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General Approach for MOF-Derived Porous Spinel AFe$_2$O$_4$ Hollow Structures and Their Superior Lithium Storage Properties

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Supporting Information

ABSTRACT: A general and simple approach for large-scale synthesis of porous hollow spinel AFe$_2$O$_4$ nanoarchitectures via metal organic framework self-sacrificial template strategy is proposed. By employing this method, we can successfully synthesize uniform NiFe$_2$O$_4$, ZnFe$_2$O$_4$, and CoFe$_2$O$_4$ hollow architectures that are hierarchically assembled by nanoparticles. When these hollow microcubes were tested as anode for lithium ion batteries, good rate capability and long-term cycling stability can be achieved. For example, high specific capacities of 636, 449, and 380 mA h g$^{-1}$ were depicted by NiFe$_2$O$_4$, ZnFe$_2$O$_4$, and CoFe$_2$O$_4$, respectively, at a high current density of 8.0 A g$^{-1}$. NiFe$_2$O$_4$ exhibits high specific capacities of 841 and 447 mA h g$^{-1}$ during the 100th cycle when it was tested at current densities of 1.0 and 5.0 A g$^{-1}$, respectively. Discharge capacities of 390 and 290 mA h g$^{-1}$ were delivered by the ZnFe$_2$O$_4$ and CoFe$_2$O$_4$, respectively, during the 100th cycle at 5.0 A g$^{-1}$.

KEYWORDS: general method, metal organic framework, spinel, hollow structure, lithium ion batteries

1. INTRODUCTION

Hollow micro/nanostructures with unique structural properties, have emerged as a key interest of research for widespread applications, such as catalysis,$^{1,2}$ drug delivery,$^{3,4}$ gas sensors,$^{5,6}$ energy conversion, and storage systems.$^{7,8}$ The nanoscale outer shell favors fast mass transfer of reactants or charge carriers, effectively utilizing the inner surface when these hollow structures are used as catalysts or in energy storage devices. On the other hand, the interior cavities can catalytically serve as a nanoreactor or function as a nanocontainer for controlled drug release applications.$^{9,10}$ Hollow-structured transition metal oxides (TMOs), especially ternary TMO with spinel structure (AB$_2$O$_4$), are promising functional materials applied in various fields ranging from electrocatalysis, chemical sensors to photonic and energy storage devices.$^{11,12}$ In particular, hollow micro/nanostructured ternary TMOs with controllable size, shape, interior architectures, and varieties of framework, compositions are highly desired, owing to their rich variety of crystallographic arrangements, low density, high porosity, high surface area, and shell permeability. Among them, Fe-based ternary oxides are known for their nature abundance, nontoxicity and cost efficiency.$^{13,14}$ In recent years, different strategies have been exploited to fabricate various hollow architectures with optimized structures and physical/chemical properties for specific applications. For example, hollow mesoporous NiCo$_2$O$_4$ nanocages have been successfully prepared via a Cu$_2$O-templated method and showed excellent oxygen evolution reaction electrochemical activity.$^{20}$ An improved microwave absorbing performance was detected using CoFe$_2$O$_4$ hollow sphere/graphene composites, which were synthesized by a facile vapor diffusion method.$^{21}$ Lou et al. have reported a two-step solution based synthesis of ZnMn$_2$O$_4$ ball-in-ball hollow microspheres, and obtained optimized lithium storage performance.$^{22}$ Although exciting progress have been achieved, controllable synthesis of ternary TMOs with well-defined complex hollow micro/nano-architectures, remains a great challenge.

Metal–organic frameworks (MOFs) assembled by metal centers/clusters with bridging organic ligands, are a fascinating class of hybrid porous crystalline material featured with structural diversity, tailorable porosity and chemical properties.$^{23,24}$ Recently, considerable attention has been focused on

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employing MOFs as self-sacrificial templates for the synthesis of novel hollow/porous metal oxide nanoarchitectures.\textsuperscript{29,30} Comparing to other strategies, metal oxides derived from MOF templates often exhibit distinct merits such as uniform size, hierarchial porosity, and large surface area and have been proven to perform extraordinarily in energy storage.\textsuperscript{31} Despite great success accomplished in the past, ultrahigh oxygen evolution activity and good mechanical durability.\textsuperscript{35} For example, a controlled pyrolysis method was utilized to synthesize hierarchically porous carbon-coated ZnO dots, which showed promising lithium storage performance when it was evaluated as anode for LIBs.\textsuperscript{34} Hybrid CoO\textsubscript{0.5}ZnO\textsubscript{0.5}porous nanowire arrays were successfully grown on Cu foil through a carbonization process of MOF and achieved novel hollow and porous structures, 0.094g cobalt acetate tetrahydrate and 0.07g zinc acetate were used with the similar methods.

