Highly Enhanced Lithium Storage Capability

Hollow micro- and nanostructures have attracted considerable attention in the past decade because of their low density, large specific surface area, and excellent loading capacity, which can serve as ideal building blocks for fabrication of lightweight structural materials and in a wide range of promising applications.[1–6] Specifically, anisotropic hollow architectures that have nonspherical shapes and well-defined regular morphologies are of particular interest, as they are expected to provide more handles to tailor the properties for different applications such as energy storage,[7–10] biomedicine[11–13] to provide more handles to tailor the properties for different applications such as energy storage,[7–10] biomedicine[11–13] and catalysis.[14–16] The most popular approach to achieve hollow structures involves the use of various removable or sacrificial templates, including hard ones such as monodispersed polymer,[17] silica[18] and carbon[19] as well as soft ones, for example, emulsion droplets[20] and gas bubbles.[21] However, the geometry of resulting hollow structures is usually spherical, possibly due to the paucity of proper nonspherical templates available and the difficulty in preserving the shape with high-curvature shells. Recently, some novel template-assisted approaches based on different principles such as galvanic replacement, Kirkendall effect, and chemical etching have been employed to prepare nonspherical hollow nanostructures.[22–27] Despite continuous progress that has been made in recent years, developing a simple and reliable method for the rational design and synthesis of anisotropic hollow structures with well-defined nonspherical geometries is highly desirable and still remains challenging.

Metal-organic frameworks (MOFs), a novel class of porous materials consisting of metal ions or clusters coordinated to organic molecules, have been intensively studied as a result of their diverse structural topologies, tunable functionalities as well as versatile applications in gas storage and separation, catalysis, and biomedical imaging.[28–31] In addition, inspired by their high surface area and porosities, MOFs have been demonstrated as promising templates or precursors to fabricate porous nanostructured materials, primarily via thermolysis.[32–46] For example, by choosing suitable MOFs with high thermal stability, their functions as both a sacrificial template and a secondary carbon precursor have been utilized to construct highly porous carbon.[32–35] Spherical MOFs have been employed as sacrificial templates to prepare multi-ball-in-ball hybrid metal oxides by taking advantage of their unique reactivity and thermal behavior.[37] Prussian blue analogues with various formulas served as removable templates or precursors in the synthesis of nonspherical hollow structures including microboxes and nanocages have also been reported.[38–42] Nevertheless, even with MOF-templating strategies, there has been rarely success in producing anisotropic hollow architectures with highly symmetric geometry configuration due to additional difficulties ranging from lack of proper uniform MOF template with regular morphology to the conversion of template with high residual stress in control.

Herein, we develop a simple and scalable approach for synthesizing monodispersed Co-based zeolitic imidazolate frameworks, [Co(mim)]_{n} \text{(ZIF-67; mim = 2-methylimidazolate)} with rhombic dodecahedral morphology at room temperature and then obtaining high symmetric Co$_3$O$_4$ hollow dodecahedra by thermal treatment of as-synthesized ZIF-67.
Zeolitic imidazolate frameworks are considered to be a new subfamily of MOFs, which frequently have expanded zeolite topologies and exceptional chemical and thermal stability.\cite{47} We chose Co$_3$O$_4$ in order to demonstrate the concept in view of hardly succeeding in the synthesis of high symmetric anisotropic Co$_3$O$_4$ hollow structures and its promising technological applications in wide range of fields. By taking advantage of the unique topology and thermal behavior of ZIF-67, we have fabricated anisotropic Co$_3$O$_4$ hollow dodecahedra through manipulation of the calcination conditions and investigated the changes of shell structure. Furthermore, these dodecahedra exhibited high specific capacity and excellent cycling performance when applied as an anode material for lithium ion batteries.

The schematic illustration for the fabrication of porous Co$_3$O$_4$ hollow dodecahedra is shown in Scheme 1. First, a novel method for the synthesis of highly uniform ZIF-67 particles with rhombic dodecahedral morphology at room temperature was developed. A subsequent two-step thermal conversion process was then introduced to transform ZIF-67 into Co$_3$O$_4$ hollow dodecahedra.

