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Engineering colloids with narrow size distribution in a three dimensional ordered macroporous carbon microreactor

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ABSTRACT

A three dimensional ordered macroporous carbon (OMC) was confirmed a proper microreactor for engineering silica based colloids by synthesizing magnetic mesoporous bioactive glass microspheres, Fe_2O_3/SiO_2 hollow microspheres and SiO_2/Ag spherical crowns. The OMC was much more chemically inert and heat resistant than the ordered macroporous polymer (OMP), thus multistep synthesis processes were carried out inside the OMC to engineer the composition, shape and structure of the silica based colloids. This work suggested that the OMC had more advantages in synthesizing colloids than the OMP, and the mechanism of engineering colloidal structures based on material wetting to the OMP was extended to designing multistep chemical reactions, limiting reaction in a closed room and material wetting to the OMC.

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1. Introduction

Mesoporous and hollow colloids are typical colloids synthesized by template-assistant strategy and have attracted great attention due to their potential application in controlled drug delivery, coatings, catalysis, and diagnostics [1,2]. Non-spherical colloids could possess optical property or catalytic activity different from their spherical counterparts [3,4]. However, the methods for synthesizing non-spherical colloids are still limited in modulating the colloid synthesis chemistry, deforming spherical colloids or surface engineering non-spherical colloids.

Three-dimensional ordered macroporous polymers (OMP) were used as templates to synthesize colloids following a material wetting mechanism [5]. The colloids were hollow when the material was wetting to the OMP template, otherwise they were solid. These colloids could be separated to be monodispersed particles by grinding or ultrasonification due to their weak connection. Compared to the OMP template, the three-dimensional ordered macroporous carbon template (OMC) was much more chemically inert and heat resistant [6]. Complicated chemical reactions could be performed one by one to prepare colloids inside the macropores of the OMC even at elevated temperatures, and the structure of the colloids could be determined by three aspects: 1) the limited space could force various nanomaterials formed in different reaction steps to mix together and the colloidal structures could be engineered by designing the multistep chemical or physical reactions; 2) the macropores could affect the shape and size of the colloids by limiting the reaction in a closed room; 3) the wetting of macropore surface by reactants could determine the colloids to be solid or hollow. In this work, the aforementioned three typical colloids, magnetic mesoporous bioactive glass microspheres (MMBGMs), hollow sphere and spherical crown were synthesized in an OMC by a single or multistep synthesis process, as illustrated in Scheme 1. These examples suggested that the method of synthesizing colloids by replicating them from ordered macroporous templates was extended by using an OMC template.

2. Materials and methods

OMC templates prepared according to a report [8] were immersed into a saturated $Fe(NO_3)_3$ aqueous solution, dried at 90 °C, and then heated to 400 °C in nitrogen to decompose $Fe(NO_3)_3$. After repeating 1–3 times, the macropores of OMC templates were filled with a certain amount of Fe_2O_3/Fe_3O_4 mixture. These OMC templates were immersed into a sol-gel precursor solution containing tetraethyl orthosilicate (TEOS, 1.56 g; $Ca(NO_3)_2\cdot 4H_2O$, 0.47 g; Pluronic F127 (a nonionic surfactant composed of polyoxyethylene-polyoxypropylene copolymers), 1.8 g; HNO_3 (2 M), 0.04 g; ethanol, 4 g), and dried at room temperature.

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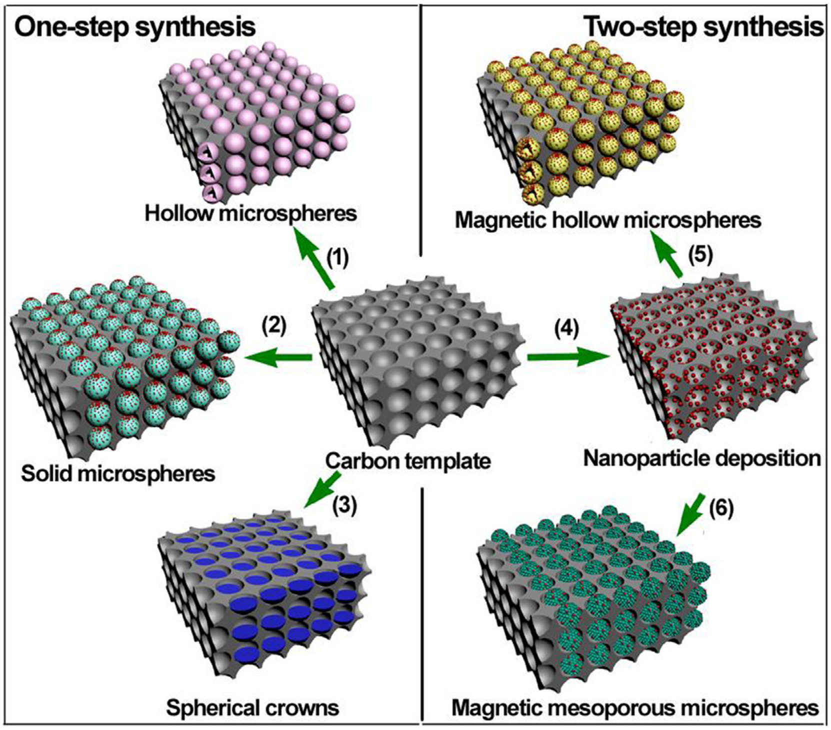

