by gas diffusion method. Their morphology, structure and hydrophobic properties were characterized by XRD, FTIR and SEM. The results show that facts including temperature, the ratio of calcium to magnesium have important effect on the morphology of calcium carbonate, while the later will influence the hydrophobic properties of the composite films.

Key Words: Chitosan, Calcium carbonate, Hydrophobic properties.

INTRODUCTION

It is an important way to synthesize calcium carbonate and other organic-inorganic composite material with superior performance using biological macromolecules and double-hydrophilic block copolymers as templates[1]. Recently, biomimetic synthesis of calcium carbonate particles induced by chitosan membrane has been studied extensively, due to chitosan has exhibited many bioactivities, such as antitumor activity, antibacterial and antioxidant activity[2,3]. Meanwhile, artificial superhydrophobic surfaces have been widely employed in many fields, such as waterproof, antifouling, self-cleaning and fluid drag reduction, since the lotus effect was reported in 1970s[4]. In this paper, calcium carbonate nanoparticle/chitosan composite films were prepared by the method of gas diffusion. Influences of the morphologies of calcium carbonate on hydrophobic properties of the film were reported.

EXPERIMENTAL

For the preparation of chitosan film, the chitosan acetic acid solution was prepared by stirring at 40 ºC and standing off the bubble. This solution was then dropped on glass slides at room temperature and made it spread evenly. To obtain calcium carbonate/chitosan film, the solution with Ca^{2+}/Mg^{2+} molar ratio the 1:0, 1:1, 1:2, 1:4 and 1:8, respectively were dropped directly onto the chitosan film. The glass slides were put on the petri dish then put into a closed desiccator. The beakers containing 5 g of ammonium carbonate which was covered with wrap punched with three holes were put into the desiccator. White products were gradually generated on the chiosan film due to the diffusion of CO_2 vapour into the mixed solutions at different temperature for a given time. The samples were collected, washed with deionized water several times and dried in an oven.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of chitosan film prepared at 10 ºC. The diffraction peaks at 23.5º, 28.5º and 32.1º indicate that the chitosan film by casting method at natural condition performs excellent crystalline form.

The scanning electron microscopy (SEM) images of calcium carbonate synthesized using chitosan film as template at 10 ºC for 60 h are shown in Fig. 2. When the concentration of calcium ion was 0.05M (Fig. 2a), calcium carbonate shows the sphere shape accumulated by square-like crystals and its surface manifested ladder layer structure. While the concentration was increased to 0.5M, calcium carbonate was formed by sheet particles and irregular shape particles, accompanying with increased number of small free particles (Fig. 2b).

The effect of concentrations of Mg^{2+} on the morphologies of calcium carbonate on the chitosam films is demonstrated in Fig. 3. The morphology of calcium carbonate changes with increasing Ca^{2+}/Mg^{2+} molar ratio. When the molar ratio is 1:2

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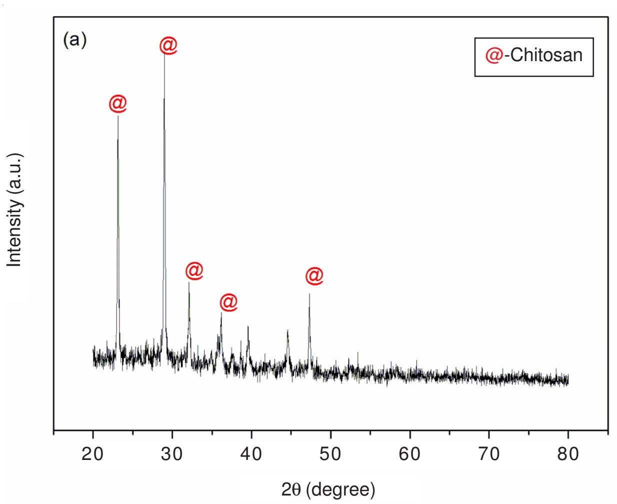

