One-pot synthesis of nanotube-based hierarchical copper silicate hollow spheres†

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A new type of hierarchical structure, copper silicate hollow spheres assembled by nanotubes, was synthesized *via* a simple one-pot route by using silica colloidal spheres as chemical template.

Hollow spheres have attracted much attention because of their potential applications in catalysis, delivery vehicles, photonic materials, optics, sensors *etc.*[1–6] Various approaches have been used to synthesize hollow spheres, such as hard or soft templating methods, and novel mechanisms like Ostwald ripening and the KerKendall effect were also introduced to fabricate hollow spheres.[7–10] Recently, hierarchical hollow spheres with the shell constructed of many kinds of nanostructure including nanobubbles or one-dimensional structures have been focused on for their structural characteristics, which endows them with a wide range of potential applications.[11–13] Therefore, the fabrication of a combinatorial structure would be of great significance.

Silicates are the most interesting and complicated class of minerals by far. Approximately 30% of all minerals are silicates and 90% of the Earth's crust is made up of silicates. The basic unit of silicates is a tetrahedron shaped anionic group with a negative four charge, which can be linked to each other in different modes and form as single units, double units, chains, sheets, rings and framework structures. The structure offers attractive chemical and physical properties in fields such as catalyst support, molecular sieve, gas adsorption and separation and so on.[14–17] In this communication, a simple chemical template method is used to fabricate a novel hierarchical structure of copper silicate hollow spheres with nanotube assembled shells. To the best of our knowledge, this kind of hierarchical structure has not been reported before. When used as dye adsorbent, the hierarchical cooper silicate hollow spheres exhibited excellent dye removal capability.

In a typical synthesis, monodispersed silica colloidal spheres were synthesized according to the Stöber method.[18] At room temperature, analytical grade $Cu(NO_3)_2 \cdot 3.5H_2O$ (0.7 mmol) and $NH_3 \cdot H_2O$ (1 mL) were mixed in 30 mL deionized water; silica colloidal spheres (0.13 g) were homogeneously dispersed into deionized water (20 mL). The above two solutions were mixed by magnetic stirring. Then the homogeneous solution was transferred into an autoclave (70 mL) for 10 h at 140 °C, the blue products were collected by centrifugation and rinsed

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with distilled water for several times until the pH was 7. Finally, the product was dried in vacuum oven at 60 °C for several hours. When the amount of $Cu(NO_3)_2 \cdot 3.5H_2O$ was increased to 1.5 mmol, while other conditions were maintained, copper silicate hollow spheres with thicker shells were obtained.

The X-ray powder diffraction (XRD) analysis was performed on an X-ray diffractometer (Philips X'pert diffractometer with Cu-Kα radiation). All the peaks of XRD pattern (Fig. 1) can be clearly indexed to copper silicate (JCPDS 03-0219). The apparent broadening of these peaks indicates that the as-prepared product was composed of nanoscaled crystals. The morphologies of the products were studied by field emission scanning electron microscope (FESEM, Sirion 200). Fig. 2a shows that the sample consists of uniform spheres with diameters of 600 nm, and the surface is rough over the whole spheres. It was further characterized by transmission electron microscope (TEM, JEOL 2010, 200 kV). The as-prepared product with black edge and white center (Fig. 2b) indicates the hollow sphere structure with uniform size in both diameter and shell thickness.

The detailed surface morphology was further investigated by high magnification TEM images. As shown in Fig. 3a, a single hollow sphere composed of a lot of nanotubes can be clearly observed. Most of the nanotubes stand vertically on the surface of the spheres with open ends, the diameter of all the nanotubes have a narrow size distribution. Many holes can be seen on the shell surface due to the open ends of the nanotubes parallel to the electron beam, and a magnified
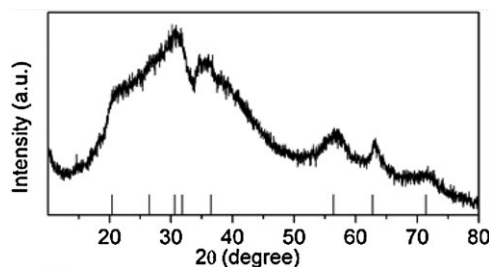

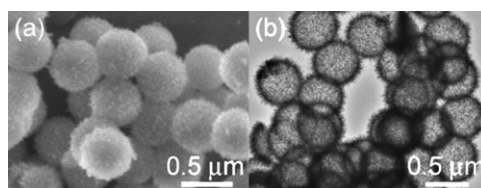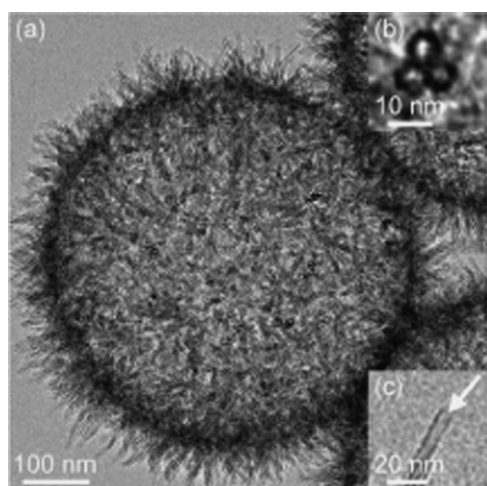**Fig. 1** XRD pattern of the as-prepared copper silicate hollow spheres.