### 2. CHARACTERIZATION

2.1. Material Synthesis. 2.1.1. Preparation of Fe-Containing MOF Fe\textsubscript{4}(Fe(CN)\textsubscript{6})\textsubscript{3} (Prussian Blue, PB) Cubes.\textsuperscript{40} In a typical procedure, 4 g of polyvinylpyrrolidone (PVP, K30, MW ~ 40 000) was dissolved into 50 mL of HCl solution (0.1 M) under magnetic stirring for 30 min to obtain a clear solution. Then, 0.12 g of K\textsubscript{4}Fe(CN)\textsubscript{6}·3H\textsubscript{2}O was added into above solution. After stirring for another 30 min, a clear light yellow solution was obtained. The bottle was sealed and then placed into an electric oven for 24 h at 80 °C. The final obtained blue product was filtered and washed three times with ethanol and distilled water. Finally, the sample was dried in a vacuum oven at 70 °C for 12 h.

2.1.2. Preparation of AFe\textsubscript{2}O\textsubscript{4} Microcubes. The conversion of the Fe-based MOFs precursor microcubes into hollow and porous spinel AFe\textsubscript{2}O\textsubscript{4} microcubes is as follows: Using NiFe\textsubscript{2}O\textsubscript{4} as an example, stoichiometric amount of Fe-based MOFs precursor and nickel acetate tetrahydrate (e.g., 0.1 g of Fe-based MOFs precursor and 0.094 g of nickel acetate tetrahydrate) were dispersed into 20 mL of ethanol under constant stirring. After stirring for 10 min, the solution was heated to 70 °C to evaporate the ethanol. After all the solvent evaporated, the product was collected and ground for 5 min. The ground mixture was then heated to 700 °C with a temperate ramp of 2 °C min\textsuperscript{-1} for 6 h in air. For the preparation of CoFe\textsubscript{2}O\textsubscript{4} and ZnFe\textsubscript{2}O\textsubscript{4} hollow and porous structures, 0.094g cobalt acetate tetrahydrate and 0.07g zinc acetate were used with the similar methods.

### 3. RESULTS AND DISCUSSION

The crystal structure of the as-prepared Prussian blue (PB) was confirmed by X-ray diffraction (XRD) analysis. All the diffraction peaks (Supporting Information Figure S1a) of PB can be indexed to Fe\textsubscript{4}(Fe(CN)\textsubscript{6})\textsubscript{3} with a cubic structure (JCPDS card no. 00-010-0239). Fourier transform infrared spectroscopy (FTIR) analysis (Supporting Information Figure S1b) shows the characteristic stretching peaks of −C≡N− groups at 2083 cm\textsuperscript{-1} and the Fe\textsuperscript{3+}−CN−Fe\textsuperscript{3+} groups at 499 cm\textsuperscript{-1}, indicating the formation of PB.\textsuperscript{5,44} A vibrational band at 2154 cm\textsuperscript{-1} of Raman spectrum (Supporting Information Figure S1c) corresponds to the stretching vibration of −C≡N− groups.\textsuperscript{5,46} From the thermogravimetric analysis (TGA) (Supporting Information Figure S1d), it is observed that the thermal decomposition of PB starts at around 285 °C in air. Low-magnification field-emission scanning electron microscopy (FESEM) image (Supporting Information Figure S1e) reveals uniformly distributed cubes with an average lateral size of around 1 μm. Further observation (Supporting Information Figure S1f) indicates that the surfaces of the micron-sized cubes are smooth. TEM image (Supporting Information Figure S1g)
verifies the solid nature of the PB. The specific surface area of PB is calculated to be 4.35 m² g⁻¹ based on the Brunauer–Emmett–Teller (BET) analysis of the nitrogen absorption/desorption isotherm (Supporting Information Figure S1h).

