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Accurate Control of Multi-shelled Co_3O_4 Hollow Microspheres for High-Performance Anode Materials in Lithium Ion Batteries**

Jiangyan Wang, Nailiang Yang, Hongjie Tang, Zhenghong Dong, Quan Jin, Mei Yang, David Kisailus, Huijun Zhao, Zhiyong Tang, Dan Wang*

Thanks 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] As an example, the anode electrodes made of transition-metal oxides have been explored to exhibit reversible capacities about two- or three-times as large as those based on the conventional graphite materials ($<372 \text{ mAh g}^{-1}$).^[1b] Among various types of transition-metal oxides, cobalt oxide (Co_3O_4) receives special attention since it is expected to have a high capacity (about 1000 mAh g^{-1}) and excellent cycling performance.

Unfortunately, although the best capacity of Co_3O_4 to date has increased to 1450 mAh g^{-1} by using Co_3O_4 micro-/nano-materials,^[2] the practical use of Co_3O_4 as anode electrodes for LIBs is still largely hindered due to their poor capacity retention upon cycling and/or low rate capability.^[3] To circumvent these issues, hollow micro-/nano-structures are used to replace the solid micro-/nano-structures as the LIB anode materials based on the following considerations:^[4] (1) The larger surface area of the hollow structures enables more access for Li ions due to an increased electrode-

electrolyte contact area. (2) The hollow interior provides additional free volume for alleviating the structural strain associated with repeated Li^+ insertion/extraction processes, resulting in the improved cycling stability. (3) Properly prepared multi-shelled hollow micro-/nano-structures not only allow for significantly reduced diffusion paths for both Li ions and electrons (leading to a better rate capability), but also provide more lithium storage sites, resulting in a higher overall capacity.

Recently, significant efforts have been devoted to the fabrication of hollow spheres with multiple shells.^[5] Different metal oxides with the multi-shelled hollow sphere structures have been synthesized based on the soft/hard template methods.^[6] It should be noted that 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 to prepare metal oxide hollow microspheres by using carbonaceous microspheres (CMSs) as the sacrificial templates. The number of shells can be controlled by adjusting the heating conditions and the concentration of metal ions.^[4,7] However, due to the large radii of hydrated cobalt ions, we failed to achieve control over the number of multi-shelled Co_3O_4 hollow microspheres.

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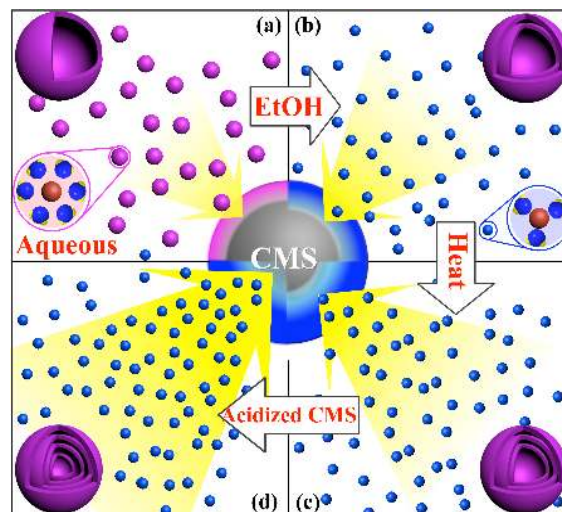


Figure 1. Scheme of the formation mechanism of the multi-shelled Co_3O_4 hollow microspheres under different adsorption conditions.

In order to precisely control the synthesis of multi-shelled Co_3O_4 hollow microspheres using CMSs as templates, we modified our strategy through controlling not only the size and diffusion rate of the hydrated metal cations, but also the absorption capability of CMSs. A pink solution of hydrated cobalt ions ($[\text{Co}(\text{H}_2\text{O})_6]^{2+}$) is observed when the solvent is only deionized water (Fig. 1a), and only single-shelled Co_3O_4 are obtained after calcination (Fig. S1).