Fig. 2 (a) SEM and (b) TEM images of the as-prepared copper silicate hollow spheres.
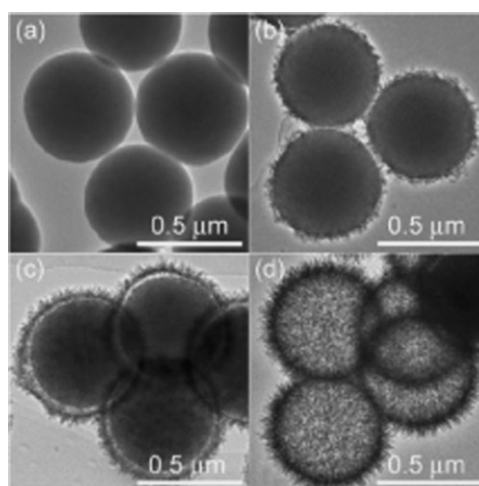
Fig. 3 TEM images of (a) single copper silicate hollow spheres; (b) three holes on the surface of a shell; (c) single nanotube on the shell.

Fig. 4 TEM images of the products collected at 140 °C for different reaction times: (a) 0 h; (b) 1 h; (c) 2 h and (d) 10 h.

image of the holes with the black edge and white center is shown in Fig. 3b, in which three holes have an average outer and inner diameter about 8 nm and 3.5 nm, respectively. One single nanotube on the shell (Fig. 3c) exhibits two parallel dark lines and darkish center, and open-ended structure as labeled by the arrow (Fig. 3c), which clearly indicates the unit of the shell is open-ended nanotubes.

Nitrogen adsorption and desorption analysis was further employed to observe the pore structure of the nanotube-based hierarchical copper silicate hollow spheres (Fig. S1). The pore size distribution calculated from the desorption branch by the Barrett–Joyner–Halenda (BJH) method (inset of Fig. S1) centred at 3.2 nm which agrees well with the inner diameter of the nanotubes observed by TEM. The Brunauer–Emmett–Teller (BET) surface area is 270 $m^2\ g^{-1}$, and the total pore volume is 0.6 $cm^3\ g^{-1}$.

Here the growth process of hierarchical hollow spheres was investigated by time-dependent experiments, and the TEM images of the corresponding products are shown in Fig. 4. The silica colloids in the present experiment are of 500 nm in diameter as shown in Fig. 4a, and the smooth surface of silica colloidal sphere can be seen clearly. With the reaction proceeding for 1 h, the surface of colloidal spheres became rough and bestrewed with particles (Fig. 4b). After 2 h reaction, the clearly blank boundary which appears indicates the formation of a core shell structure, and a complete thin shell with an obvious rough surface was observed around the silica colloidal spheres (Fig. 4c). When the reaction was prolonged for 10 h, obvious voids appeared, indicating that copper silicate hollow spheres were obtained (Fig. 4d), and the thickness of the shell was found to be uniform and thicker than that of the sample shown in Fig. 4c.

A growth mechanism of the hollow spheres is proposed according to the above experimental results. As we know the template, common silica colloidal spheres, is often used as a physical template in the fabrication of the core shell structure, and the hollow spheres are usually obtained after the silica cores are dissolved in an alkaline condition.[18,19] The dissolving property implies that the silicon–oxygen bonds could be broken to form silicate ions. Here the alkaline condition was

provided by using ammonia solution. The chemical process of the generation of copper silicate hollow spheres in the experiment could be described as follows. The ammonia was used as the source of hydroxide ions based on ionization, and it also can be coupled with copper ions in the form of complex ions which dispersed in solution homogeneously. When silica colloidal spheres were heated at high temperature in ammonia solution, the silicate ions would generate and react with the copper ions around the silica colloidal spheres, then the copper silicate formed and preferentially deposited on the surface of silica colloidal spheres. With the reaction proceeding, the silica colloidal spheres were consumed and more copper silicate generated from the copper–ammonia complex ions, and then the shell became complete gradually. The boundary shown in Fig. 4c could be ascribed to the consumption of silica cores during the reaction. The copper silicate shells continued growing thicker until all the copper ions were transformed into copper silicate according to the above reaction process. Finally, the silica cores left were dissolved by surplus hydroxide ions at high temperature, which led to the formation of copper silicate hollow spheres. It should be pointed that the critical amount of ammonia was 0.7 mL to dissolve silica completely in the present system. In the whole process, the silica colloidal spheres played two roles both as template and source of silicate ions, and the reagent ammonia provided hydroxyl ions and coupled with copper ions, all these together offered a proper condition for the formation of copper silicate hollow spheres. In addition, the thickness of the shell can be controlled by adjusting the reaction parameters, such as the copper silicate hollow spheres with thicker shell were obtained by increasing the initial concentration of copper ions (Fig. S2).

