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Lithium-Ion Batteries

Accurate Control of Multishelled Co_3O_4 Hollow Microspheres as High-Performance Anode Materials in Lithium-Ion Batteries**

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Owing to their high energy density, light weight, and long cycle life, rechargeable lithium-ion batteries (LIBs) have become one of the dominant power sources for portable electronic devices. With the growing need for higher capacity and safety, numerous efforts have been made to develop alternative high-performance electrode materials for next-generation LIBs.[1] For example, anode electrodes made of transition-metal oxides have been found to exhibit reversible capacities about two or three times as large as those based on conventional graphite materials ($< 372\ \mathrm{mA\,h\,g^{-1}}$).[1b] Among various types of transition-metal oxides, cobalt oxide (Co_3O_4) has received special attention, since it is expected to have a high capacity (about $1000\ \mathrm{mA\,h\,g^{-1}}$) and excellent cycling performance.

Unfortunately, although the best capacity of Co_3O_4 to date has increased to $1450\ \mathrm{mA\,h\,g^{-1}}$ through the use of Co_3O_4 micro-/nanomaterials,[2] the practical use of Co_3O_4 anode electrodes for LIBs is still largely hindered by their poor capacity retention upon cycling and/or low rate capability.[3] To circumvent these issues, hollow micro-/nanostructures have been used instead of solid micro-/nanostructures as LIB anode materials on the basis of the following considerations:[4] 1) The larger surface area of the hollow structures enables better access for lithium ions as a result of the increased electrode–electrolyte contact area. 2) The hollow interior provides additional free volume to alleviate the structural strain associated with repeated Li^+-insertion/extraction processes and thus leads to improved cycling stability. 3) Properly prepared multishelled hollow micro-/nanostructures not only allow for significantly reduced diffusion paths for both lithium ions and electrons, but also provide more lithium-storage sites: The shorter diffusion paths lead to a better rate capability, and the overall capacity is higher as a result of the larger number lithium-storage sites.

Recently, significant effort has been devoted to the fabrication of hollow spheres with multiple shells.[5] Different metal oxides with multishelled hollow-sphere structures have been synthesized on the basis of the soft-/hard-template methods.[6] However, these methods are only suitable for specific metal oxides and cannot be applied generally to a wide range of materials. Recently, we reported a facile and general strategy for the preparation of metal-oxide hollow microspheres by the use of carbonaceous microspheres (CMSs) as sacrificial templates. The number of shells can be controlled by adjusting the heating conditions and the concentration of the metal ions.[4,7] However, owing to the large radii of hydrated cobalt ions, we were unable to control the number of Co_3O_4 microsphere shells.

To enable precise control over the synthesis of multishelled Co_3O_4 hollow microspheres with CMS templates, we modified our strategy by controlling not only the size and diffusion rate of the hydrated metal cations, but also the absorption capability of the CMSs. A pink solution of hydrated cobalt ions ($[Co(H_2O)_6]^{2+}$) was observed when the solvent was only deionized water (Figure 1 a), and only single-shelled Co_3O_4 microspheres were obtained after calcination (see Figure S1 in the Supporting Information). When the solvent was changed to a mixture of ethanol and water (1:1, v/v), the solution turned blue-violet, which suggested a decrease in the number of the aquo groups (H_2O) within the coordination sphere of the cobalt ion ($[Co(H_2O)_{(6-x)}]^{2+}$, $x = 3$–6).[8] The decreased hydration within the coordination sphere led to a decrease in the size of the cobalt ions and thus an increased ability to diffuse into CMS templates (Figure 1 b); as a result, double-shelled Co_3O_4 microspheres were formed (Figure 2 a,d). To further enhance the diffusion rate, we increased the volume fraction of ethanol in the solvent to 75 vol% and heated the solutions to higher temperatures. According to the Arrhenius equation,[9] at a higher temperature, a higher diffusion rate coefficient can be reached, and thus cobalt ions can be adsorbed by CMSs more readily (Figure 1 c). Thus, triple-shelled Co_3O_4 resulted (Figure 2 b,e). Besides altering the solution conditions, we modified the CMSs by immersing them in 0.5 M aqueous HCl for 2 days. The measured BET specific surface area of the resulting