When the solvent is changed to a mixture of ethanol and water (1:1, v/v), the color of the solution turns blue-violet, suggesting a

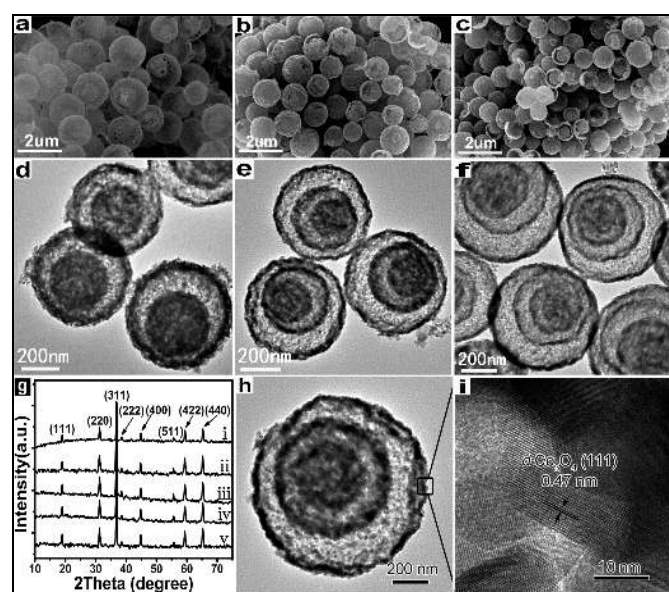


Figure 2. a,b,c) SEM and d,e,f) TEM images of double-, triple-, quadruple-shelled Co_3O_4 hollow microspheres. g) XRD patterns of commercial Co_3O_4 and as-prepared products (i, ii, iii, iv and v represent single-, double-, triple-, quadruple-shelled and commercial Co_3O_4 , respectively). e,f) TEM and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

reduction of aquo groups (H_2O) within the cobalt ion's coordination sphere ($[\text{Co}(\text{H}_2\text{O})_{(6-x)}]^{2+}$, $x = 3-6$).^[8] The reduced hydration within the coordination sphere leads to a reduction in the size of the cobalt ions and a subsequent increased ability to diffuse into CMS templates (Fig. 1b), resulting in double-shelled Co_3O_4 (Fig. 2a and 2d). To further enhance the diffusion rate, the volume fraction of ethanol in the solvent is improved to 75 vol%, and the solutions are heated 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 easily (Fig. 1c), resulting in triple-shelled Co_3O_4 (Fig. 2b and 2e). Besides altering the solution conditions, we have modified the CMSs by immersing them in 0.5 M HCl solution for 2 days. The measured BET specific surface area is 18.8% higher than those without acid treatment, as well as a higher pore volume (Table S2). The larger surface area allows for penetration of more cobalt ions (Fig. 1d), resulting in quadruple-shelled Co_3O_4 (Fig. 2c and 2f). Through the above-mentioned methods, we have yielded multi-shelled Co_3O_4 hollow microspheres with an unprecedented high yield and purity. Based on analysis of more than one hundred Co_3O_4 hollow microspheres for each sample, it was determined that (i) all the multi-shelled Co_3O_4 hollow microspheres had similar sizes (Fig. S2) and (ii) the yield of each type of Co_3O_4 hollow microspheres was very high: 80%, 70%, 75%, and 75%, for single-, double-, triple-, and quadruple-shelled Co_3O_4 microspheres, respectively. For instance, in the preparation of the quadruple-shelled Co_3O_4 hollow microspheres, 75% had quadruple shells and 25% had triple shells (with no observed single- or double- shelled structures) (Fig. S3). Impressively, the prepared Co_3O_4 exhibits excellent rate capacity, good cycling performance and ultrahigh capacity.