Fig. 1. XRD pattern of chitosan film prepare by casting method

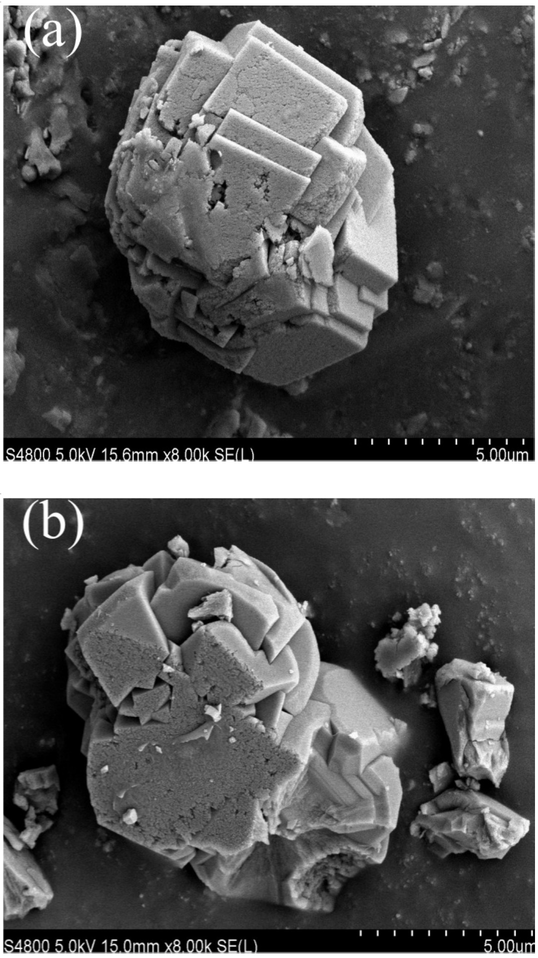

Fig. 2. SEM images of calcium carbonate used chitosan film as templates in absence of magnesium ion: (a) $[Ca^{2+}]$ = 0.05 M and (b) $[Ca^{2+}]$ = 0.5 M

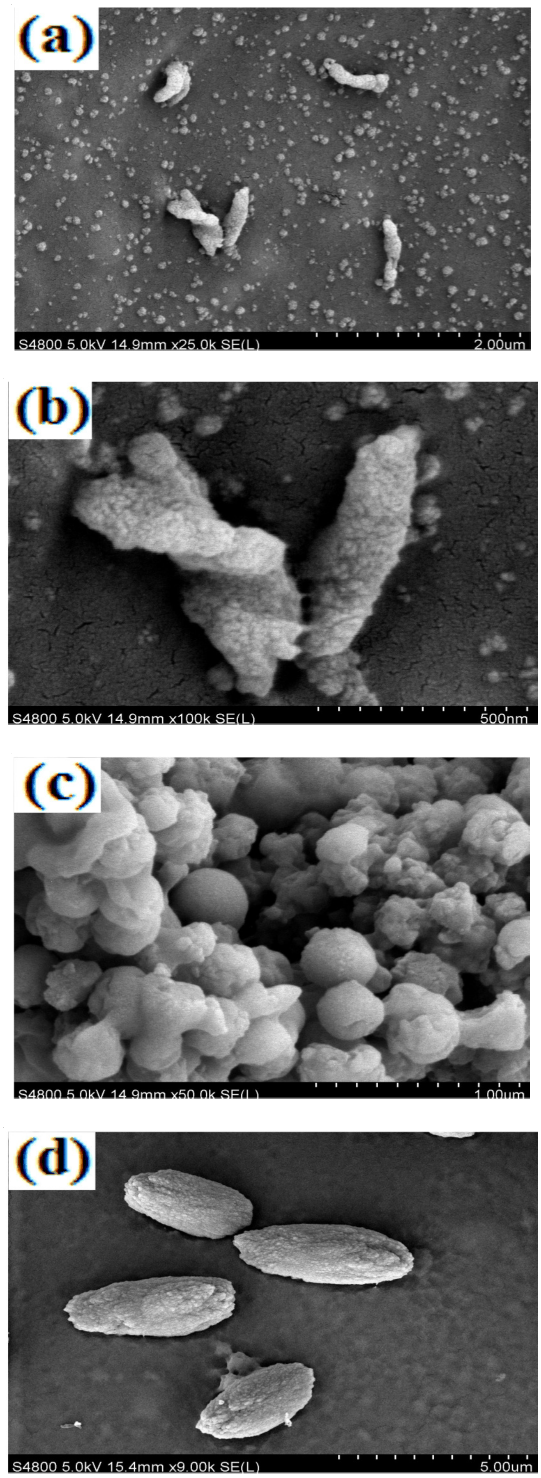

Fig. 3. SEM images of products on the chitosan film at 10 ºC and $[Ca^{2+}]$ = 0.05 M in presence of $[Ca^{2+}]/[Mg^{2+}]$ molar ratio: (a) 1:2; (b) enlarged image of (a); (c) 1:4 and (d) 1:8. The reaction time is 60 h