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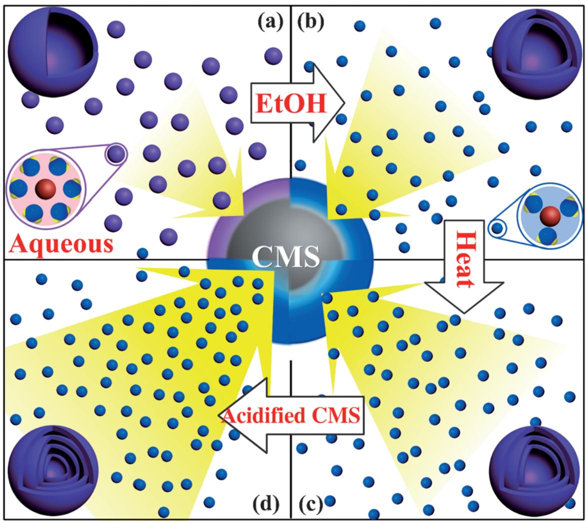

Figure 1. Mechanism for the formation of the multishelled Co_3O_4 hollow microspheres under different adsorption conditions.

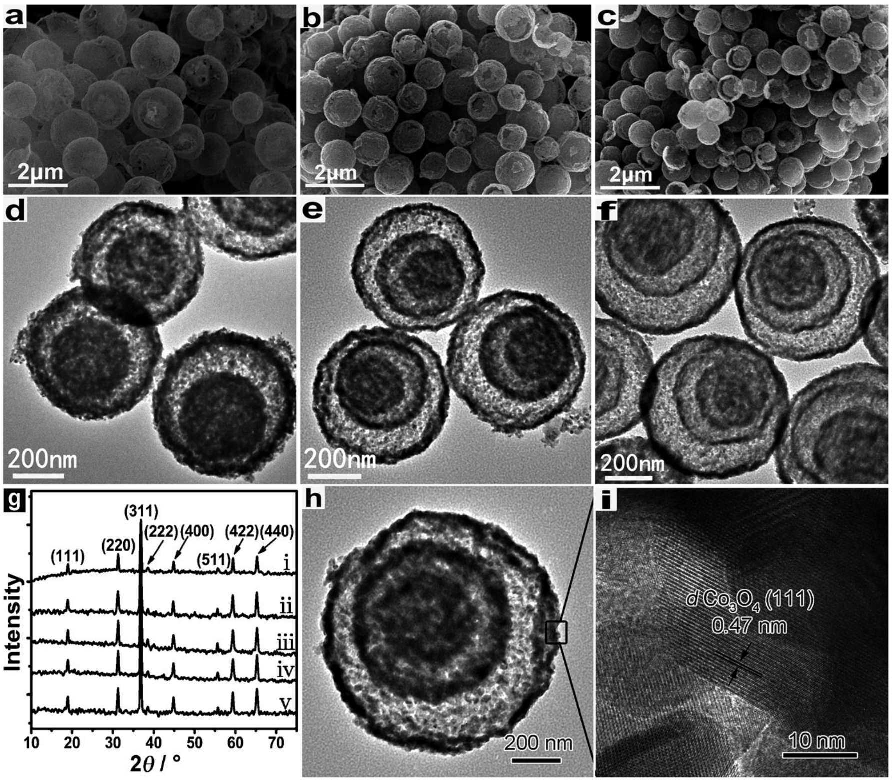

Figure 2. a,b,c) SEM and d,e,f) TEM images of double-, triple-, and quadruple-shelled Co_3O_4 hollow microspheres. g) XRD patterns of the as-prepared i) single-, ii) double-, iii) triple-, and iv) quadruple-shelled microspheres and v) commercial Co_3O_4. h) TEM and i) HRTEM images of an individual triple-shelled Co_3O_4 hollow microsphere.

CMSs was 18.8% higher than that of CMSs without acid treatment, and their pore volume was greater (see Table S2 in the Supporting Information). The larger surface area enables the penetration of more cobalt ions (Figure 1 d) and resulted in the formation of quadruple-shelled Co_3O_4 (Figure 2 c,f).

By the methods described above, we obtained multishelled Co_3O_4 hollow microspheres in unprecedented high yield and purity. On the basis of the analysis of more than 100 Co_3O_4 hollow microspheres for each sample, we determined that all multishelled Co_3O_4 hollow microspheres had a similar size (see Figure S2) and that the yield of each type of Co_3O_4 hollow microsphere was very high: 80, 70, 75, and 75% for single-, double-, triple-, and quadruple-shelled Co_3O_4 microspheres, respectively. For example, in the preparation of the quadruple-shelled Co_3O_4 hollow microspheres, 75% of the product microspheres had quadruple shells and 25% had triple shells (with no observed single- or double-shelled structures; see Figure S3). Impressively, the synthesized Co_3O_4 exhibited an excellent rate capacity, good cycling performance, and an ultrahigh specific capacity.