The crystalline structures of the prepared Co_3O_4 hollow microspheres were investigated by X-ray diffraction (XRD), with

commercial Co_3O_4 powder for comparison (Fig. 2g). All the reflection peaks were indexed to a pure cubic spinel Co_3O_4 (JCPDS card no. 42-1467, space group: $\text{Fd}3\text{m}$, $a=8.084 \text{ \AA}$),^[3a] with no additional peaks detected. X-ray photoelectron spectroscopy (XPS) was also utilized to understand the chemical composition of as-prepared and commercial Co_3O_4 (Fig. S4). Two characteristic broad peaks encompassing the Co^{2+} and $\text{Co}^{3+} 2p_{3/2}$ at 780.2 eV and Co^{2+} and $\text{Co}^{3+} 2p_{1/2}$ at 795.2 eV are observed, which corresponds to the standard Co_3O_4 phase.^[10] Detailed structural observation from TEM imaging on single Co_3O_4 hollow microsphere clearly reveals nanopores inside the shells (Fig. 2h), probably formed by gas evolution during calcination.^[11] Furthermore, high-resolution TEM (HRTEM) imaging demonstrates the highly crystalline nature of the Co_3O_4 nanoparticles in the shells with the (111) lattices commonly observed (Fig. 2i). Evidently, the porous features of the shells and the preferential (111) orientation of nanoparticles will benefit the application of the Co_3O_4 hollow microspheres in LIBs.^[12]

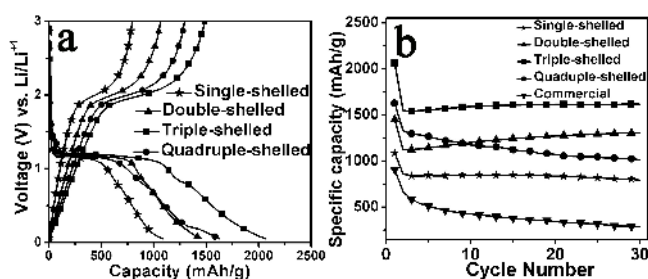


Figure 3. a) First cycle discharge-charge curves of the multi-shelled Co_3O_4 hollow microspheres at a current density of 50 mA g^{-1} between 0.05 and 3.0 V. b) Discharge capacities versus cycle number for the prepared Co_3O_4 hollow microspheres and commercial Co_3O_4 products at a current density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

The lithium storage properties of the multi-shelled Co_3O_4 hollow microspheres as the anodes are evaluated using the standard $\text{Co}_3\text{O}_4/\text{Li}$ half-cell configuration. Figure 3a shows the first discharge-charge voltage profiles of four Co_3O_4 hollow microsphere samples at a current density of 50 mA g^{-1} and in a 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 cut-off voltage of 0.05 V, similar to previous reports.^[2,3b,13] And the longer the plateau we can observe, the higher power-output behavior we can achieve.^[14] The initial capacities of single-, double-, triple-, and quadruple-shelled Co_3O_4 microspheres are 1087.2, 1450.0, 2063.7 and 1626.2 mAh g^{-1} , respectively. All of these are higher than their theoretical values (890 mAh g^{-1}), which is usually ascribed to irreversible reactions such as the decomposition of the electrolyte.^[15]

Figure 3b highlights that all multi-shelled structures show much better cycling performance than the commercial Co_3O_4 , with triple-shelled Co_3O_4 microspheres showing the highest specific capacity and best cycling performance. Here, after 30 cycles at a current density of 50 mA g^{-1} , the specific capacities of single-, double-, triple-, and quadruple-shelled Co_3O_4 microspheres remain as high as 792.7, 1303, 1615.8 and 1011.5 mAh g^{-1} , respectively, while which of commercial Co_3O_4 is only 287.5 mAh g^{-1} . The extra capacity in addition to the redox reaction may be due to the formation of a thicker solid electrolyte interface (SEI) film,^[16] or interfacial lithium storage mechanism.^[17] Interestingly, we also notice that both double- and triple-shelled Co_3O_4 microspheres show a remarked

increase in capacity, delivering unusual negative fading rates of -0.56% and -0.16% on cycling up to 29 cycles from the second cycle, which is different from the commonly observed cases including 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]

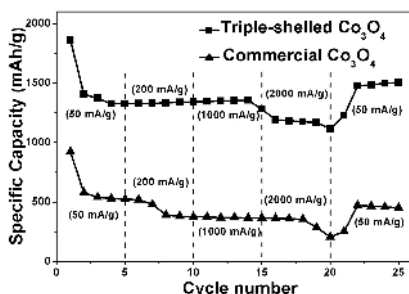


Figure 4. Discharge curves of the triple-shelled Co_3O_4 hollow microspheres and commercial Co_3O_4 at different current densities.

