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Feature Article

Solution-phase synthesis of inorganic hollow structures by templating strategies

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The solution-phase synthesis of hollow micro- and nanostructures by using suitable templates such as hard templates, soft templates and reactive templates has attracted considerable attention in recent years. This paper is focused on the template synthesis of inorganic hollow structures with tailored size, morphology, and architecture, with emphasis on the templating strategies recently developed in our lab for the facile solution-phase synthesis of novel inorganic hollow structures. The formation mechanisms of the hollow structures via different kinds of templates are discussed in depth to show the general concepts for the preparation processes. The properties and applications of hollow structures are briefly described, demonstrating the promising and broad application fields of hollow materials.

1. Introduction

The controlled synthesis of hollow micro-/nanostructures has received considerable attention in recent years because of their potential applications in controlled drug delivery, catalysis, sensors, lightweight fillers, low-dielectric-constant thin films, photonic crystals, confined-space chemical reactors, biomedical diagnosis and therapy, and so on [1–7]. Many methodologies have been developed for the synthesis of micro- and nanostructures with hollow interiors, which can basically be separated into two parts: the synthesis with and without templates. The synthesis of hollow structures without templates involve ultrasonication [8,9], spray drying or pyrolysis [10,11], laser pyrolysis [12], etc. These template-free methods are usually one-pot synthesis with simple processes. However, their disadvantages such as less control over the size and shape of hollow structures, less understood mechanisms and difficulty in developing general strategies for the synthesis largely limit their applications. In contrast, the synthesis of hollow structures with the assistance of templates shows its remarkable advantages such as the designed controls on the size, shape, and composition, clear mechanisms, and variability of templates. In general, the templates being used for the synthesis of hollow structures include hard templates, soft templates, and reactive templates. A variety of soft templates, such as liquid droplets, microemulsions, polymer complex aggregates, and gas bubbles, have been used in the synthesis of hollow micro- and nanostructures under mild conditions by solution-phase method. There have been several excellent reviews describing the recent progress in the synthesis and applications of hollow micro-/nanostructures [1–3,6,7,13]. In this feature articles, we will focus on the template synthesis of inorganic hollow structures with tailored size, morphology, and architecture, with emphasis on the templating strategies recently developed in our lab for the facile solution-phase synthesis of novel inorganic hollow structures. However, the synthesis of one-dimensional hollow structures or hollow tubes will not be covered in this article since such tubular structures have been introduced in many review articles [14–18].

This article is organized as follows. Firstly, three typical kinds of templates used for the fabrication of hollow structures, i.e., hard templates, soft templates such as emulsions and copolymer complex micelles, and reactive templates based on Kirkendall Effect, selective etching, and Ostwald ripening, are introduced in detail in this paper. Secondly, the special properties and applications of inorganic hollow structures reported in the recent years are briefly summarized. Finally, an outlook on the future development in this area is presented.

2. Template synthesis of hollow structures

2.1. Hard templates

Colloidal particles have been widely used as hard templates for the effective fabrication of hollow structures. In general, this approach involves the four major steps illustrated in Scheme 1 [1]: (1) preparation of hard templates; (2) functionalization/modification of template surface to achieve favorable surface properties; (3) coating the templates with designed materials or their precursors by various approaches, possibly with post-treatment to form compact shells; and (4) selective removal of the templates to

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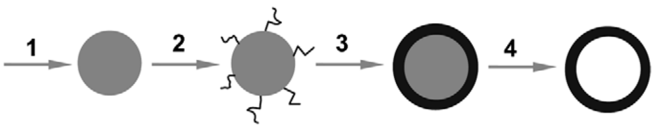

Scheme 1. Schematic illustration of a conventional hard templating process for hollow sphere synthesis. Reprinted from [1] with permission from Wiley InterScience.

obtain hollow structures. The synthesis based on hard templates is conceptually straightforward and is suitable for a broad range of materials. Considerable efforts have been focused on preparing uniform colloidal particles as desirable hard templates and developing flexible or versatile coating schemes for the accurate control over the composition, cavity size, and shell thickness of the hollow structures.