Scheme 1. Colloids of varied structures could be prepared by one- or multi-step synthesis process in an OMC. Hollow microspheres (1) or solid microspheres (2) were prepared depending on the material wetting to an OMC; spherical crowns were prepared when reactant in an OMC was pyrolyzed and released huge amount of gas (3); highly magnetic hollow and mesoporous microspheres were prepared by predepositing reactant and rationally designing the components of colloids ((4), (5) and (6)).

Monodispersed MMBGMs were obtained after calcinations at 600 °C in air and ultrasonification in water. Magnetic hollow $Fe_2O_3/Fe_3O_4/SiO_2$ microspheres were prepared by repeating the preparation process of MMBGMs without F127 and $Ca(NO_3)_2 \cdot 4H_2O$. SiO_2/Ag microspheres were prepared by immersing OMC templates into a silica sol-gel precursor containing $AgNO_3$ and calcination in air at 600 °C, when the content of $AgNO_3$ in the sol-gel precursor was low (i.e. TEOS, 1.6 g; $AgNO_3$, 0.1 g; H_2O, 0.6 g; ethanol, 6 g; HNO_3 (2 M), 0.08 g). SiO_2/Ag spherical crowns were obtained when the content of $AgNO_3$ was increased to 0.3 g in above recipe.

3. Results and discussion

The first example is the synthesis of MMBGMs with uniform shape and size. Doping CaO into silica network is a well known method to prepare bioactive glasses (BG) [7]. MMBGMs could be a potential drug carrier because BGs possess excellent biocompatibility, biodegradability, bone conduction and induction properties [8,9]. BG microspheres combined with magnetic particles are also highly desirable for biosensor, bioseparation, magnetic control and magnetic resonance imaging [10].

The reported methods for synthesizing magnetic mesoporous silica microspheres include solvothermal treating ferric precursor absorbed in the mesopores of silica microspheres [11], growing a mesoporous silica shell on magnetic cores [12], and mixing maghemite ferrofluid with silica sol in the aerosol-assisted method [13]. In order to prepare MMBGMs, ferric and calcium nitrates must be melted into a silica network. However, adding huge amount of nitrates into a silica sol-gel precursor makes it more difficult to form an ordered mesoporous structure because metal ions could damage the morphology of surfactant assemblies and nitrates could release a huge amount of gas during pyrolysis and damage the mesoporous structure and spherical shape. A multistep synthesis could be carried out in the ordered macropores of the OMC (Fig. 1a), avoiding interference of chemical reactions to each other in the formation process of different materials ((4), (5) and (6) in Scheme 1). All the MMBGMs showed spherical shapes and narrow size distribution replicating from the OMC, and their ordered mesoporous structure was perfect because the Fe_2O_3/Fe_3O_4 nanoparticles preformed in the first step did not interfere with the microphase-separation of F127 in the sol-gel process of the second step (Fig. 1b-f). These Fe_2O_3/Fe_3O_4 nanoparticles dispersed well in MMBGMs as pointed by the arrows (Fig. 1e), and the saturation magnetization could be controlled by the repeating number of the first step (Fig. 1g). MMBGMs dispersed in water were moved by a magnetic bar when their saturation magnetization was higher than 7.5 emu/g (Fig. 1h).

The second example showed that multistep chemical reactions in an OMC template could affect the structure of colloids. By repeating the deposition of $Fe(NO_3)_3$ for three times, the Fe_2O_3/Fe_3O_4 content in the $Fe_2O_3/Fe_3O_4/SiO_2$ microspheres increased and Fe_2O_3/Fe_3O_4 nanoparticles were adhered by silica. TEM confirmed the $Fe_2O_3/Fe_3O_4/SiO_2$ microspheres were hollow (Fig. 2a), and XRD confirmed both Fe_2O_3 and Fe_3O_4 formed (Fig. 1b). The reason that hollow microspheres formed in this example, but solid mesoporous microspheres were obtained in the first example could be that Fe_2O_3/Fe_3O_4 deposited on the macropore surface of the OMC template induced formation of silica gel on the macropore surface; however, in the case of MMBGMs, F127 could offer a cohesive force to resist the interaction between Fe_2O_3/Fe_3O_4 and the OMC template and force silica gel to aggregate. Solid BG microspheres were obtained without pre-depositing Fe_2O_3/Fe_3O_4 (not shown here), confirming that pre-synthesized Fe_2O_3/Fe_3O_4 on the macropore surface in the first step was a key for the formation of hollow structure.

The third example was the preparation of SiO_2/Ag spherical crowns. The macropores of an OMC were numerous microreactors.

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