The size and morphology of the as-synthesized ZIF-67 was investigated by field-emission scanning electron microscopy (FESEM), as shown in Figure 1a. It can be clearly seen that the formation of ZIF-67 particles have good uniformity with size ca. 1.5 μm. A magnified FESEM image in Figure 1b depicts the very smooth surface over the whole particle, indicating the single-crystal-like feature of the ZIF-67. A single ZIF-67 crystal from different view positions reveals that it has regular rhombic dodecahedral morphology and is enclosed by 12 well-defined [110] facets on the surface, as shown in I, II and III. Figure 1c presents X-ray diffraction (XRD) patterns of the ZIF-67 and their simulated results. All the diffraction peaks of the formed ZIF-67 in the 2θ range of 5–40° match well with the simulated as well as the published results.\cite{48} The N$_2$ adsorption measurement of ZIF-67 (Figure S1, Supporting Information) shows a type I isotherm and gives a Brunauer-Emmett-Teller (BET) specific surface area of 1562 m$^2$ g$^{-1}$, which is comparable to those of ZIF-8 (1630 m$^2$ g$^{-1}$).\cite{47} To the best of our knowledge, this is the first synthesis of single-crystalline ZIF-67 MOFs with perfect rhombic dodecahedral morphology. Figure 1d gives the thermogravimetric analysis (TGA) curves of ZIF-67. It is clearly found that ZIF-67 underwent significant weight loss when heating to 350 °C in air and 500 °C in nitrogen atmosphere, respectively. On the basis of TGA results, the as-synthesized ZIF-67 template was first heated at 350 °C in nitrogen gas and then annealed at the same temperature in flowing air to obtain the final products. It is noticeable that thermal treatment in nitrogen gas is favorable for preserving the configuration of ZIF-67 due to the fact that carbon generated at the first calcination might act as a temporal buffer, effectively hindering further contraction of MOFs.\cite{43}

The crystallographic structure and phase purity of the product after calcination was examined by XRD (Figure 2a). All diffraction peaks correspond well to a pure cubic spinel
Co$_3$O$_4$ (JCPDS card No. 42–1467, space group: Fd3m, lattice constant a = 8.084 Å). No diffraction peaks from residues or impurities are observed, suggesting that the product is of high purity. Figure 2b shows an FESEM image of the products, demonstrating that they preserve well the uniform size and rhombic dodecahedral morphology of the MOF precursor particle. Magnified FESEM images of Co$_3$O$_4$ dodecahedra oriented nearly along the [100] and [110] axes and the corresponding model illustration are presented in Figures 2c–e. It is found that the surface of dodecahedra is very rough, indicating the formation of pores during the calcination process. The interior structure of the Co$_3$O$_4$ dodecahedra is further elucidated by transmission electron microscopy (TEM) and selected-area electron diffraction (SAED). The highly symmetric dodecahedral shell structures can be observed more distinctly and the hollow interiors are clearly revealed by the sharp contrast between the centers and edges of dodecahedra from the TEM image in Figure 2f. The magnified TEM image further confirms that this dodecahedral-like structure is porous and composed of nanoparticles with a size of a few nanometers (Figure 2g). The high-resolution TEM image (Figure 2h) taken near the dodecahedra edges displays distinct lattice fringes with d spacings 0.29 and 0.24 nm, which are in good agreement with the (220) and (311) lattice planes of Co$_3$O$_4$, respectively. In addition, a large number of steps/kinks can be observed in the exterior surfaces of the composed nanoparticles. The SAED pattern (Figure 2h inset) shows multiple diffraction circles, implying the polycrystalline features of these Co$_3$O$_4$ dodecahedra. The elemental mapping measurement confirms the co-existence and homogenous dispersion of Co and O elements within the dodecahedra (Figures 2i–k). The texture and porosity of Co$_3$O$_4$ hollow dodecahedra was quantified by measuring the N$_2$ adsorption-desorption isotherm (Figure S2, Supporting Information). The uniform Co$_3$O$_4$ hollow dodecahedra are found to have a moderate BET specific surface area of 54.5 m$^2$ g$^{-1}$. In addition, the pore size distribution curve (the inset in Figure S2) obtained using Barrett-Joyner-Halenda (BJH) method reveals a bimodal nature with a narrow distribution centered at 10 nm and a relatively wide distribution centered at 18 nm.

To understand the influence of calcination temperatures on the morphology and structure of the products, the ZIF-67 were treated at 425, 500 and 575 °C, respectively. At the temperature of 425 °C, the products still retained well the geometries and dimensions of the ZIF-67 template, whereas a few holes occurred on their surfaces (Figures S3a and b, Supporting Information). As the temperature increases to 500 °C, the products could only maintain a basic framework of dodecahedra and their porous shell shrunk into a complex hierarchical structures constructed by worm-like Co$_3$O$_4$ subunits (Figures S3c and d, Supporting Information). Further increasing the temperature to 575 °C,

