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Lithium Storage **Very Important Paper**

General Synthesis of Multi-Shelled Mixed Metal Oxide Hollow Spheres with Superior Lithium Storage Properties[**]

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Abstract: *Complex hollow structures of transition metal oxides, especially mixed metal oxides, could be promising for different applications such as lithium ion batteries. However, it remains a great challenge to fabricate well-defined hollow spheres with multiple shells for mixed transition metal oxides. Herein, we have developed a new "penetration–solidification–annealing" strategy which can realize the synthesis of various mixed metal oxide multi-shelled hollow spheres. Importantly, it is found that multi-shelled hollow spheres possess impressive lithium storage properties with both high specific capacity and excellent cycling stability. Specifically, the carbon-coated* $CoMn_2O_4$ *triple-shelled hollow spheres exhibit a specific capacity of* $726.7\,mA\,h\,g^{-1}$ *and a nearly 100 % capacity retention after 200 cycles. The present general strategy could represent a milestone in design and synthesis of mixed metal oxide complex hollow spheres and their promising uses in different areas.*

Hollow spheres, in particular those with complex shell structures, have recently stimulated tremendous research interest because the multi-level architecture could enable functional materials with optimized properties in vaious applications including catalysis, drug delivery, gas sensors, energy storage systems and many others.[1–6] Researchers have recently paid considerable efforts on exploring different effective strategies which could manipulate the shell structure of hollow spheres aiming to optimize their physical/chemical properties for specific applications. As a result, many types of hollow spheres with multi-shelled structures have been fabricated through different synthesis routes.[7–13] For example, Wang and coworkers carried out the controlled synthesis of multi-layered ZnO hollow spheres through the hard template assisted strategy and found strong correlation between the perfomance and shell-structure when applied in solar cells.[9] In addition, several types of Cu_2O multi-level hollow spheres were recently fabricated using different methods such as soft templating and Ostwald ripening process.[10,11] Despite these exciting progresses, there are still great challenges in general synthesis of complex hollow spheres. First, most of the current methods are only suitable for synthesizing complex hollow spheres of some specific materials, which undoubtedly hinders practical applications of these complex hollow structures. On the other hand, existing strategies could only be feasible for the synthesis of simple binary metal oxide hollow spheres, which will largely limit the opportunities for studing other multi-component metal oxide functional mateirals. Therefore, a general strategy for mixed metal oxide hollow spheres with multiple shells is highly dirable.

Transition metal oxides (TMOs), especially those mixed valence oxides invloving different metal elements, have recently found great potentials as electrode materials for energy storage devices including fuel cells, lithium-ion batteries (LIBs) and electrochemical capacitors (ECs).[14–19] Although this class of materials exhibits very high theoretical capacity for LIBs, the poor cycling performance presumably caused by the large volume variation during repeated charge/discharge processes[20] becomes the major obstacle for their practical applications. As one of the promising solutions, construction of TMOs hollow spheres with multi-shelled structures has recently received considerable amount of attention.[13,21,22] Specifically, hollow spheres enables better access for Li^+ ions since a porous structure with high surface area can be achieved, which will lead to the increased electrode–electrolyte contact area. More importantly, the hollow interior could provide extra voids to effectively alleviate the volume change and mechanical strain derived from the repeated Li^+ insertion/extraction processes. Moreover, multi-shelled structures could further reduce diffusion paths for Li^+ ions and provide better structural support and utilization of the void interior. For example, binary Co_3O_4 hollow spheres with controlled shell structures have been recently shown to exhibit optimized lithium storage performance.[22] Nonetheless, it remains a great challenge to construct multi-shelled mixed metal oxide hollow spheres, which could be exceptionally desirable for lithium storage.[23] Here, we report a general "penetration–solidification–annealing" strategy for the synthesis of multi-shelled hollow spheres of various mixed metal oxides, including $CoMn_2O_4$, $Co_{1.5}Mn_{1.5}O_4$, $MnCo_2O_4$, $ZnMn_2O_4$, $ZnCo_2O_4$, and $NiCo_2O_4$. Remarkably, it is found that the complex hollow spheres exhibit largely enhanced lithium storage properties.

