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Shape-controlled hollow silica nanoparticles synthesized by an inorganic particle template method

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ABSTRACT

Shape-controlled hollow silica nanoparticles have been successfully synthesized by an inorganic particle template method, which involves sol–gel silica coating over surfaces of the template and followed by acid-dissolution removal of the template. This work demonstrates shape control of the hollow particle using calcium carbonate as the template with a variety of shapes such as cubic, rough-surfaced spherical and rod-like particles. Inner size and shape of hollow silica nanoparticles synthesized were exactly reflected to outer size and shape of template used, and existence of micropores in the silica shell wall was verified by nitrogen gas adsorption analysis.

1. Introduction

Owing to hollow structure comprised of inner void surrounded by solid shell, hollow particles have superior properties as compared to dense ones, such as low bulk density, high specific surface area, low thermal conductivity, capsulation capacity and unique optical characteristic, and hence have been applied in many areas including drug delivery [1], bioencapsulation [2], medical diagnostics [3], catalysis [4], plasmonics [5], and composite electronic and structural materials [6]. Control of size and shape of the hollow particles has been becoming attractive technique for innovation of further functionalized materials [7].

A number of methods to fabricate hollow inorganic particles had been reported. Spray pyrolysis [8] and fluidized bed reactor [9] are simple technique to produce hollow particles without any templates, but difficult to control their size and shape. Layer-by-layer (LbL) adsorption [10] and sol–gel method with template [11] have been reported as useful techniques to synthesize hollow particles. Caruso et al. employed LbL method with polystyrene (PS) template [10]. Silica nanoparticles were adsorbed on the PS surface due to electrostatic attractive force to form core–shell particles. After repeat of the adsorption process for controlling the shell thickness, the PS template was removed by calcination. Such organic particle template method is effective to obtain hollow particle with a relative narrow size distribution, but the particle shape is usually limited to only sphere with size not less than hundred nanometers, except for specific cases: use of organic fiber core to prepare hollow silica fiber [12] or applying micelle template to form silica hollow spheres with a diameter of 30 nm [13]. Moreover, removal process of the organic template such as calcination or dissolution with organic solvents is not environmentally-friendly.

We have developed an inorganic particle template method, in which cubic-shaped calcium carbonate ($CaCO_3$) is employed as a template to synthesize hollow silica particles [14]. An overview of the method is shown in Fig. 1. Surfaces of the $CaCO_3$ core are coated by silica, which is synthesized by hydrolysis of TEOS and following condensation and polymerization under a basic condition with addition of ammonium aqueous solution. The formed core–shell particles are subjected to acid treatment to remove the $CaCO_3$ core, and eventually silica shell walls remain keeping the hollow structure. This method has some advantages: one is actually low environmental burden for the core removal as the $CaCO_3$ is easily dissolved by week acid without calcination process which is necessary for the organic particle template method; the other is shape control of the hollow particles as $CaCO_3$ is one of inorganic crystals with crystalline anisotropy, of which crystal growth is controllable by chemical conditions in nanoscale such as cubic calcite, rod-like aragonite and so on [15]. In this study, we have expanded the proposed technique to obtain shape-controlled hollow silica structure in nanoscale using three kinds of $CaCO_3$ as templates such as cubic, spherical with rough surface or rod-like ones.

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