

## New synthetic route for preparing rattle-type silica particles with metal cores

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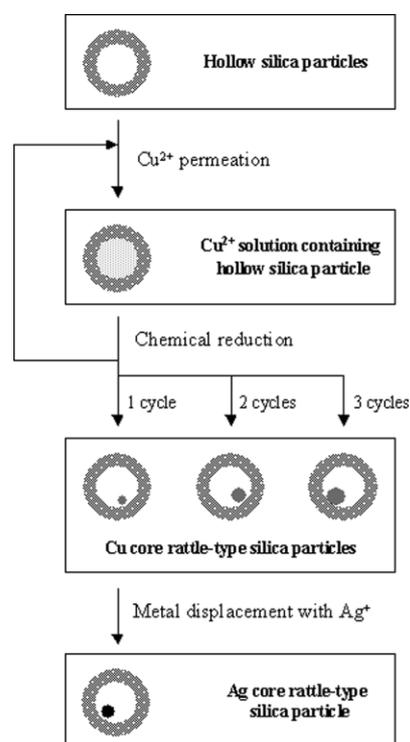
Rattle-type silica particles with metal cores, applicable to catalysts and metal/inorganic composite coating materials, were prepared by the pre-shell/post-core method that can control the size of metal cores inside silica capsules and exchange from metal cores into different ones with a metal displacement reaction.

Core-shell composite materials and micro- or nanosized capsules have received considerable attention for their technological importance in many fields.<sup>1–3</sup> An important extension of core-shell particles is the subsequent removal of the core by either thermal decomposition or chemical dissolution,<sup>4–7</sup> forming hollow spheres. Applications of such particles are as capsule agents for drug delivery, catalysis, and protecting sensitive agents such as proteins and enzymes. A variety of procedures currently used to fabricate a wide range of stable hollow spheres of various compositions have been reported.<sup>4,8–12</sup> Notably, rattle-type spheres with metal cores have been studied with tailored properties in recent years. The spheres have mostly been synthesized by templating strategies that are composed of the formation of outer shell on metal-silica core-shell particles and the subsequent removal of silica templates. The earlier literature reported on the rattle-type spheres with metal cores, including Au@polymer,<sup>13,14</sup> Au@silica,<sup>13,15</sup> and Au@carbon.<sup>13–15</sup> In this communication, we describe the preparation of Cu core rattle-type silica particles by pre-shell/post-core method, a new synthetic route, that involves the formation of metal cores within preformed shells. The Cu cores can be increased by performing the experimental procedure repeatedly. Moreover, the Cu cores inside silica shells can be exchanged for Ag cores by a metal displacement reaction.

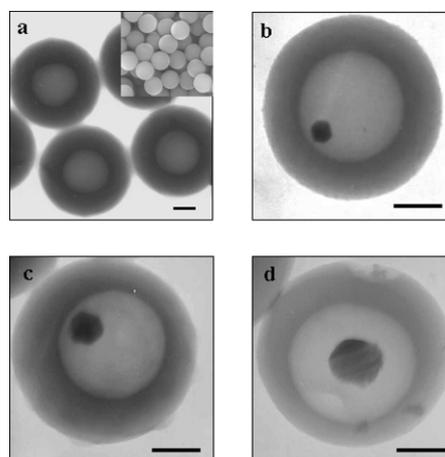
The schematic procedure for the preparation of rattle-type silica particles with metal cores is shown in Scheme 1. The first step involved the permeation of Cu<sup>2+</sup> ions into the preformed silica shells. In the next step, Cu metal cores were formed in the interior of silica shells by chemical reduction. For obtaining Ag core rattle-type silica particles, a metal displacement reaction should be performed additionally. A typical synthesis of metal core rattle-type silica particles follows. Hollow silica particles were prepared by a template-free method as described previously.<sup>16</sup> The particles (0.5 g) were added to a 50 ml of ethanolic solution ( $4.1 \times 10^{-2}$ – $3.3 \times 10^{-1}$  M) containing copper nitrate hydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ). After sonication for 1 h in an ultrasonic bath, more than 4 eq. of hydrazine monohydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) was added to the mixture solution with stirring and further reacted for 3 h under reflux. The solution was allowed to stand without agitation for several minutes at ambient temperature, and copper aggregates settled down to the bottom of the container. Supernatant solution containing the resulting particles was collected by several centrifugation/dispersion cycles at ~1000 rpm. The resultant particles were collected from the solution with a membrane filter and washed with ethanol several times. The particles were dried for 4 h in a vacuum oven at ambient temperature. The iteration of the above procedure resulted in the size growth of Cu cores in the interior of silica shells. The Cu cores of the particles as prepared were exchanged for Ag metal cores by a metal displacement reaction that used  $\text{AgNO}_3$  instead of the copper salt in the above procedure.

Fig. 1 shows the electron microscope images of the particles synthesized by the pre-shell/post-core method. Obviously, the

silica capsules are monodisperse in particle size and internal diameter, given as ca. 400 nm and ca. 230 nm, respectively (Fig. 1a). The size and wall thickness of the silica shells can be controlled by the variation of experimental conditions.<sup>16</sup> In this study, the silica shells shown in Fig 1a were used as nanoreactors, in which metal particles were formed from metal salts. After a cycle of



**Scheme 1** Schematic for the preparation of rattle-type silica particles with metal cores by pre-shell/post-core method.