The schematic illustration for the general synthetic process of the spinel AFe₂O₄ hollow structures is depicted in Figure 1. A second metal ion (A⁺) is uniformly mixed with PB by grinding. During the annealing process, the outer surface of PB and A⁺ react with oxygen forming a shell of AFe₂O₄. Simultaneously, a core/shell-structured intermediate is formed. Then small voids are generated when the inner core PB diffuses (J_PB) out and across the AFe₂O₄ forming new oxide layers. After all PB is consumed, a cubic hollow shell forms.²⁹,⁴⁷,⁴⁸ By changing the composition of the second salt, different ternary TMO hollow structures can be obtained. To validate the generality of this method, we synthesized hollow structured NiFe₂O₄, CoFe₂O₄, and ZnFe₂O₄. By employing the above process, we achieved large-scale synthesis of other single-phase mixed valence metal oxides with hollow architectures.

For the as-obtained NiFe₂O₄, all the diffraction peaks (Figure 2) can be assigned to the cubic NiFe₂O₄ structure (JCPDS card no. 00-010-0325) without additional peaks from other phases. The cube morphology of the PB is well maintained after thermal treatment. The FESEM images in Figure 3a,b display the homogeneously distributed NiFe₂O₄ cubes with a uniform size of around 1 μm, and the surface of the cube is rougher than the PB as it is composed of lots of nanocrystals. Transmission electron microscopy (TEM) images (Figure 3c,d) validate that the nanocrystal is of 15–30 nm in size and the wall of the hollow cube is around 250 nm in thickness. Magnifying on one nanocrystal, a lattice spacing of 4.82 Å is observed (Figure 3e) which can be indexed to the {111} set of planes of cubic NiFe₂O₄. The indexed fast Fourier transform (FFT) pattern (Figure 3e inset) taken from the marked region of Figure 3e further confirms that it is single crystalline. An elemental distribution investigation was carried out by energy-filtered TEM technique (Figure 3g–i) of the whole area of Figure 3f, which clearly demonstrates the coexistence and homogeneous distribution of Fe, Ni, and O elements.

Figure 2. XRD patterns of the NiFe₂O₄ hollow cubes.

Figure 3. (a and b) FESEM images at different magnifications of the porous NiFe₂O₄ hollow cubes. (c and d) TEM images of the porous NiFe₂O₄ hollow cubes. (e) HRTEM image showing the assembled nanoparticles of NiFe₂O₄ hollow cubes and (inset) FFT pattern of the marked region. (f) HRTEM image showing the lattice fringes of cubic NiFe₂O₄. (f–i) Elemental mappings of the porous NiFe₂O₄ hollow cubes.

Figure 4. XRD patterns of the CoFe₂O₄ and ZnFe₂O₄ hollow cubes.

Pure CoFe₂O₄ (cubic structure, JCPDS card no. 00-022-1086) and ZnFe₂O₄ (cubic structure, JCPDS card no. 00-022-1012) phases are formed without any other detectable impurities. FESEM images of CoFe₂O₄ (Figure 5a,b) and ZnFe₂O₄ (Figure 5d,e), reveal similar cube morphology with uniform sizes (about 1 μm). Their hollow interiors can be readily formed, which are unambiguously disclosed by TEM images (Figure 5c for CoFe₂O₄ and Figure 5f for ZnFe₂O₄).

Ternary TMOs, especially Fe-based metal oxides, have found great potential in energy storage application in recent years. The lithium storage properties of the hollow structured ternary metal oxides were evaluated using a half-cell configuration with Li metal as the counter-electrode and reference electrode in the
voltage range of 0.005–3.0 V. The electrochemical behavior of NiFe$_2$O$_4$ was analyzed by performing cyclic voltammetry (CV) at a scan rate of 0.2 mV s$^{-1}$. As indicated in Figure 6a, a minuscule hump and a dominant peak, located at 1.35 and 0.35 V, are detected in the first cathodic curve. The small hump may be due to intercalation of Li into the NiFe$_2$O$_4$ lattice. The dominant peak corresponds to the reduction of Ni$^{2+}$ and Fe$^{3+}$ to metallic Ni and Fe nanoparticles, and is accompanied by the formation of a solid electrolyte interphase (SEI) film. In the following anodic sweep, it can be observed that one pronounced peak is at 1.73 V, a shoulder peak is at 2.12 V, and they are associated with the reoxidation of Ni and Fe, respectively (eqs 2 and 3). From the second curve onward, the main cathodic peak shifts to 0.8 V with a shoulder peak at 1.2 V, indicating a different reduction mechanism (eq 2). The second and third curves almost overlap with each other, suggesting good reversibility of the electrochemical reactions.