The initial dodecahedral framework had entirely collapsed and some agglomerates with irregular shape were found in the products (Figures S3e and f, Supporting Information). XRD analysis confirmed that all annealed samples at 425, 500 and 575 °C can be assigned to a pure cubic spinel Co$_3$O$_4$ (Figure S4, Supporting Information). Nevertheless, the diffraction peaks of Co$_3$O$_4$ became more intense and shaper with increasing calcination temperature, indicating the growth of crystallites and improved crystallinity. Furthermore, thermally converted products at elevated temperature were accompanied by a considerable decrease in the BET specific surface area, from 40.25 m$^2$ g$^{-1}$ for the porous Co$_3$O$_4$ hollow dodecahedra obtained at 425 °C to only 9.72 m$^2$ g$^{-1}$ for the Co$_3$O$_4$ irregular agglomerates obtained at 575 °C (Figure S5, Supporting Information). Co$_3$O$_4$ hollow dodecahedra fabricated by this strategy have highly porous shells consisting of small particles with size of several nanometers and posses a BET surface area ranging from 40.25 to 54.5 m$^2$ g$^{-1}$. The existence of mesopores in Co$_3$O$_4$ hollow dodecahedra could increase the interfacial contact between the electrolyte and the electrode material, which may provide efficient penetration of the electrolyte into the active materials and greatly enhance the diffusion kinetics within the electrode.

Based on the above observations, the transformation of ZIF-67 into porous Co$_3$O$_4$ hollow dodecahedra may undergo a non-equilibrium inter-diffusion process.[44,49] At the beginning of the thermal oxidation of ZIF-67, an initial intermediate shell was formed on their surface. Although this initial layer acting as an interface separated the inner ZIF-67 from the outside atmospheric oxygen, the out diffusion of ZIF-67 still occurred due to the interface consisting of an intermediate shell with lots of vacancies. The out diffusion rate of ZIF-67 is larger than that of atmospheric oxygen during the oxidation reactions, which may lead to a hollow cavity. Owing to the volume loss and release of internally generated gaseous i.e. CO$_2$, H$_2$O and N$_2$O$_3$ during the inter-diffusion process, the porous dodecahedra composed of nanoparticles were finally formed. However, as the temperatures increases, the non-equilibrium inter-diffusion and gas release accelerated, and the porous hollow architectures gradually collapsed.

We also investigated the effect of varying the morphology of the initial ZIF-67 particles on the formation of final Co$_3$O$_4$ products. The initial ZIF-67 templates could be prepared as truncated dodecahedra rather than rhombic dodecahedra by adjusting the concentration of reactants and using H$_2$O as solvents (Figures S6a and b). These initial ZIF-67 templates with truncated dodecahedral morphology were heated at 350 °C for the formation of final products. As seen in Figure 3a and Figure S6c, the obtained Co$_3$O$_4$ products are high symmetric polyhedrons with particle sizes ranging from 500 nm to 1 µm. Two typical magnified FESEM images of polyhedrons in different orientations further illustrate that they have a well-defined porous shell, inheriting well the overall truncated dodecahedral morphology of the templates with 18 facets exposed (Figure 3b and Figure S6d, Supporting Information). TEM images as given in Figure 3c and d further reveal these Co$_3$O$_4$ truncated dodecahedra are hollow and their shells are constructed of compactly arranged nanoparticles, which are similar to that of the previous dodecahedra.

To explore the advantages of the porous Co$_3$O$_4$ hollow dodecahedra, we studied their lithium storage properties as anodes with the standard half-cell configuration. Figure 4a shows the first five consecutive cyclic voltammetry (CV) curves of the electrodes fabricated by porous Co$_3$O$_4$ hollow dodecahedra at a scan rate of 0.1 mV s$^{-1}$. In the first cycle, there is an intense peak at around 0.85 V in the discharge process, corresponding to the initial reduction of Co$_3$O$_4$ to metallic Co accompanying with the formation of Li$_2$O. Meanwhile, a broad peak at about 2.1 V in the charge process, which should be ascribed to the oxidation of metallic Co to Co$_3$O$_4$ and the decomposition of Li$_2$O. From the second cycle, the reduction peak shifts to a higher potential of about 1.05 V, while the oxidation peak position remains almost unchanged. The subsequent CV curves exhibit good reproducibility and overlap very well, indicating the good reversibility of the electrochemical reactions. Figure 4b shows the representative charge–discharge voltage curves of the Co$_3$O$_4$ hollow dodecahedra at a current density of 100 mA g$^{-1}$ in the voltage range of 0.01–3 V, which is consistent with typical charge–discharge
Figure 4. Electrochemical properties of the porous Co$_3$O$_4$ hollow dodecahedra electrode. (a) Cyclic voltammetry curves of the initial 5 cycles scanned at the rate of 0.1 mV s$^{-1}$. Galvanostatic charge–discharge voltage profiles at a current density of 100 mA g$^{-1}$. (c) Cycling performance and Coulombic efficiency at a current rate of 100 mA g$^{-1}$. (d) Rate capabilities at various current rates between 1 C and 10 C.