The unit of the shell was uniform nanotubes which were observed in the above images and the formation process was proposed as follows. The copper silicate generated in the reaction has a clay-type structure, and is composed of asymmetric alternating sheets of silica tetrahedra and copper oxide octahedra.[14] According to the theory of L. Pauling who has pioneered studies on the crystal structures of layered silicates, if the two crystal faces of a constituent layer in a layer crystal are not equivalent, there would be a tendency for

the layer to curve, one face becoming concave and one convex, and this tendency would in general not be overcome by the relatively weak force between adjacent layers.[20,21] Meanwhile, the layer structure tended to curl at an elevated temperature and pressure according to the scrolling mechanism that was put forward to explain the formation of nanowires and nanotubes previously by many researchers.[22–24] In our experiment, from further observation of the product prepared at the initial stage (Fig. 4b), the magnified image of the particles around the silica colloidal spheres were seen to exhibit lamellar particles without nanotubes (Fig. S3), while the final product exhibited a nanotube structure. From this we propose that the cooperation effect of the elevated temperature and pressure in a closed reaction system and the intrinsic asymmetric structure formed during the reaction process, makes the layer-structured copper silicate scroll in-situ along one certain axis of the layered copper silicates. Here it is worth noting that the nanotubes almost have a uniform diameter as shown in Fig. 2a, which implies that the lamellas may have a similar wideness before scrolling, and determining whether there is a critical scrolling wideness of lamellas in particular conditions is under way in our group.

The large specific surface area and thermal stability of silicate combined to enhance the potential applications of hierarchical copper silicate hollow spheres. Here the as-obtained hierarchical copper silicate hollow spheres were used to investigate the application in waste-water treatment. The adsorption isotherm was obtained by varying the initial concentration of methylene blue (MB) solution without any additives. The adsorption isotherm (Fig. 5a) indicates that 1 g new as-prepared hierarchical copper hollow spheres can remove 162 mg MB, which is much higher than that of the natural sepiolite with an adsorption capacity of 58 mg g^{-1},[25] indicating a better adsorption performance of the hierarchical porous copper silicate hollow spheres. The copper silicate hollow spheres containing MB could be renewed by combustion at 300 °C in air for 4 h, and the renewed copper silicate hollow spheres still exhibit a large adsorption performance as shown by the curve in Fig. 5b. The above results show that the as-prepared hierarchical copper silicate hollow spheres provide a novel material for the
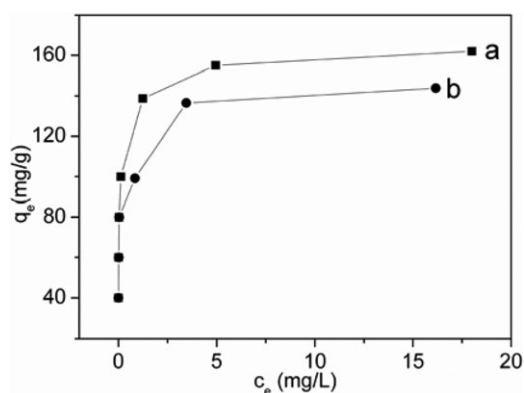
removal of weakly biodegradable pollutants which indicates a great potential application in the practical dye removal treatment.

In summary, silica colloidal spheres were successfully used as sources of silicate ions and templates in the synthesis of hierarchical copper silicate hollow spheres. The characterization and evolution process have been investigated. The formation mechanism of nanotube-based hierarchical structure was proposed that the generated lammellar copper silicate scrolled in-situ around the silica colloidal spheres. The whole synthesis procedure was done in one step and this simple in-situ reaction method will cast new light on the development of new superstructures. The hierarchical copper silicate hollow spheres exhibited large specific surface area and excellent adsorption capability of dye, meanwhile it also was expected to be applied potentially in other fields such as catalyst support.

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Fig. 5 Adsorption isotherm of MB on (a) new as-prepared; (b) renewed hierarchical copper silicate hollow spheres, respectively, c_e (mg L^{-1}) is the equilibrium concentration of the MB solution and q_e (mg g^{-1}) is the amount of MB adsorbed at equilibrium.