The colloidal particles that have been used as hard templates include mesoscale silica spheres, polystyrene (PS) beads and nanoparticles of various materials such as carbon, metals, and metal oxides. Uniform silica particles and PS beads are the most commonly employed hard templates with availability of a wide range of sizes from commercial sources. Colloidal polymer spheres have been used as sacrificial hard templates for the fabrication of hollow oxide spheres with controlled shell thickness and cavity size through sol–gel coating [19,20] and a wide range of hollow structures by the layer-by-layer (LbL) techniques [2,21,22]. The LbL assembly refers to sequential deposition of oppositely charged polymer species on substrates mediated by non-covalent interactions including electrostatic interactions, followed by removal of the decomposable colloidal core [23]. The LbL technology becomes very popular and fast growing in recent years because of the highly controlled engineered features of hollow capsules including size, shape, composition, thickness, permeability, and function [2]. Inorganic hollow capsules such as hollow spheres of silica [23], titania [24] were first prepared via alternating deposition of polymers and nanoparticles onto PS particles by LbL technique. Fig. 1 shows the transmission electron microscopy (TEM) images of the uncoated PS lattices and the hollow silica spheres with different shell thickness obtained by coating silica nanoparticles and poly(diallydimethylammonium chloride) (PDADMAC) via LbL technique, followed by calcination [25]. The hollow silica spheres retained the spherical shape of the original PS particle templates. The high uniformity of the capsule walls is evident. The LbL method was also used for the synthesis of hollow capsules of a range of other nanoparticle building blocks such as metals [26–28], oxides [29,30], semiconductors and composites [31,32]. Besides the above mentioned simple hollow capsules, more complicated capsules such as shell-in-shell microcapsules were also fabricated by LbL technique [33]. This technique involves the fabrication of spherical ball-in-ball particles consisting of two concentric calcium carbonate compartments that can be independently loaded with biopolymers [33]. Despite its versatility and the growing popularity, the LbL method suffers from three major drawbacks, i.e., complicated preparation processes, unavailability for preparing hollow nanospheres, and lacking mechanical toughness, which partially limit its applications.

Other than LbL technique, various methods such as direct chemical deposition, chemical adsorption [34–36], and nanocasting [37–40] have been widely used in the synthesis of hollow structures via hard templates. Yang et al. managed to synthesize titania-polymer capsules and hollow titania spheres with tunable cavity size and shell thickness using sulfonated-polystyrene core–shell gel particles as hard template through sol–gel process [20]. Hollow spheres of a variety of materials such as TiO_2 [41], SnO_2 [42], NiO [43,44], ZnS [45], carbon [46], and Au@Y2O3:Eu^{3+} [47] have been prepared by depositing shell materials or shell precursors on the surface of the hard templates, followed by a post-treatment to remove the templates. Moreover, hollow spheres of Pd [34], Ga_2O_3[36], TiO_2 [35], and Fe_3O_4 [35] were fabricated using hard templates via chemical adsorption–calcination method. Hollow spheres with mesoporous shells of different materials such as carbon [37,39] and silicon oxycarbide [38] have been prepared using spherical templates with solid core and mesoporous shell structure via nanocasting.

As a recent example, we recently synthesized hollow titania microparticles about 20–60 μm in size and hollow titania/carbon composite microparticles about 30–90 μm in size by employing Sephadex G-100 beads as the hard template as well as the carbon precursor via chemical deposition [48]. Calcination of the hollow titania/G-100 hybrid microparticles in air resulted in the formation of hollow titania microparticles. A typical scanning electron microscopy (SEM) image of dry Sephadex G-100 beads is displayed in Fig. 2a. Fig. 2b shows the titania/G-100 hybrids obtained after reaction for 8 h, which were was then calcined into hollow titania hollow spheres in air at 500 °C (Fig. 2c). Calcinations of the hollow titania/G-100 hybrid microparticles in flowing nitrogen led to the formation of hollow microparticles of titania/carbon composites (Fig. 2d). Compared with the hollow titania microparticles, the hollow titania/carbon composite microparticles exhibited remarkably enhanced photocatalytic activity on the photodegradation of Rhodamine B. It is noteworthy that commercial Sephadex G-100 beads were used both as the hard template and the carbon precursor for the synthesis of titania/carbon hollow microparticles in this work. This strategy may be extended to the synthesis of other inorganic/carbon composite hollow spheres.

2.2. Soft templates

The synthesis via hard templates has been regarded as a very effective and most common method for the synthesis of hollow

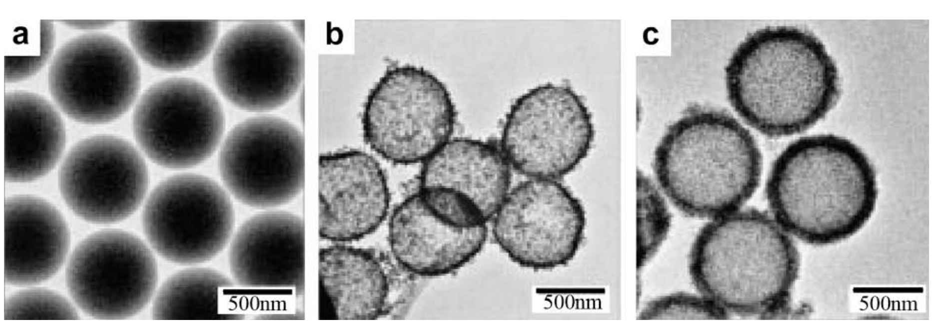

Fig. 1. TEM micrographs of (a) uncoated PS lattices and hollow silica spheres produced by calcining PS lattices coated with (b) a single SiO_2/PDADMAC layer pair, and (c) three SiO_2/PDADMAC layer pairs. Reprinted from [25] with permission from Wiley InterScience.