The crystalline structures of the prepared Co_3O_4 hollow microspheres were investigated by X-ray diffraction (XRD) along with the structure of commercial Co_3O_4 powder for comparison (Figure 2 g). All reflection peaks were indexed to a pure cubic spinel Co_3O_4 structure (JCPDS card no. 42-1467, space group: $Fd3m$, $a = 8.084$ Å),[3a] with no additional peaks detected. X-ray photoelectron spectroscopy (XPS) was also used to investigate the chemical composition of as-prepared and commercial Co_3O_4 (see Figure S4). Two characteristic broad peaks encompassing the Co^{2+} and Co^{3+} $2p_{3/2}$ states at 780.2 eV and Co^{2+} and Co^{3+} $2p_{1/2}$ states at 795.2 eV were observed; these peaks correspond to the standard Co_3O_4 phase.[10] Detailed structural observation by TEM imaging of a single Co_3O_4 hollow microsphere clearly revealed nanopores inside the shells (Figure 2 h). These nanopores are probably formed by gas evolution during calcination.[11] Furthermore, high-resolution TEM (HRTEM) imaging demonstrated the highly crystalline nature of the Co_3O_4 nanoparticles in the shells: (111) lattices were commonly observed (Figure 2 i). The porous nature of the shells and the preferential (111) orientation of nanoparticles should be beneficial for the application of the Co_3O_4 hollow microspheres in LIBs.[12]

The lithium-storage properties of the multishelled Co_3O_4 hollow microspheres as anodes were evaluated with the standard Co_3O_4/Li half-cell configuration. Figure 3 a shows the first-cycle discharge–charge voltage profiles of four samples of Co_3O_4 hollow microspheres at a current density of 50 mA g^{-1} in the potential range from 0.05 to 3.0 V. In the first-discharge curves, the potential quickly falls to a 1.1 V plateau and then gradually declines to the cutoff voltage of

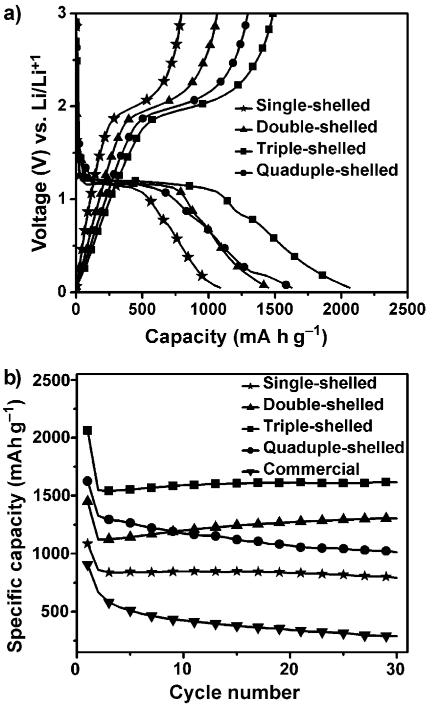

Figure 3. a) First-cycle discharge–charge curves for the multishelled Co_3O_4 hollow microspheres at a current density of 50 mA g^{-1} between 0.05 and 3.0 V. b) Discharge capacity versus cycle number for the prepared Co_3O_4 hollow microspheres and commercial Co_3O_4 at a current density of 50 mA g^{-1}.

0.05 V, in analogy with the behavior of previously reported similar systems.[2,3b,13] The longer the observed plateau is, the higher the achievable power output is.[14] The initial capacity of single-, double-, triple-, and quadruple-shelled Co_3O_4 microspheres is 1087.2, 1450.0, 2063.7, and 1626.2 mA h g^{-1}, respectively. All of these values are higher than the theoretical capacity (890 mA h g^{-1}). The difference between the theoretical and observed capacity is usually ascribed to irreversible reactions, such as the decomposition of the electrolyte.[15]

Figure 3 b highlights the better cycling performance of all multishelled structures with respect to that of the commercial Co_3O_4 sample, wherein triple-shelled Co_3O_4 microspheres showed the highest specific capacity and best cycling performance. After 30 cycles at a current density of 50 mA g^{-1}, the specific capacity of single-, double-, triple-, and quadruple-shelled Co_3O_4 microspheres remained as high as 792.7, 1303, 1615.8, and 1011.5 mA h g^{-1}, respectively, whereas that of commercial Co_3O_4 was only 287.5 mA h g^{-1}. The extra capacity above that offered by the redox reaction may be due to the formation of a thicker solid electrolyte interface (SEI) film[16] or an interfacial lithium-storage mechanism.[17] Interestingly, both double- and triple-shelled Co_3O_4 microspheres showed a remarkable increase in capacity: unusual negative fading rates of −0.56 and −0.16 % were observed during up to 29 cycles after the second cycle, in contrast to the behavior commonly observed for such systems, including that of single- and quadruple-shelled Co_3O_4 samples.[2,13] To our knowledge, the performance of the Co_3O_4-based anode materials for LIBs presented here is the best to date.[2,15b]