Figure 1 illustrates the general "penetration–solidification–annealing" process for the formation of multi-shelled

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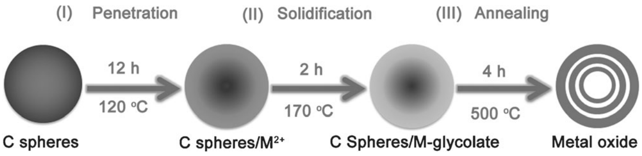

Figure 1. Schematic illustartion of the "penetration–solidification–annealing" process for the formation of complex metal oxide multi-shelled hollow spheres.

mixed metal oxide hollow spheres in a unified polyol system. First, carbonaceous spheres obtained by a previously reported hydrothermal method[24] are well dispersed into an ethylene glycol solution of metal acetate precursors. Second, in order to realize the deep "penetration" of metal ions into the carbonaceous spheres, the reaction solution is heated up to 120 °C in an oil bath and kept stirring at this temperature for 12 h. Third, the "solidification" process is then carried out by further increasing the temperature to 170 °C and kept refluxing for another 2 h. During this process, the metal glycolate will be formed in both the interior and outer surface of carbonaceous spheres.[21,25] At last, multi-shelled hollow spheres can be easily generated through a thermal annealing treatment in air. In our method, one of the important features compared with previously reported template-engaged methods for hollow spheres is that the "penetration" and "solidification" processes are separated. Therefore, the similar chemical properties of different transition metal ions in the polyol process make the method universal for various transition metal oxides, which is especially advantageous for synthesis of mixed metal oxide hollow spheres.

In order to validate the generality of the method, multi-shelled hollow spheres of $Co_xMn_{3-x}O_4$ with controlled molar ratios of Co and Mn are first synthesized. Figure 2 shows some representative field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of triple-shelled hollow spheres of $CoMn_2O_4$ (Figure 2 A,B), $Co_{1.5}Mn_{1.5}O_4$ (Figure 2 C,D) and $MnCo_2O_4$ (Figure 2 E,F). As can be seen, FESEM images (Figure 2 A,C,E) of these three types of hollow spheres exhibit similar features in shape, size and uniformity. The average diameters for these hollow spheres are in the range of 600–800 nm. TEM images (Figure 2 B,D,F) provide the direct evidence that triple-shelled structures are formed for all these three types of hollow spheres while there is a slight difference in the shell thickness which is estimated in the range of 30–50 nm. X-ray powder diffraction (XRD) analysis (Figure S1, see Supporting Information) of these different materials confirms their phase purity while the molar ratio of metal elements in each compound is determined through energy-dispersive x-ray spectroscopy (EDS) analysis (Figure S2).

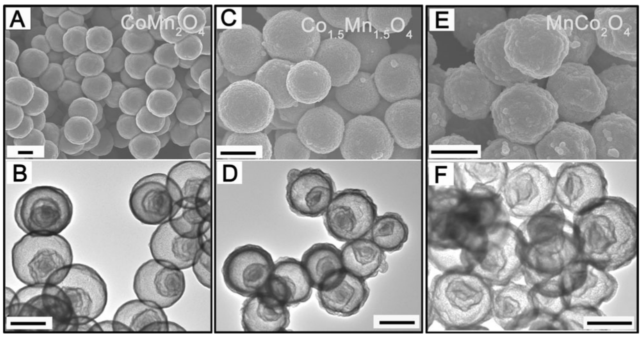

Figure 2. A,C,E) FESEM and B,D,F) TEM images of complex hollow spheres of mixed metal oxides: A,B) $CoMn_2O_4$; C,D) $Co_{1.5}Mn_{1.5}O_4$; E,F) $MnCo_2O_4$. The scale bars are 500 nm.

To further demonstrate the versatility of our method, multi-shelled hollow spheres of three other mixed metal oxides including $ZnMn_2O_4$, $ZnCo_2O_4$ and $NiCo_2O_4$ are fabricated by simply using the respective precursors. Figure 3 shows the typical FESEM and TEM images of $ZnMn_2O_4$ (Figure 3 A,B), $ZnCo_2O_4$ (Figure 3 C,D) and $NiCo_2O_4$ (Figure 3 E,F) triple-shelled hollow spheres. The formation of compounds is confirmed by the corresponding XRD patterns (Figure S3) and EDS results (Figure S4). Compared with $Co_xMn_{3-x}O_4$ hollow spheres, the morphological features are quite similar in terms of both size and shape. Again, TEM images clearly indicate that a triple-layered shell structure can be readily formed for different materials. While the shells observed here are mostly triple shells, it should be possible to tune the number of shells by controlling the experimental conditions. Our preliminary results suggest that the number of shells is highly related with two factors, i.e., the "penetration" time in step 1 (see Figure 1) and the diameter of carbon spheres used during the synthesis. The shell number for the hollow spheres can be manipulated by adjusting the "penetration" time, which can generate single-shelled, double-shelled hollow spheres for different oxide materials. In addition, the diameter of carbon spheres could be another important factor influencing the number of shells formed in the hollow spheres. Larger carbon spheres could enable more space to generate more shells in hollow spheres, which means that four- or even five-shelled hollow spheres could be possible if larger carbon spheres are used.

