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Formation of multi-layered chitosan honeycomb spheres via breath-figure-like approach in combination with co-precipitation processing

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ABSTRACT

Highly ordered, multi-layered, regular hexagonally patterned and size controlled honeycomb magnetic chitosan hydrogel beads were successfully fabricated by a facile method combining breath-figure templating and co-precipitation processing. The chitosan honeycomb beads were characterized and the unique structure formation mechanism was outlined. The diameter of pores in the hexagonally patterned structure was ~10 μm, and the saturation magnetization of the chitosan honeycomb containing Fe_3O_4 nanoparticles (*ca.* 5 ± 2 nm) was around 12 emu/g.

1. Introduction

Nowadays, functional porous beads have become an appealing topic due to their unique structure and functions such as greater pore accessibility, higher surface area, lower density, faster molecular diffusion-transfer and more controllable inner pore volume [1,2]. Porous materials based on natural biomasses have attracted great attention owing to their remarkable performance in various applications including filtration separation [3], adsorption [4], energy devices [5], catalysis [6] and chromatography [7], especially spherical hollow-shell spheres, which are frequently encountered in engineering industries [8].

Plenty of methods based on gas foaming [9], melt-molding and particle-leaching [10,11], air incorporation [12], freeze-drying [13], and emulsion templating [14] have been developed to fabricate highly porous materials [15], which always involved multi-step operation and used toxic emulgators and pore-formed template [16,17]. The Breath Figure (BF) methodology is particularly suitable for the preparation of honeycombed polymer films with ordered porous structure [18]. Most of known techniques are able to produce breath figure films formed on solid substrates in two dimension [20]. It is worth noting that only a few new findings have been reported in this area, limiting pursuits of novel 3D architectures [19].

Herein, we report a simple method for fabrication of honeycomb chitosan hydrogel beads by a method analogous to breath figure approach in combination with *in situ* co-precipitation and gel condensation process. Our findings provide a significant insight into the polymer gel condensation in liquids for Breath Figure templating applications.

2. Experimental

2.1. Materials

Chitosan (95% deacetylation), $FeCl_3{\cdot}6H_2O$, $FeCl_2{\cdot}4H_2O$, acetic acid, sodium hydroxide, and sodium citrate were obtained from Aladdin Reagent Factory (Shanghai, China). All compounds are commercially available chemicals and were used without further purification.

2.2. Preparation of stock solutions

The Fe^{2+}/Fe^{3+}mixture solution: The Fe^{2+}/Fe^{3+}mixture solution (molar ratio = 2) was prepared by dissolving 2.956 g of $FeCl_3{\cdot}6H_2O$

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and 1.087 g of $FeCl_2{\cdot}4H_2O$ in 12.5 mL ultra-pure water. *2.0 % acetic acid solution:* 2.0 % acetic acid solution was prepared by adding 2 mL acetic acid into 250 mL ultra-pure water. *Alkaline solution:* The alkaline soaking solution was prepared by dissolving 12.500 g of sodium hydroxide in 250 mL ultra-pure water.

2.3. Preparation of chitosan honeycombs

First, 0.8 g of chitosan was dissolved in 24 mL 2.0% acetic acid solution, and stirred for 30 min at 3000 r/min. Next, 2 mL of Fe^{3+}/Fe^{2+} mixture solution of molar ratio 2 was added to the chitosan solution and stirred for another 30 min, which resulted in a color change of solution from intensive yellow to dark red. Then, the resulted mixture was added dropwise slowly into alkaline solution by peristaltic pump and rested for 24 h. The formed beads were extensively washed with deionized water to remove the residual alkali and vacuum dried.

2.4. Measurements

For scanning electron microscope (SEM, Hitachi S-3000N, Japan) observations, the samples were coated with gold-palladium (80/20) film prior to scanning. The transmission electron microscopy (TEM, FEI Tecnai-G20, Japan) samples were prepared by placing a drop of alcohol suspensions of chitosan powder onto a 400 mesh, carbon-coated copper grid. The elemental analysis was performed (effective area *ca.* 80 mm^2, typical resolutions MnKa 125 eV) by EDS (Oxford X-Max, UK). The magnetic property was measured by vibrating sample magnetometer (VSM, MPMS SQUID, USA) at room temperature in the range of −7 T to 7 T.

3. Results and discussion

We employed chitosan and iron salts as the components for *in situ* co-precipitation reaction and facilitation of the breath figure formation to fabricate multi-layered chitosan honeycomb beads. As shown in Fig. 1, the honeycomb-like chitosan beads were fabricated on the basis of an effective and straightforward chelation of Fe^{2+}/Fe^{3+} with chitosan, generation of Fe_3O_4 by *in situ* co-precipitation, and formation of chitosan honeycomb beads accompanied by breath figure appearance.