(Fig. 3a), calcium carbonate nanoparticles with size *ca.* 50 nm disperse well throughout the chitosan film, however, aggregates of calcium carbonate with strip structure were founded. As shown in Fig. 3b, the aggregates with the length of 1 µm show irregular and distorted shape. When the Ca^{2+}/Mg^{2+} molar ratio is 1:4 (Fig. 3c), the size of nanoparticles with sphere shape increases to 800 nm, which is due to the formation of $Mg(OH)_2$ acts as the nuclei for the growth of calcium carbonate. When the molar ratio is 1:8 (Fig. 3d), calcium carbonate shows the spindle-shaped structure with the size of 7 µm. This is due to that the high concentration of magnesium makes part of the Mg^{2+} adsorb on the surface of calcium carbonate crystals, which lead to the formation of calcium carbonate with the spindle-like structure.

The micromorphologies of calcium carbonate particles prepared at higher temperature, 25 ºC, on the composite film are demonstrated in Fig. 4. Compared to the low temperature, the morphologies of products obtained at 25 ºC have not changed significantly. However, with the increase of Ca^{2+}/Mg^{2+} molar ratio, the size of calcium carbonate increases from 300-600 nm. This is due to chitosan film partly dissolves at high temperature and leads to the film undergo changes from the original tie-like structure to a certain degree of chain structure and the chain structure on the surface of film can make the calcium carbonate particles reunite due to winding effects.

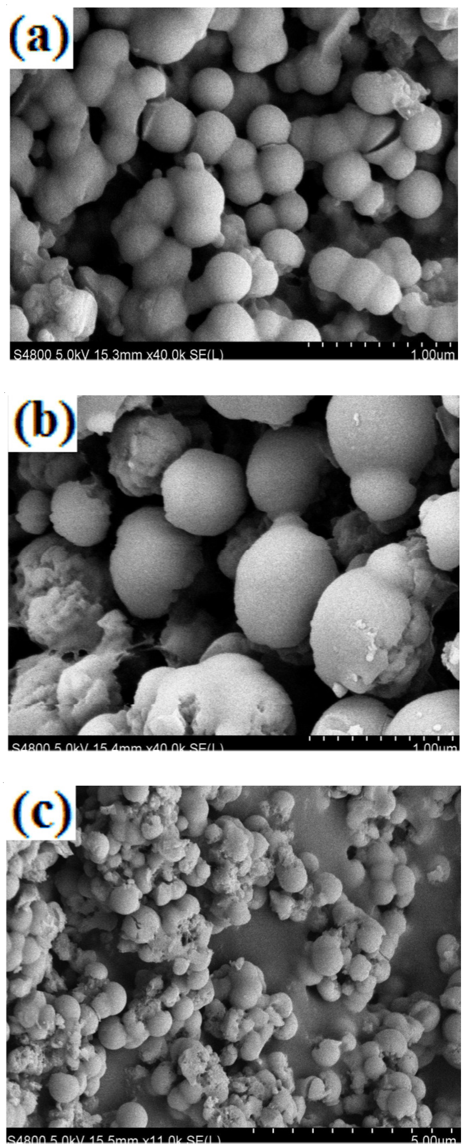

Fig. 4. SEM images of products on the chitosan film at 25 ºC and $[Ca^{2+}]$ = 0.05 M in presence of $[Ca^{2+}]/[Mg^{2+}]$ molar ratio: (a) 1:2; (b) 1:4; and (c) 1:8. The reaction time is 60 h

Fig. 5 shows the FT-IR spectra of calcium carbonate nanoparticles/chitosan composite membranes. The peaks located at 1421, 1082 and 876 cm^{-1} in Fig. 5a correspond to the antisymmetric stretching vibration, symmetric stretching vibration and out-of-plane blending modes of CO_3^{2-}, respectively, which can be assigned to the characteristic peak for calcite[5]. Fig. 5b shows the FT-IR spectra of the membrane with Ca^{2+}/Mg^{2+} molar ratio is 1:8. The peaks located at 1421 and 853 cm^{-1} can be assigned to the characteristic peak for aragonite[6].