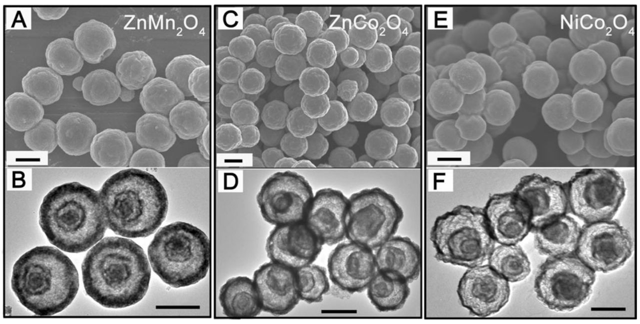

Figure 3. A,C,E) FESEM and B,D,F) TEM images of complex hollow spheres of mixed metal oxides: A,B) $ZnMn_2O_4$; C,D) $ZnCo_2O_4$; E,F) $NiCo_2O_4$. The scale bars are 500 nm.

The lithium storage properties of carbon-coated $CoMn_2O_4$ triple-shelled hollow spheres are then evaluated as an anode material for LIBs. The carbon coating is performed through a modified hydrothermal method using glucose as the carbon precursor.[26] After carbonization, the content of amorphous carbon in the nanocomposite is determined to be about

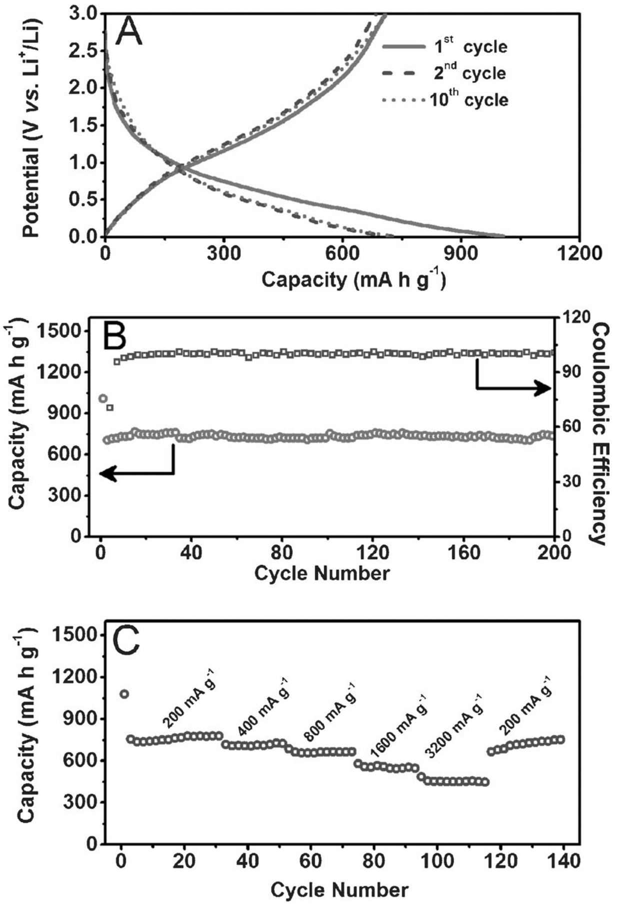

Figure 4. Lithium storage properties of carbon-coated $CoMn_2O_4$ triple-shelled hollow spheres: A) discharge–charge voltage profiles of the first, second, and tenth cycles in the voltage range of 0.01–3 V; B) cycling performance and corresponding Coulombic efficiency at a current density of 200 mAg^{-1}; C) rate performance at various current densities from 200 mAg^{-1} to 3200 mAg^{-1}.

17.6 wt% by thermogravimetric analysis (Figure S5). TEM images (Figure S6) reveal uniform coating of carbon layer with a rough thickness of about 16 nm while keeping the shell structure and phase of the $CoMn_2O_4$ hollow spheres unaltered (Figure S7). In this study, the mass of the active material in the electrode configuration includes both the metal oxide and coated carbon in order to reasonably evaluate the specific capacity. Figure 4A shows typical discharge–charge voltage profiles for the first, second and tenth cycles of the carbon-coated $CoMn_2O_4$ triple-shelled hollow sphere electrode at a current density of 200 mAg^{-1}. As can be seen, the first discharge capacity is around 1006.6 mAhg^{-1}, whereas the corresponding charge capacity is around 708.9 mAhg^{-1}. This corresponds to an initial Coulombic efficiency of 70.4%, which is similar to the values reported in previous literatures.[15,18] The discharge–charge curves for the second and tenth cycles almost coincide with each other, indicating the good cycling stability.[20,27] Figure 4B shows the cycling performance of carbon-coated $CoMn_2O_4$ triple-shelled hollow spheres at a current density of 200 mAg^{-1}. As shown, the discharge capacity of the carbon-coated $CoMn_2O_4$ triple-shelled hollow sphere electrode is around 726.7 mAhg^{-1} in the second cycle, and it is very stable with almost 100% capacity retention for at least 200 cycles. This cycling performance is remarkable compared to previously reported results for mixed metal oxide electrodes.[15,18,21,28,29] From the corresponding Coulombic efficiency curve shown in Figure 4B, the Coulombic efficiency quickly increases to around 96.5% for the second cycle and reaches a value higher than 99% after several cycles. Furthermore, the rate capability is evaluated with current densities ranging from 200 to 3200 mAg^{-1} (Figure 4C). As can be seen, the average specific capacities are 775.1, 706.3, 656.1, 557.6 and 449.8 mAhg^{-1} at the current densities of 200, 400, 800, 1600 and 3200 mAg^{-1}, respectively. After the high-rate charge–discharge cycling, a specific capacity as high as 746.3 mAhg^{-1} can be restored when the current density is reduced to 200 mAg^{-1}. The above results clearly imply the excellent lithium storage properties of carbon-coated $CoMn_2O_4$ triple-shelled hollow spheres as an anode material for LIBs.