The excellent electrochemical performance of our products can be explained by their unique anisotropic hollow structure with a variety features. First, the composed nanometer-sized subunits would shorten the Li$^+$ ions diffusion distance and improve the kinetics of charge carrier. Second, the presence of a large number of atomic steps and kinks in the facets of composed subunits might be more beneficial to the reaction of Li with Co$_3$O$_4$.[55] Last, the void space within the hollow dodecahedra and the hierarchically porous shells provide abundant channels and sites for efficient electrolyte penetration, enhance the contact area between the electrode and electrolyte, and buffer the large volume changes induced by lithium insertion/extraction.

In summary, high symmetric porous Co$_3$O$_4$ hollow dodecahedra with nanometer-sized building blocks have been synthesized through a simple strategy, which involves the preparation of Co-containing ZIF-67 template with rhombic dodecahedral morphology and subsequent two-step thermal annealing the template at moderate temperature. The effects of the annealing temperatures on the morphology of the final products have been investigated and the formed hollow dodecahedra may undergo a non-equilibrium inter-diffusion process. Benefiting from their unique structural features, these elegant anisotropic hollow dodecahedra exhibit high lithium storage capacities and excellent cycling performance as anode materials for lithium ion batteries. Furthermore, since MOFs can be prepared with desired compositions and morphologies, the current MOFs-templated strategy is quite versatile and can be easily extended for synthesis of other well-defined hollow metal oxides, which may have promising applications in energy conversion and storage, catalysis, and drug delivery systems.
Experimental Section

Synthesis of ZIF-67: Co(NO$_3$)$_2$$\cdot$6H$_2$O (1.455 g, 0.5 m mol) was dissolved in the binary mixture of 40 ml methanol (MeOH) and 40 ml ethanol (EtOH). 2-methylimidazole (1.642 g, 2 m mol) was dissolved in another mixture of 40 ml MeOH and 40 ml EtOH. The above two solutions were then mixed vigorously for 30 s, and the resulting solution was incubated at room temperature for 24 h. The resulting purple precipitates were collected by centrifugation and washing with ethanol several times and finally vacuum-dried at 80 °C. ZIF-67 with truncated dodecahedral morphology was synthesized by the same procedure except mixing the solution of 145.5 mg Co(NO$_3$)$_2$$\cdot$6H$_2$O in 5 ml H$_2$O and 3.284 g 2-methylimidazole in 15 ml H$_2$O.

Preparation of High Symmetric Co$_3$O$_4$ Hollow Dodecahedra: A combustion boat loaded the powder of ZIF-67 was placed in a tube furnace and then heated to 350 °C at a rate of 5 °C min$^{-1}$ and maintained at this temperature for 30 min under nitrogen gas flow. After that, the nitrogen gas was switched off and the furnace was still kept at this temperature for another 30 min in air. Last, the product was taken out and its color was found to change from purple to black.

Characterization: The crystal phase of the prepared samples was characterized by X-ray powder diffractometer (Bruker D8 Advance) with Cu Kα radiation (λ = 1.5406 Å). The morphology and structure of the as-received products were studied using field emission scanning electron microscope (FESEM, JEOL JSM-7600F) and transmission electron microscope (HRTEM, JEOL JEM-2100F), respectively. Energy-dispersive X-ray (EDX) analysis and elemental mapping were obtained using the energy-dispersive X-ray spectroscopy attached to the JSM-2100F. The thermogravimetric analysis (TGA) was conducted by using a Shimadzu-60 thermo-analyzer under a nitrogen and air flow at 10 °C min$^{-1}$ from room temperature to 600 °C, respectively. The N$_2$ adsorption-desorption isotherm were measured by using a Quantachrome Instruments Autosorb AS-6B equipment.

Electrochemical Measurements: Electrochemical measurements were carried out at room temperature based on a coin-type half cell configuration. The working electrode was fabricated by mixing active materials, super-P carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10 in N-methyl-2 pyrrolidinone (NMP) solvent. The resulting slurry was coated onto Cu foil and dried at 60 °C for 12 h. The coin cells were assembled in argon filled glove box with moisture and oxygen concentrations less than 1 ppm by using lithium metal as counter electrode, Celgard2400 membrane as the separator, and 1 M LiPF$_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) as the electrolyte. The cells were tested on a NEWARE multichannel battery test system with galvanostatic charge and discharge (voltage window of 0.01–3 V). Cyclic voltammetry was carried out on a CHI660C electrochemical workstation.

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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