Facile fabrication of manganese carbonate and oxides shell structure

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Manganese compounds, with economical and low toxical advantages, have been widely used in industry and environmental protection. Manganese oxides with different valencies of manganese (MnO_x), e.g., Mn_2O_3, Mn_3O_4, and MnO_2, have been successfully applied as catalysts, ion sieves, electrocatalysts and magnetic materials [1]. In these fields, the control of morphology, size, and texture of materials is of pivotal importance because of the complicated surface/interface reactions [2]. Therefore, a variety of manganese oxides with different morphologies such as single crystals, nanowires, nanosheets, nanoparticles, and thin films [1, 3–8] have been synthesized to meet different demands.

Shell structures are known to have many advantages as catalysts, fillers, drug carriers, chemical sensors and photonic crystals owing to their low density, high surface area, and surface permeability [1d, 9, 10]. Large amounts of inorganic [11], organic [12] and organic-inorganic hybrid [13] shell structures have been prepared and have exhibited their unique properties. Manganese oxides with shell structures, as a kind of promising functional materials, are also highly desired. Suib *et al.* [1d] has shown outstanding superior catalytic performance of hollow nanospheres (diameter ≈ 400 nm) of γ-MnO_2 compared with the conventional γ-MnO_2, and Sasaki *et al.* [10] has predicted the applications of hollow Mn_2O_3 nanoshells in catalysis and electrochemistry. Herein, a facile route is proposed to fabricate hollow MnO_x (Mn_2O_3 and Mn_3O_4) shells through the controlled precipitation of $MnCO_3$ on polyelectrolyte-modified hexagonal mesoporous silica (HMS) spheres in a solution containing manganese sulfate and urea, followed by calcining these $MnCO_3$ shells in different atmospheres. In this method, urea acted as both the precipitator for Mn^{2+} and the corrosive agent for mesoporous silica through its hydrolysis at elevated temperature, which effectively avoided the core-etching step in conventional routes for hollow structures. Additionally, the porosity of the HMS core facilitated the corrosion of itself.

HMS spheres with an average particle size of 1.1 μm were synthesized according to the literature [14]. After calcination at 600 °C for 4 hr to remove the surfactant, the HMS spheres were immersed in a solution of polydialyldimethylammonium chloride (PDDA) for 15 min to make their surfaces positively charged. Then they were washed with distilled water to remove the excessive PDDA and dried at 70 °C. Afterwards, the PDDA-modified HMS spheres were dispersed in an aqueous solution containing 0.16 mol L^{-1} manganese sulfate and 0.40 mol L^{-1} urea with solid content of 150 mg L^{-1}. After stirred for 2 hr at room temperature, the dispersion was transferred into an oil bath at 85 °C and stirred for another 1.5 hr. Finally, this system was quenched in an ice–water bath to stop the reaction. The products were centrifugated, washed and then dried at 70 °C.

The scanning electron microscope (SEM) image of the samples (Fig. 1a) shows that the as-prepared materials well retained the monodisperse spherical morphology of original HMS, despite the rough surface, composed of nanoparticles. The corresponding transmission electron microscopy (TEM) image (Fig. 1b) indicates that the sample was hollow structured with the shell thickness of ca. 100 nm, which can be further confirmed by the SEM image of the broken microsphere (Fig. 1b inset). The structure of the hollow spheres can be maintained after sonicated for 10 min in a sonic bath of 50 Hz, in which their good mechanical strength is well shown. The X-ray Diffraction (XRD) pattern (Fig. 2a) of the sample demonstrates its pure crystalline phase of $MnCO_3$. Elemental analysis by energy-dispersive X-ray (EDX) reveals that most of the SiO_2 of the HMS cores had been *in-situ* removed during the synthetic process.

Manganese oxides with shell structure, e.g., Mn_3O_4 (Fig. 3a) and Mn_2O_3 (Fig. 3b) could be easily obtained via calcining the $MnCO_3$ hollow spheres at 700 °C for 1 hr in nitrogen and air, respectively. The TEM image (Fig. 3) illustrates that the shell structure was well retained. The XRD patterns (Figs 2b and c) show that

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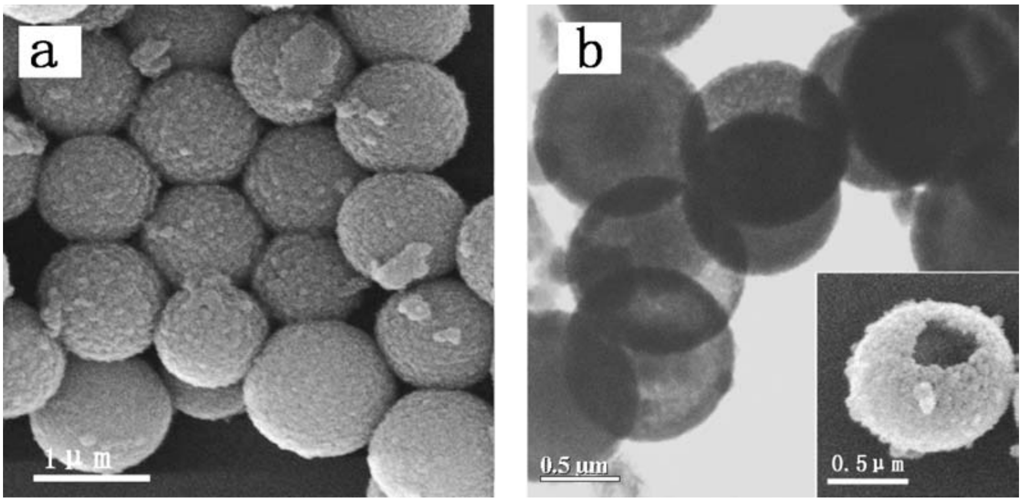

Figure 1 (a) SEM and (b) TEM images of the hollow $MnCO_3$ spheres.