\[
\begin{align*}
\text{NiFe}_2\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- & \rightarrow \text{Ni} + 2\text{Fe} + 4\text{Li}_2\text{O} \quad (1) \\
\text{Ni} + \text{Li}_2\text{O} & \leftrightarrow \text{NiO} + 2\text{Li}^+ + 2\text{e}^- \quad (2) \\
2\text{Fe} + 3\text{Li}_2\text{O} & \leftrightarrow \text{Fe}_2\text{O}_3 + 6\text{Li}^+ + 6\text{e}^- \quad (3)
\end{align*}
\]

The first three cycles of galvanostatic discharge–charge voltage profiles of the NiFe$_2$O$_4$ electrode are investigated at a current density of 0.1 A g$^{-1}$ between 0.005 and 3.0 V. As shown in Figure 6b, the initial discharge and charge capacities of 1629 and 1176 mA h g$^{-1}$ are delivered by NiFe$_2$O$_4$ electrode, corresponding to a Coulombic efficiency of 72.2%. The capacity loss in the initial cycle can be attributed to the irreversible SEI formation. In the second cycle, the NiFe$_2$O$_4$ electrode displays high discharge and charge capacities of 1189 and 1143 mA h g$^{-1}$, respectively, with a high Coulombic efficiency of 96.1%.

Cycling performance of NiFe$_2$O$_4$ electrode was evaluated at different current densities of 0.5, 1.0, and 5.0 A g$^{-1}$. A five-cycle precondition at 0.1 A g$^{-1}$ was used before testing the electrodes at 5.0 A g$^{-1}$. As presented in Figure 6c, after 100 cycles at 0.5 A g$^{-1}$ the NiFe$_2$O$_4$ electrode delivers a high discharge capacity of 1387 mA h g$^{-1}$. It is worth mentioning that there is a slight increase of the capacity after 65 cycles, which may be due to the activation process, as observed in previous studies. When the current density is increased to 1.0 A g$^{-1}$, a high discharge capacity of 841 mA h g$^{-1}$ is achieved by the NiFe$_2$O$_4$ electrode after 100 cycles. When it is discharged at a high current density of 5.0 A g$^{-1}$, the NiFe$_2$O$_4$ electrode still maintains a capacity of 447 mA h g$^{-1}$ after 100 cycles.

The ultrafast charging and discharging capability of the NiFe$_2$O$_4$ electrode was evaluated at various current densities, ranging from 0.1 to 8.0 A g$^{-1}$. As depicted in Figure 6d, NiFe$_2$O$_4$ electrode delivers a high capacity of 1189 mA h g$^{-1}$ at...
0.1 A g\(^{-1}\) during the second discharge cycle. When the current densities are increased to 0.5, 1.0, and 4.0 A g\(^{-1}\), the second-cycle discharge capacities become 1024, 888, and 747 mA h g\(^{-1}\), respectively. At high current densities of 6.0 and 8.0 A g\(^{-1}\), the NiFe\(_2\)O\(_4\) electrode still depicts high capacities of 690 and 636 mA h g\(^{-1}\), respectively. More importantly, a stable and high capacity of 1085 mA h g\(^{-1}\) can still be retained when the current density changes from 8.0 to 0.1 A g\(^{-1}\).

The lithium storage properties of the CoFe\(_2\)O\(_4\) and ZnFe\(_2\)O\(_4\) hollow structures are also evaluated. Figure S2 (Supporting Information) gives the cycling performance of the CoFe\(_2\)O\(_4\) and ZnFe\(_2\)O\(_4\) electrodes at constant current densities of 1.0 and 5.0 A g\(^{-1}\). The CoFe\(_2\)O\(_4\) electrode shows a relatively stable cycling performance. During the 100th cycle, CoFe\(_2\)O\(_4\) electrode and delivers a high capacity of 770 mA h g\(^{-1}\) at 1.0 A g\(^{-1}\) and manages to stabilized at 290 mA h g\(^{-1}\) at 5.0 A g\(^{-1}\). A more stable cycling performance is achieved by the ZnFe\(_2\)O\(_4\) electrode. When the ZnFe\(_2\)O\(_4\) electrode is cycled at constant current densities of 1.0 and 5.0 A g\(^{-1}\), it displays high capacities of 947 and 390 mA h g\(^{-1}\), respectively, during the 100th cycle. The capability of the CoFe\(_2\)O\(_4\) and ZnFe\(_2\)O\(_4\) electrodes in achieving high power density was examined by performing cycling test at various current densities (Supporting Information Figure S2b). When a high current density of 8.0 A g\(^{-1}\) is applied, CoFe\(_2\)O\(_4\) and ZnFe\(_2\)O\(_4\) electrodes reach high discharge capacities of 380 and 449 mA h g\(^{-1}\), respectively. High capacities of around 900 and 850 mA h g\(^{-1}\) can be obtained by CoFe\(_2\)O\(_4\) and ZnFe\(_2\)O\(_4\) electrodes, respectively, when the current density is reduced from 8.0 A g\(^{-1}\) back to 0.1 A g\(^{-1}\).

