

Controlled synthesis of mesoporous $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell microspheres with tunable chamber structures *via* a self-template method†

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Mesoporous $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell microspheres with tunable chamber structures have been synthesized by the reaction between $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ and SiO_2 microspheres *via* a simple self-template approach.

Nanostructured inorganic materials with hierarchical morphologies have attracted considerable attention in the field of catalysis, separation technology, microelectronic devices, and biomaterials engineering.^{1–9} In particular, the fabrication design of spherical materials with hollow interiors has been intensively pursued due to their specific structures, interesting properties that differ from their solid counterparts,^{10–16} and their potential uses as low-density capsules for controlled release of drugs, dyes and inks, development of artificial cells, protection of proteins, enzymes and DNA, catalysis, biotechnology, and materials science.^{17–25} Various methods have been developed for preparing hollow structures. For example, $\text{SiO}_2/\gamma\text{-Fe}_2\text{O}_3$ core-shell structures and $\gamma\text{-Fe}_2\text{O}_3$ hollow spherical nanoparticles are obtained by spray drying techniques, which use a nozzle system to disperse individual liquid droplets of uniform size.²⁶ The template synthesis is another simple and common method for obtaining core-shell structures and hollow spheres. The templates used mainly include polystyrene latex spheres,^{15,27} liquid crystal,²⁸ surfactants,²⁹ microemulsion droplets,³⁰ and some inorganic nanoparticles.³¹ Recently, Tsunoda and co-workers reported biomimetic synthesis of lysozyme-silica hybrid hollow particles using sonochemical treatment.³² Wang and Caruso reported the preparation of hollow LiNbO_3 spheres using polyelectrolyte-coated colloid spheres as templates in *in situ* sol-gel reactions.³³ Also, recent progress has shown that many hollow nanostructures can be readily synthesized by using the nanoscale Kirkendall effect.^{34–42} In a nanoparticle system, the Kirkendall effect refers to preferred outward elemental diffusion leading to a net material flux across the spherical interface and the consequent formation of a single void at the center.^{43,44}

Porous solid materials are important in many areas of modern science and technology, including ion exchange, molecular separation, catalysis, chromatography, microelectronics and energy storage.^{45–47} More importantly, the ability to

manipulate the structure and morphology of porous solids on a nanometer scale would enable greater control of the local chemical environment.^{48–50} For example, nano- to microscale porous silicon is used as a cell interface for bone-tissue engineering.⁵¹ Mesoporous crystalline $\beta\text{-MnO}_2$ is used as a reversible positive electrode for rechargeable lithium batteries⁵² and ultrasound-triggered smart drug release from a poly(dimethylsiloxane)-mesoporous silica composite.⁵³ Also, 3D mesoporous silica foam can enhance the aldol reaction using an aldolase I antibody.⁵⁴

Herein, we report a novel, self-template approach to fabricating mesoporous $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell microspheres and $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow microspheres. In comparison with the traditional synthesis of hollow microspheres, this one-step self-template route can avoid subsequent complicated procedures for the removal of templates.

To demonstrate the procedure used to synthesize $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell microspheres and $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow microspheres, controlled experiments dependant on the molar ratios of Si and Ni were carried out. The morphologies and structures of the resulting products were characterized by SEM and TEM. Fig. 1 presents SEM and TEM images of the resulting products synthesized with different molar ratios of Si and Ni. As the molar ratio of Si and Ni decreases from 4 : 3 to 1 : 2, SEM images (Fig. 1(a), (c), (e) and (g)) reveal that the products are composed of a large amount of microspheres with diameters of about 350 nm. Interestingly, many intersected two-dimensional nanosheets with thickness of 10 nm exist on the surfaces of the microspheres to form mesoporous structures. In some broken microspheres in Fig. 1(a), (c) and (e), one can see clearly that there is a separate SiO_2 core in a hollow microsphere. The typical core-shell structures of $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ microspheres are further confirmed by TEM images (Fig. 2(b), (d) and (f)). As the molar ratio of Si and Ni decreases from 4 : 3 to 1 : 2, $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ microspheres, $\text{SiO}_2/\text{voids}/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell structures, and $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow microspheres are formed, respectively. When the molar ratios of Si and Ni are 4 : 3, 1 : 1 and 2 : 3, the diameters of SiO_2 core are about 300, 200 and 50 nm, and the shell thickness are about 40, 60 and 80 nm, respectively. $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow microspheres with shell thickness of 100 nm can be obtained with the molar ratio of Si and Ni increased to 1 : 2.