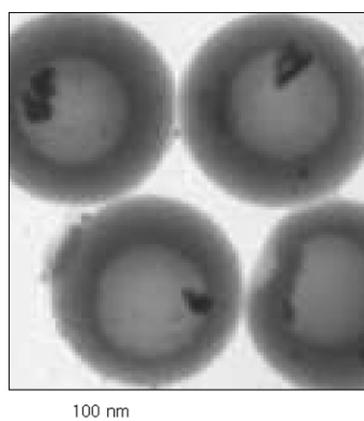


**Fig. 1** EM micrographs of hollow silica particles (a) and Cu core rattle-type silica particles (b: 1 cycle; c: 2 cycles; d: 3 cycles). Bar scale is 100 nm.

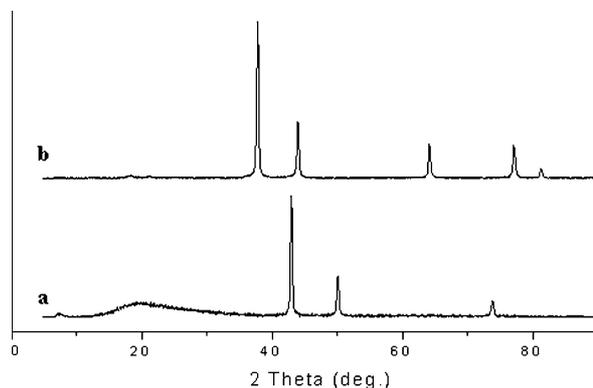
experimental procedure as shown in Scheme 1, rattle-type silica capsules with Cu cores were obtained. The Cu cores in the resulting particles are *ca.* 40 nm in size (Fig. 1b). The growth of Cu cores can be achieved by repeating the experimental procedure. It is shown that the size of Cu cores is *ca.* 70 nm after the second cycle of procedure and *ca.* 100 nm after the third cycle (Figs. 1c and 1d). The growth of metal cores can also be controlled by the concentration of metal salts. The size of the metal cores increases slightly with the concentration of metal salts, which may be due to the limited size of the hollows within the silica capsules. Therefore, a stepwise increase in the size of the metal cores within the silica capsules can be accomplished by successive repeats of the experimental procedure, as shown in Fig. 1.

As mentioned above, the rattle-type silica capsules with Cu cores could be prepared by chemical reduction following the introduction of the corresponding metal ions into the preformed silica shell interior. However, this approach is not suitable for the preparation of Ag core rattle-type silica capsules, as it leads instead to Ag-coated silica capsules. However, Ag core rattle-type silica capsules can be prepared by a metal displacement reaction. As described earlier, Cu core rattle-type silica capsules are prepared, and then upon exposure to Ag<sup>+</sup> the Cu particles oxidize to Cu<sup>2+</sup> ions and the Ag<sup>+</sup> ions are reduced to yield zerovalent Ag cores within the silica capsules. The rattle-type silica capsules with Ag cores as prepared are shown in Fig. 2. The metal cores of resulting particles from a metal displacement reaction, being designated as Ag particles, are identified by powder X-ray diffraction (XRD) as shown in Fig. 3. The intrinsic peaks of Cu metal disappear and those of only Ag metal are observed in the XRD patterns after the reaction (JCPDS No.: 04-0836 (Cu) and 04-0783 (Ag)). The metal core rattle-type silica particles as prepared could be used to form metal-containing silica coating films. This could be made possible by a feature of silica shells described in an earlier report,<sup>16</sup> which is selective solubility in organic solvents. Fig. 4 shows a TEM image of a metal-containing silica film after solvent treatment. Using an ethanolic solution containing Cu core rattle-type silica particles, a film was prepared on a substrate material by the dip coating method. Acetone treatment led to the formation of a Cu-containing silica coating film without the presence of silica particles in shape.

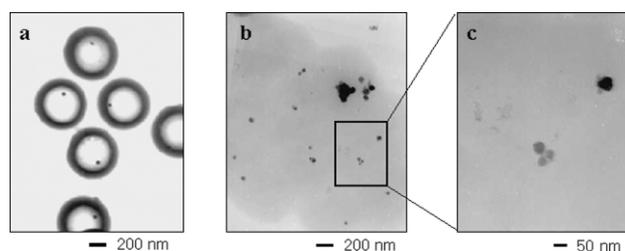
In summary, a new synthetic route preparing metal-entrapping hollow core/silica shell particles has been described that allows the formation of metal particles within the interior of preformed hollow silica particles. These rattle-type silica particles with Cu cores were synthesized by the permeation of metal salts into the hollow and their subsequent chemical reduction. Here, the silica hollow particles were used as nanoreactors for the fabrication of metal



**Fig. 2** TEM micrograph of Ag core rattle-type silica particles prepared by metal displacement reaction.



**Fig. 3** XRD patterns of Cu core (a) and Ag core rattle-type silica particles (b) prepared by pre-shell/post-core method.



**Fig. 4** TEM micrographs of Cu core rattle-type silica particles (a) for film preparation and a metal-containing silica film (b and c) formed after acetone treatment.

particles. The metal core sizes within the hollow could be increased by repeating the reaction procedures. Furthermore, the metal cores could be exchanged by a metal displacement reaction. Upon exposure to Ag<sup>+</sup>, the Cu particles within the hollow oxidized to Cu<sup>2+</sup> ions and Ag<sup>+</sup> ions were reduced to yield Ag particles. This reaction can be applied to other noble metal salts with higher reduction potentials. The metal core rattle-type silica particles as prepared could be used to form metal-containing silica coating films, making use of a feature of silica shells described in an earlier report.<sup>16</sup> Moreover, these particles may be applicable to catalysis.

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