To achieve an in-depth understanding of the composition and structural information on the electrodes after cycling, XRD and FESEM characterizations were performed on the electrodes after 100 cycles at a current density of 1.0 A g\(^{-1}\). On the basis of FESEM images before and after cycling, the cube morphologies of the NiFe\(_2\)O\(_4\) (Supporting Information Figure S3a,d) and CoFe\(_2\)O\(_4\) (Supporting Information Figure S3b,e) electrodes that are assembled by numerous nanoparticles are maintained. This confirms that the hollow structure is rigid enough to withstand deformation induced by repeated lithium intercalation/extraction. As for ZnFe\(_2\)O\(_4\) (Supporting Information Figure S3c,f), though pulverization is observed, the primary nanoparticles and the porous structure can still be observed. The XRD patterns (Supporting Information Figure S3g–i) of the cycled samples do not show clear peaks corresponding to the respective oxide phases. This is possibly because the formed grain size is very small to give a long-range ordering peak in the XRD pattern.

Therefore, the obtained hollow structured ternary TMOs demonstrate good stability during cycling and excellent rate capabilities at high charge−discharge current densities. These outstanding lithium storage performances can be attributed to the hierarchically assembled hollow structures. Compared to its bulk counterpart, the nanoparticles in the hollow cubes offer large electrode/electrolyte contact area and allow a short diffusion distance for the charge carriers. A short diffusion distance is also achieved by the porous frameworks and hollow interior. This is because this configuration provides the easy accessibility of the electrolyte to the active materials from multiple directions and allows effective interaction between the electrolyte and the electrodes. This is crucial for the excellent rate capability. Moreover, the hollow interior space and the voids between nanoparticles cushion the volume changes during the charge/discharge process, which are of paramount importance for the cycling stability.

4. CONCLUSION

In summary, we have developed a general and simple approach for large-scale synthesis of porous hollow spinel AFe\(_2\)O\(_4\) nanoarchitectures via MOF self-sacrificial template strategy. The successful synthesis of uniform NiFe\(_2\)O\(_4\), ZnFe\(_2\)O\(_4\), and CoFe\(_2\)O\(_4\) hollow architectures manifests the versatility of this method. The well-defined hollow structured AFe\(_2\)O\(_4\) cubes are hierarchically assembled by numerous nanoparticles. These distinguishing structural features make the ternary AFe\(_2\)O\(_4\) viable in a wide range of applications. When the obtained NiFe\(_2\)O\(_4\), ZnFe\(_2\)O\(_4\), and CoFe\(_2\)O\(_4\) hollow microcubes are used as anode for LIBs, ultrahigh rate capability and long-term cycling stability can be achieved by all three metal oxides. In particular, high specific capacities of 636, 449, and 380 mA h g\(^{-1}\) were achieved by NiFe\(_2\)O\(_4\), ZnFe\(_2\)O\(_4\), and CoFe\(_2\)O\(_4\), respectively, at a high current density of 8.0 A g\(^{-1}\). NiFe\(_2\)O\(_4\) exhibits high specific capacities of 841 and 447 mA h g\(^{-1}\) after 100 cycles at 1.0 and 5.0 A g\(^{-1}\), respectively. Stable capacities of 390 and 290 mA h g\(^{-1}\) were maintained by ZnFe\(_2\)O\(_4\) and CoFe\(_2\)O\(_4\), respectively, after 100 cycles at 5.0 A g\(^{-1}\). In addition, as the metal ions in MOF and the structure of MOF can be easily tuned, we believe this strategy can be extended to the preparation of other hollow or unique structured materials for vast applications.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b08741.

- XRD patterns; FESEM images; TEM images of the PB; cycling and rate capability of CoFe\(_2\)O\(_4\) and ZnFe\(_2\)O\(_4\); FESEM images and XRD of NiFe\(_2\)O\(_4\), CoFe\(_2\)O\(_4\), and ZnFe\(_2\)O\(_4\) electrodes after cycling. (PDF)

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Notes
The authors declare no competing financial interest.

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