To further study the formation process of $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell microspheres and $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow microspheres, time-dependent experiments were performed using a molar ratio of Si and Ni of 1 : 2. Representative

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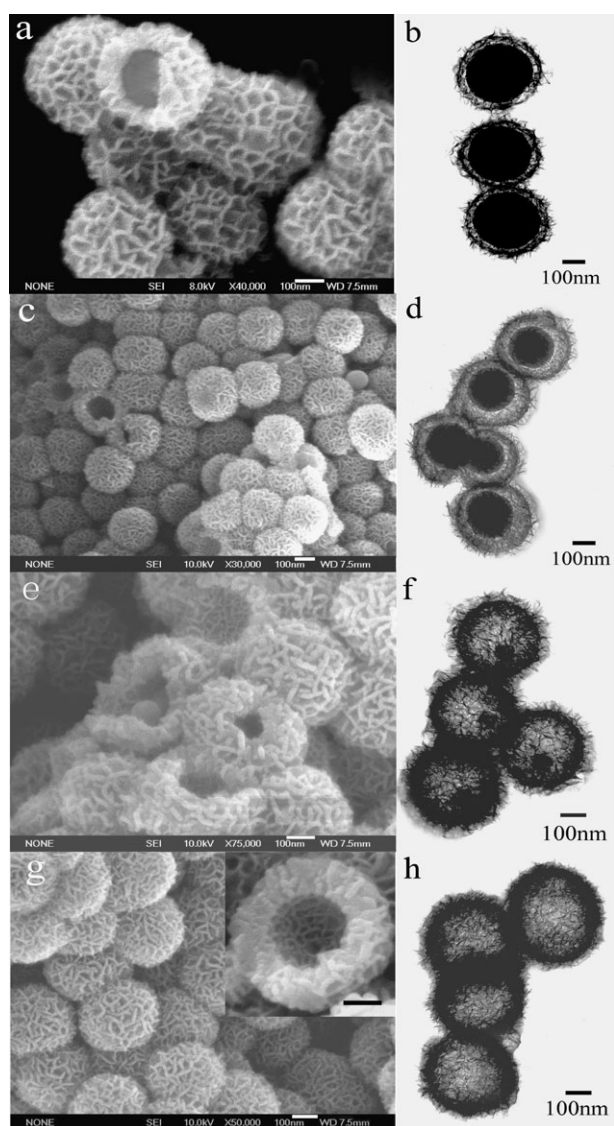


Fig. 1 SEM and TEM images of as-synthesized products: (a), (c), (e) and (g) show the SEM images of the as-synthesized products corresponding to molar ratios of Si and Ni of 4 : 3, 1 : 1, 2 : 3 and 1 : 2, respectively. (b), (d), (f) and (h) are the TEM images of the as-synthesized products corresponding to molar ratios of Si and Ni of 4 : 3, 1 : 1, 2 : 3 and 1 : 2, respectively.

TEM images of the products at different reaction times are presented in Fig. 2. As shown in Fig. 2(a), at the early stage of the reaction (3 h), the main products consist of core-shell microspheres, and the outer shell contacts with the silica core closely. With the reaction proceeding (6 h), the shells began to separate from the cores with increasing thickness of the shells. The TEM image reveals that the sheetlike phase did not contact with the silica core closely as shown in Fig. 2(b), forming a unique sphere-in-sphere structure, which might cause this separation. Interestingly, as the reaction time is extended to 12 h, the inner-sphere size reduces continuously with increasing thickness of the shells as shown in Fig. 2(c). On further extension to 24 h, the inner spheres disappear, and the $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow sphere structures are obtained as shown in Fig. 2(d). Accompanying this interesting structural

