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General Approach for MOF-Derived Porous Spinel AFe_2O_4 Hollow Structures and Their Superior Lithium Storage Properties

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S Supporting Information

ABSTRACT: A general and simple approach for large-scale synthesis of porous hollow spinel AFe_2O_4 nanoarchitectures via metal organic framework self-sacrificial template strategy is proposed. By employing this method, we can successfully synthesize uniform NiFe_2O_4 , ZnFe_2O_4 , and CoFe_2O_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_2O_4 , ZnFe_2O_4 , and CoFe_2O_4 , respectively, at a high current density of 8.0 A g^{-1} . NiFe_2O_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_2O_4 and CoFe_2O_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,^{3–6} gas sensors,⁷ energy conversion, and storage systems.^{8–12} 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.¹³ Hollow-structured transition metal oxides (TMOs), especially ternary TMO with spinel structure (AB_2O_4), are promising functional materials applied in various fields ranging from electrocatalysis, chemical sensors to photonic and energy storage devices.^{14–16} 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.^{17–19} 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_2O_4 nanocages have been successfully prepared via a Cu_2O -templated method and showed excellent oxygen evolution reaction electrochemical activity.²⁰ An improved microwave absorbing performance was detected using CoFe_2O_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_2O_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.^{23–28} 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.^{29,30} Comparing to other strategies, metal oxides derived from MOF templates often exhibit distinct merits such as uniform size, hierarchical porosity, and large surface area and have been proven to perform extraordinarily in energy storage,³¹ catalysis,^{24,32} drug delivery,³³ and photocatalysis.³¹ 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.³⁴ Hybrid Co_3O_4 -carbon porous nanowire arrays were successfully grown on Cu foil through a carbonization process of MOF and achieved ultrahigh oxygen evolution activity and good mechanical durability.³⁵ Despite great success accomplished in the past, only a few attempts were made on the synthesis of ternary TMOs structures.^{36–39} Several challenges in the synthesis of ternary systems have been encountered: (1) If the other metal ion is added via a solution-based method, then achieving homogeneous dispersion of MOF in solution is difficult due to the extremely low dissolution rate of MOF in any solvent, and morphological and structural retentions of the MOF are difficult to achieve as high temperature is necessary to convert the ionic precursors into the metal oxides. (2) If the other metal is added by modification of the MOF, then the feasibility depends on the radius and chemical bonding of the metal ions. Moreover, the ratio of two metal ions in MOF is fixed so there will be stoichiometric problems when converting to metal oxides with different ratios. As a result, in an effort to explore synthetic approaches for TMOs derived from MOF, there are still obstacles in accurately controlling the morphologies and structures, especially for the complicated ternary systems.

Here, we present a simple and general approach toward the large-scale synthesis of porous hollow spinel AFe_2O_4 nanoarchitectures based on a MOF self-sacrificial template strategy. By employing this method, we successfully synthesized hollow hierarchically assembled microcubes including NiFe_2O_4 , ZnFe_2O_4 and CoFe_2O_4 . These hollow AFe_2O_4 microcubes demonstrated superior lithium storage properties. For example, high specific capacities of 636, 449, and 380 mA h g^{-1} were achieved by NiFe_2O_4 , ZnFe_2O_4 , and CoFe_2O_4 , respectively, at a high current density of 8.0 A g^{-1} . NiFe_2O_4 exhibits high specific capacities of 841 and 447 mA h g^{-1} during the 100th cycle at 1.0 and 5.0 A g^{-1} , respectively. Discharge capacities of 390 and 290 mA h g^{-1} were delivered by the ZnFe_2O_4 and CoFe_2O_4 , respectively, during the 100th cycle at a current density of 5.0 A g^{-1} .

2. EXPERIMENTAL SECTION

2.1. Material Synthesis. **2.1.1. Preparation of Fe-Containing MOF $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ (Prussian Blue, PB) Cubes.**^{40–42} 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 $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ 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_2O_4 Microcubes. The conversion of the Fe-based MOFs precursor microcubes into hollow and porous spinel AFe_2O_4 microcubes is as follows: Using NiFe_2O_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 temperature ramp of 2 °C min^{-1} for 6 h in air. For the preparation of CoFe_2O_4 and ZnFe_2O_4 , hollow and porous structures, 0.094 g cobalt acetate tetrahydrate and 0.07 g zinc acetate were used with the similar methods.