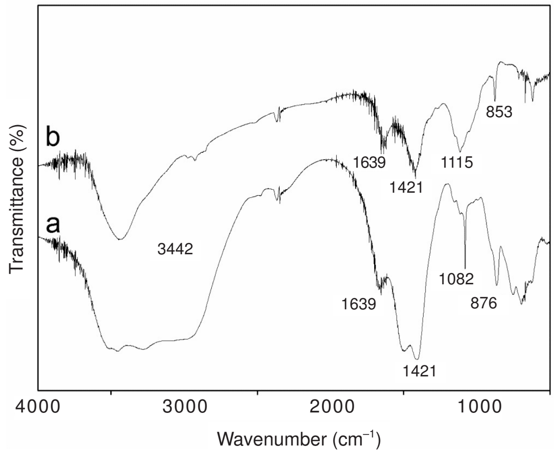

Fig. 5. FT-IR of calcium carbonate nanoparticles/chitosan composite membrane: (a) $[Ca^{2+}]$ = 0.05 M and (b) [Ca] = 0.05 M, $n[Ca^{2+}]/n[Mg^{2+}]$ = 1:8

The hydrophobic properties of the film are demonstrated in Fig. 6 and Table-1. The water contact angles of composite film decrease from 122.8º of sample No. 1 to 92.3º of sample No. 3, which is close to the level of super-hydrophobic. However, the average size of calcium carbonate on the composite films decreases from 7.0-0.8 µm then rises to 7.0 µm. Compared with sample No. 3, the film (No. 4) prepared at 25 ºC shows higher water contact angle, 115.2º; the average size of calcium carbonate on the composite film decreases to 0.6 µm. According to the results, it is postulated that the hydrophobic properties of this kind of composite film depend on the morphology and polymorph of calcium carbonate. For sample No. 1, micro-mastoid calcium carbonate particles accumulated by flake-like microcrystal appear on the composite film, which is similar to the structure of lotus leaf and results in the contact angle of composite film close to the level of superhydrophobic property[7]. But for sample Nos. 2 and 3, no micro/nano mastoid structure has been observed. When come to sample 4, high reaction temperature leads to nano-calcium carbonate agglomerate seriously caused by the twist of free chitosan chains. The surfaces of calcium carbonate therefore are full of pores, which is advantageous to improve the degree of roughness and enhance the hydrophobic property.

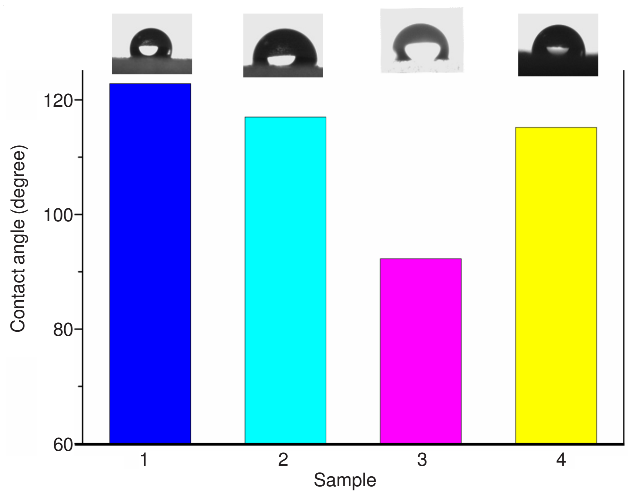

Fig. 6. Hydrophobic properties of the composite films

TABLE-1
CONTACT ANGLE OF THE FILMS

Sample number	Ca^{2+}/Mg^{2+} molar ratio	Temperature (ºC)	Contact angle (º)	Average size of calcium carbonate (µm)	Morphology and polymorph of calcium carbonate on the composite film
1	1:0	10	122.8	7.0	Sheet-like microcrystas;calcite
2	1:4	10	117.0	0.8	Sphere;aragonite
3	1:8	10	92.3	7.0	Spinde-like; aragonite
4	1:8	25	115.2	0.6	Agglomeration with full pores on the surface; aragonite

Conclusion

Calcium carbonate/chitosan composite films have been prepared by the method of gas diffusion. It was found that the addition of magnesium ion could influence the nucleation and growth of calcium carbonate crystals, while the high temperature promoted the formation of the pores on the surface of calcium carbonate. The films show good hydrophobic property; the morphology, polymorph and size of calcium carbonate on the composite film have key roles on the hydrophobic property of film.

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