The impressive cycling stability and excellent rate performance of carbon-coated $CoMn_2O_4$ triple-shelled hollow spheres could be attributed to the following aspects. First, the relatively strong mechanical stability of $CoMn_2O_4$ triple-shelled hollow spheres allows the uniform coating of a thin carbon layer on the surface. The carbon coating could further strengthen the mechanical stability of the hollow spheres, and more importantly could well alleviate the stress generated by large volume variation during the repeated lithium insertion/extraction processes. Second, the carbon layer will certainly enhance the electrical conductivity of metal oxides after the thermal annealing treatment, which could contribute to the rate performance. Moreover, the multi-shelled hollow structure might be better able to withstand the mechanical stress during the charge-discharge processes compared to single-shelled hollow structures.

In conclusion, a "penetration–solidification–annealing" process has been developed for the first time to realize the general synthesis of various mixed metal oxide multi-shelled hollow spheres, including $Co_xMn_{3-x}O_4$, $ZnMn_2O_4$, $ZnCo_2O_4$ and $NiCo_2O_4$. The method is quite universal which holds the potential to be further extended to other materials. As demonstrated, the multi-shelled hollow spheres possess excellent lithium storage properties as anodes for lithium ion batteries. The present work makes a significant contribution to not only the synthetic methodology of hollow structures, but also the application of transition metal oxides as negative electrodes in lithium ion batteries.

Experimental Section

In a typical synthesis, carbonaceous spheres are firstly obtained through a reported hydrothermal method.[24] Take the synthesis of $CoMn_2O_4$ hollow spheres as an example, 0.5 mmol of cobalt acetate tetrahydrate and 1 mmol of manganese acetate tetrahydrate are dissolved into 30 mL of ethylene glycol under stirring to form a transparent solution. Then, 30 mg of carbonaceous sphere powder is dispersed into the above solution through sonication to form a uniform dispersion. After this, the solution is transferred to a flask and heated to 120 °C in an oil bath and kept at 120 °C for 12 h to allow the sufficient penetration of metal ions into the carbonaceous spheres. The solution is then further heated to 170 °C and kept refluxing for another 2 h, followed by naturally cooling down to room temperature. The precipitation is then collected by centrifugation and washed with deionized water and ethanol for several times to get rid of possible residues on the surface. The triple-shelled hollow spheres are generated through a thermal annealing treatment in air at the temperature of 500 °C for 4 h with a heating rate of $3\,^{\circ}\mathrm{C\,min^{-1}}$. The synthesis procedures of other mixed metal oxides are the same as that for $CoMn_2O_4$ hollow spheres except for using different metal acetate precursors. The carbon coating is performed through a hydrothermal method using glucose as the carbon source. First, 60 mg of the $CoMn_2O_4$ triple-shelled hollow spheres is dispersed into 50 mL of glucose aqueous solution with a concentration of 0.06 M. The solution is then transferred to an 80 mL Teflon-lined autoclave and heated to 170 °C for 4 h. The obtained product is washed with ethanol for several times and dried in an oven, followed by a carbonization step in N_2 at 450 °C for 4 h.

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advanced X-Ray Diffractometer. Field-emission scanning electron microscope (FE-SEM) images and energy-dispersive X-ray spectroscopy (EDS) spectra were obtained on a JEOL JSM 6700F microscope. Transmission electron microscope (TEM) images were taken on a JEOL 2010 microscope.

The electrochemical measurements were carried out using CR2016 coin-type half-cells. The working electrode consisted of active material, carbon black (Super-P-Li), and polymer binder (polyvinylidene fluoride; PVDF) in a weight ratio of 80:10:10. Lithium foil was used as both the counter and reference electrode. 1.0 M $LiPF_6$ in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate was used as the electrolyte. Cell assembly was carried out in an Ar-filled glovebox with moisture and oxygen concentrations below 1.0 ppm. The galvanostatic charge–discharge tests were performed on a NEWARE battery test system.

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