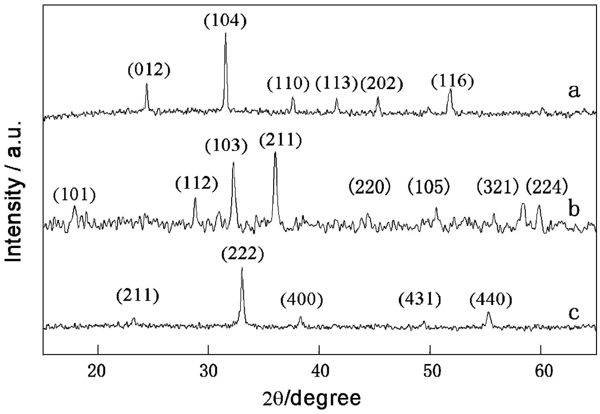

Figure 2 XRD patterns of (a) $MnCO_3$, (b) Mn3O4 and (c) Mn_2O_3 hollow spheres.

their diffraction peaks corresponded to the crystalline phase of Mn_3O_4 and Mn_2O_3, respectively. The BET specific surface area of the hollow Mn_2O_3 shells was determined to be 56 $m^2\ g^{-1}$. As reported formerly, Mn_2O_3 and Mn_3O_4 were efficient catalysts for many environmental reactions and the synthesis of organic compounds [15], as well as promising candidates of humidity sensors [16], batteries [17], and starting materials for manufacturing soft magnetic materials [18]. The features of the well-defined hollow structure with nanoscale shells may generate a series of new properties complementary to those of the MnO_x crystal itself, and consequently improve or widen the applications of manganese oxides.

In our experiments, the fabrication of integrated hollow $MnCO_3$ shells was the premise to obtain the MnO_x hollow structure. It was found that the concentration of Mn^{2+} in the synthesis system played an important role in the formation of shell structure. Excessive manganese ions led to the independent precipitation and agglomeration of large $MnCO_3$ particles in the solution, while insufficient manganese ions not only failed to coat the HMS spheres uniformly but also resulted in large amounts of residue of SiO_2 cores in the shells. This phenomenon could be explained by the assumption that the consumption of the $CO_3{}^{2-}$ during the precipitation of the $MnCO_3$, accelerated the decomposition of urea, and the resulted proper alkalinity of the solution is the key factor for the dissolving of the silica core. Therefore, insufficient $MnCO_3$ precipitation would not lead to the etching of the HMS spheres.

Another important factor that influenced the quality of the produced $MnCO_3$ shells was whether the HMS spheres were pre-modified with positively-charged polyelectrolyte. As mentioned in the literature, the

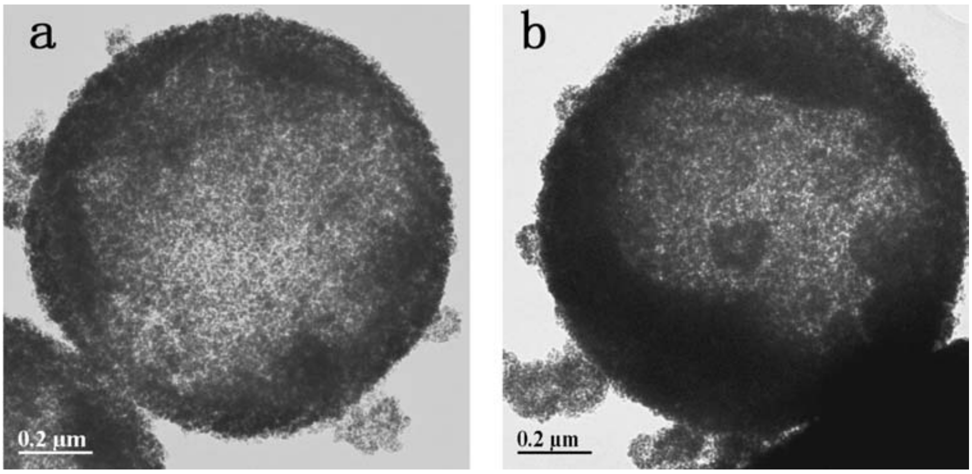

Figure 3 TEM images of hollow shells of (a) Mn_3O_4 and (b) Mn_2O_3.

isoelectric point (i.e.p.) of manganese carbonate was about 5.8 [19], thus the $MnCO_3$ nanoparticles formed in the alkaline solution were negatively charged. As a result, negatively-charged $MnCO_3$ would tend to deposit onto the surface of PDDA-modified electropositive HMS cores through the electrostatic interaction. Otherwise, if non-modified HMS spheres with negative charges in the alkaline solution (the i.e.p. of silica is below 4) [20] served as the template, no hollow structures could be obtained.

In summary, a simple route has been developed for the preparation of hollow shells of $MnCO_3$ with uniform size, and the subsequent calcinations in proper atmospheres would produce hollow MnO_x shells with desired oxidation states, which may broaden the application of manganese oxides. HMS cores were *in-situ* dissolved in the synthetic solution whose alkalinity was controlled by the decomposition of urea. Therefore, the necessary template-etching process in the previous approaches was successfully avoided. This method has also been proved to be a versatile way to synthesize other hollow metal carbonates with similar crystalline propensity with manganese carbonate, such as cadmium carbonate and calcium carbonate. Detailed work is in progress in our laboratory.

Acknowledgements

The authors thank the NSFC (20273016, 20233030, 20303003, 20325313) and the SNPC (0249nm028, 03DJ14004) and the Major State Basic Research Program of China (2000077500, 2003CB615807) for financial support.

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Received 23 November 2004
and accepted 25 April 2005