As the rate capability is also critical for practical applications, we measured discharge curves at different current densities for the triple-shelled Co_3O_4 microspheres and the commercial Co_3O_4 sample (Figure 4). Even at a high current density of 2000 mA g^{-1}, the triple-shelled Co_3O_4 microspheres can still deliver a capacity of at least 1117.3 mA h g^{-1}, which is far higher than the 205.9 mA h g^{-1} observed for commercial Co_3O_4. In other words, the discharge or charge process can be completed in about 33 min, while a relatively high capacity is maintained; this result is significantly superior to those previously reported (a capacity of only 450 mA h g^{-1} was observed at a similar current density).[18] Remarkably, a stable high capacity of 1505 mA h g^{-1} can still be attained when the current density is decreased to 50 mA g^{-1}. This result suggests that the elastic multishelled structures might indeed be very "breathable".[19]

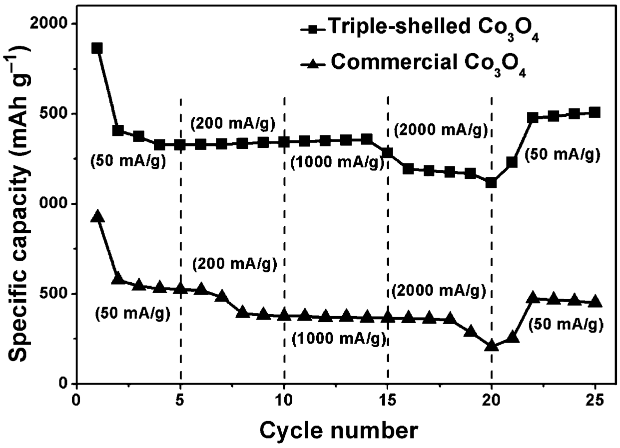

Figure 4. Discharge curves for the triple-shelled Co_3O_4 hollow microspheres and commercial Co_3O_4 at different current densities.

The LIB performance of the triple-shelled Co_3O_4 microspheres was clearly superior to that of the other three types of multishelled Co_3O_4 hollow microspheres synthesized. This discrepancy may be explained by the different volume-occupying rates of the different microsphere types after Li uptake. A smaller volume-occupying rate is unfavorable for a high volumetric specific capacity, whereas a larger volume-occupying rate has a negative effect on the structural stability and thus leads to electrode failure and poor cycling performance (see Figures S5 and S6).[13] An appropriate volume-occupying rate, such as that of the triple-shelled Co_3O_4 microspheres, guarantees a high volumetric specific capacity as well as good structure stability and thus leads to the highest lithium storage and excellent cycling performance.

In this study, the electrodes composed of the multishelled Co_3O_4 hollow microspheres displayed significantly better electrochemical performance than those made from commercial Co_3O_4. The most likely interpretation of these results is based on a combination of observations. First, when the particle size is decreased, there are more atoms residing on the surface, with respect to the volume of the particle, and as a result, the particle is more active for the lithium electrochemical reaction. Second, the unique multishelled structures and the increased porosity of the shells lead to an increase in the electrolyte/Co_3O_4 contact area, a decrease in the effective diffusion distance for both lithium ions and electrons, and thus better rate capabilities.[2] Third, the interior cavities enhance the specific capacity by providing extra space for the storage of Li^+ and improve the cycling performance by buffering against the local volume change during Li^+-insertion/extraction processes.[4]

In summary, uniform multishelled Co_3O_4 hollow microspheres were successfully synthesized in high yield with high purity by a hard-template method. By controlling the size and diffusion rate of the hydrated metal cations and the ion-absorption capability of CMSs we can accurately control the number of shells and the interior structures. When tested as the anode materials for LIBs, these multishelled Co_3O_4 hollow microspheres exhibited excellent rate capacity, good cycling performance, and an ultrahigh specific capacity (1615.8 $mA\,h\,g^{-1}$ at the 30th cycle). The superior performance in LIBs originates from the porous hollow multishelled microstructure, which guarantees more lithium-storage sites, a shorter lithium-ion diffusion length, and sufficient void space to buffer the volume expansion. Given their facile synthesis and improved performance, it can be expected that these multishelled Co_3O_4 hollow microspheres will open a new avenue for the development of the next generation of LIBs with a higher specific capacity, better cycling performance, and a higher rate capacity.

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