SEM observations were conducted to study morphological features of the resulted beads (Fig. 2). As shown in Fig. 2A, the surface morphology of chitosan beads is distorted by severe wrinkles and cavities, which was caused by partial collapse of the highly porous network structure. The porous beads shrank distinctly after vacuum drying due to its high moisture content of 93%, which also reflected the highly porous inner structure. The multi-layered structure appeared clearly in the section view of the sphere (Fig. 2B). The hexagonally porous structure can be easily observed in Fig. 2C where multiple layers of hexagonal closely packed pores are obviously seen in a magnified image (Fig. 2D). This kind of ordered hexagonally-patterned chitosan honeycomb-like hydrogel beads have not been reported previously.

Formation of Fe_3O_4 nanoparticles in chitosan beads was confirmed by TEM. Fig. 3A shows well dispersed Fe_3O_4 nanoparticles of *ca.* 5 ± 2 nm in diameter. The hysteresis loop obtained from vibrating sample magnetometer (VSM) analysis showed the saturation magnetization of the honeycomb was 12 emu/g, which is consistent with the presence of Fe_3O_4 nanoparticles observed by TEM. EDS spectrum shown in Fig. 3B' contains the characteristic peaks of irons and oxygen. The presence of iron and the results of VSM are in a good agreement with the proposed co-precipitation mechanism. XRD method was employed to investigate the crystal structure of magnetic chitosan composite (see supporting information Fig. S2). The chitosan beads showed the same pattern as pure Fe_3O_4. According to the XRD analysis of pure Fe_3O_4 and magnetic chitosan beads, six diffraction peaks were observed at $2\theta = 29.6$, 34.9, 42.6, 53.2, 56.5 and 62.1, corresponding to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) crystal planes of face-centered cubic Fe_3O_4, respectively, which indicated that the crystal structure of Fe_3O_4 in magnetic chitosan composite was a cubic spinel structure.

Subsequently, in order to visualize the process of the layer-by-layer growth, one-drop of chitosan solution containing Fe^{2+}/Fe^{3+} was added to alkaline solution to monitor the bead formation

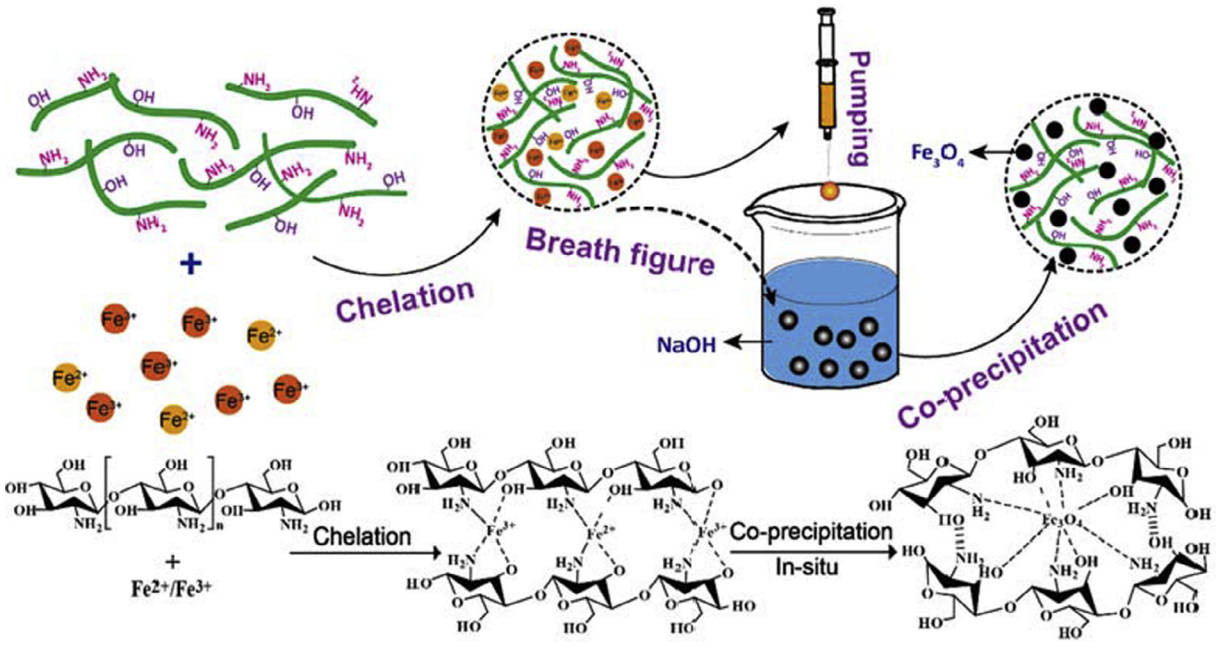

Fig. 1. Schematic illustration of preparation of chitosan honeycomb beads.