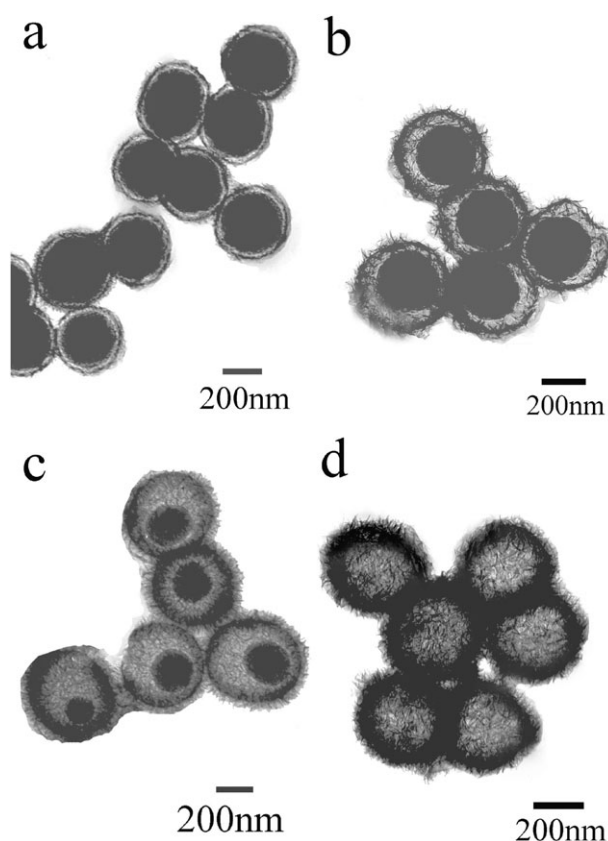


Fig. 2 TEM images of as-synthesized products: experiments were performed for a molar ratio of Si and Ni of 1 : 2. (a), (b), (c) and (d) correspond to reaction times of 3, 6, 12 and 24 h, respectively.

evolution is the observation of the inner spheres reducing continuously in size with increasing thickness of the shells. The chamber structures between the core and shell of the mesoporous $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell microspheres can also be tuned by controlling the reaction time.

The shape of the N_2 adsorption/desorption isotherm and pore diameter distribution (Fig. S2) (see ESI†) of $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell microspheres and $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow microspheres further reveals the characteristics of their porosity. The BET surface area of $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell microspheres and $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow microspheres are about 121 and 190 $\text{m}^2 \text{g}^{-1}$, respectively, which is larger than that of Raney Ni (95 $\text{m}^2 \text{g}^{-1}$).⁵⁸ The pore volume of $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell microspheres and $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow microspheres are 0.310 and 0.336 $\text{cm}^3 \text{g}^{-1}$, respectively. The mean pore diameters are 9.00 nm and 6.93 nm, respectively. A majority of the pores for $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell microspheres and $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow microspheres have diameters around 3.5 and 4.0 nm, respectively. As a result, with the decreasing of the molar ratio of Si to Ni, the pore size, and surface area of as-synthesized products increased. Apparently, such a mesoporous structure provides efficient transport pathways to their interior voids, which is critical for catalysis, delivery, and other applications. More importantly, the unique sphere-in-sphere structure allows multireflections of electromagnetic waves, such as

ultraviolet and visible light, within their interior cavities, endowing these spheres with greatly enhanced properties.

In summary, we have demonstrated a practical route to the facile synthesis of mesoporous $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell spheres with tunable chamber structure and mesoporous $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow spheres. This procedure should be extendable to many other systems that involve the use of different combinations of materials for the core and the shell. The mesoporous structured $\text{SiO}_2/\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ core-shell microspheres and $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$ hollow microspheres would open up the possibility of finding new applications or improving existing performance. To this purpose, we are currently investigating the structure of these hollow shells in more detail, as well as the incorporation of functional additives into the shells.

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