Considering that the rate capability is also critical for practical applications, discharge curves at different current densities for the triple-shelled Co_3O_4 microspheres and the commercial Co_3O_4 products are measured. 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 $1117.3 \text{ mAh g}^{-1}$, which is far higher than 205.9 mAh g^{-1} for commercial Co_3O_4 . In another word, the discharge or charge process can be completed in about 33 minutes while still obtaining a relatively high capacity, which is significantly superior to other reports (only 450 mAh g^{-1} is obtained at a similar current density).^[18] Remarkably, a stable high capacity of 1505 mAh g^{-1} can be still attained when the current density is reduced back to 50 mA g^{-1} . This result might suggest that the elastic multi-shelled structures are indeed very “breathable”.^[19]

Comparing the LIB performance of the four types of the prepared multi-shelled Co_3O_4 hollow microspheres, it is easily found that the triple-shelled Co_3O_4 microspheres are superior to all. This discrepancy may be assigned to their different volume occupying rates after Li uptake. A smaller volume occupying rate is unfavourable for the high volumetric specific capacity, while a larger one does harm to the structural stability, leading to the electrode failure and the poor cycling performance (Fig. S5 and S6).^[13] An appropriate volume occupying rate, as which of the triple-shelled Co_3O_4 microspheres, guarantees the high volumetric specific capacity as well as a good structure stability, leading to the highest lithium storage, and excellent cycling performance.

Based on these results, we can conclude that the electrodes made of the multi-shelled Co_3O_4 hollow microspheres displayed a significantly better electrochemical performance than those made from commercial Co_3O_4 . The most likely interpretation is based on a combination of observations. First, by reducing the particle size, there will be more atoms residing on the surface, making it more active for lithium electrochemical reaction. Second, the unique multi-shelled structures and the increased porosity of the shells will increase the electrolyte/ Co_3O_4 contact area and reduce the effective diffusion distance for both Li ions and electrons (leading to better rate capabilities).^[2] Third, the interior cavities not only provide extra space for the storage of Li^+ (giving rise to the enhancement of the specific capacity), but also buffer against the local volume change

during Li^+ insertion/extraction processes, hence improving the cycling performance.^[4]

In summary, the uniform multi-shelled Co_3O_4 hollow microspheres were successfully synthesized with a high yield and purity through 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 multi-shelled Co_3O_4 hollow microspheres exhibit excellent rate capacity, good cycling performance and ultrahigh specific capacity ($1615.8 \text{ mAh g}^{-1}$ at the thirtieth cycle). The superior performance in LIBs originates from the porous hollow multi-shelled microstructure, which guarantees more lithium storage sites, a shorter Li-ion diffusion length and sufficient void space to buffer the volume expansion. Considering the facile synthesis and the improved performance, it can be expected that the prepared multi-shelled Co_3O_4 hollow microspheres will open a new avenue for development of the next generation of LIBs with higher specific capacity, better cycling performance and higher rate capacity.

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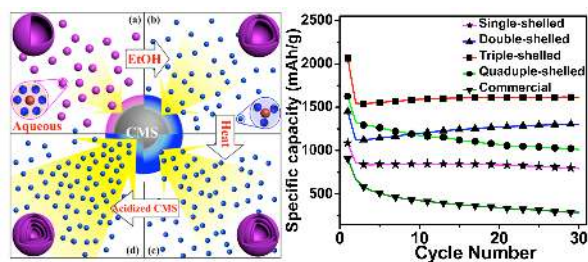
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Lithium Ion Batteries

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Multi-shelled Co_3O_4 hollow microspheres are prepared with a high yield and purity through a hard-template method. Due to the porous hollow multi-shelled microstructure, which guarantees a shorter Li^+ diffusion length and sufficient void space to buffer the volume expansion, these multi-shelled Co_3O_4 microspheres exhibit excellent rate capacity, good cycling performance and ultrahigh specific capacity ($1615.8 \text{ mAh g}^{-1}$ at the thirtieth cycle for triple-shelled Co_3O_4), as the anode materials for LIBs.