2.2. Characterization. X-ray powder diffraction (XRD) was performed on a Bruker AXS D8 advance X-ray diffractometer at the 2θ range of 10–80° using $\text{Cu K}\alpha$ radiation. The morphology of the samples was investigated with a field emission scanning electron microscope (FESEM) system (JEOL, Model JSM-7600F). Transmission electron microscopy (TEM) characterization and elemental composition analysis were performed with a JEOL 2100F operating at 200 kV with energy dispersive X-ray spectroscopy (EDS) attachment. Fourier transform infrared spectrometer (FTIR) of model spectrum GX is used to obtain the spectrum. Raman spectra were obtained by a WITeek alpha300 SR confocal microscopy Raman system with a piezocrystal controlled scanning stage. Thermogravimetry analyses (TGA, Q500) were carried out in the temperature range 30–900 °C at a heating rate of 10 °C min^{-1} in air flow. Brunauer–Emmett–Teller (BET) surface area is analyzed by surface area and porosity analyzer model ASAP 2020.

2.3. Electrochemical Measurements. The coin-type cells were assembled in an argon-filled glovebox. The electrodes were fabricated by mixing the ternary AFe_2O_4 , single-walled carbon nanotube (SWCNT) and poly(vinylidene fluoride) (PVDF) at a weight percent ratio of 70:20:10 in *N*-methyl-2-pyrrolidone (NMP) solvent. The resulting mixture was then pasted onto the aluminum foil and punched into small disks ($\phi = 14$ mm). The mass loading was around 2.0 mg.

All the electrodes were directly used as the anodes without binders or additives. The electrochemical properties of the obtained working electrodes were measured using two-electrode CR2032 (3 V) coin-type cells with lithium foil serving as both counter and reference electrodes. The electrolyte was 1 M LiPF_6 in ethylene carbonate (EC)/diethyl carbonate (DEC; 1:1, w/w). The cells were assembled in an argon-filled glovebox with both moisture and oxygen contents below 1.0 ppm. The mass loading was around 2.0 mg. In the calculation of capacity, only the mass of active materials was included. Galvanostatic discharge–charge tests were performed using a NEWARE battery tester at a voltage window of 0.005–3.0 V at ambient temperature. Cyclic voltammetry (CV) was performed with an electrochemical workstation (Solarton).

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 $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ 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 $-\text{C}\equiv\text{N}-$ groups at 2083 cm^{-1} and the $\text{Fe}^{2+}-\text{CN}-\text{Fe}^{3+}$ groups at 499 cm^{-1} , indicating the formation of PB.^{43,44} A vibrational band at 2154 cm^{-1} of Raman spectrum (Supporting Information Figure S1c) corresponds to the stretching vibration of $-\text{C}\equiv\text{N}-$ groups.^{45,46} 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)

Figure 1. Schematic illustration of the synthetic process of the Fe-based ternary metal oxides hollow structures.

verifies the solid nature of the PB. The specific surface area of PB is calculated to be $4.35 \text{ m}^2 \text{ g}^{-1}$ 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 AFe_2O_4 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^+ reacts with oxygen forming a shell of AFe_2O_4 . 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 AFe_2O_4 forming new oxide layers. After all PB is consumed, a cubic hollow structure 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 NiFe_2O_4 , CoFe_2O_4 , and ZnFe_2O_4 . 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 NiFe_2O_4 , all the diffraction peaks (Figure 2) can be assigned to the cubic NiFe_2O_4 structure (JCPDS card

Figure 2. XRD patterns of the NiFe_2O_4 hollow cubes.

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 NiFe_2O_4 cubes with a uniform size of around $1 \mu\text{m}$, 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 $4.82 \text{ \AA}$ is observed (Figure 3e) which can be indexed to the $\{111\}$ set of planes of cubic NiFe_2O_4 . The indexed fast Fourier transform (FFT) pattern (Figure 3e inset) taken from the marked region of Figure 3e (zone axis of $[111]$) 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 3. (a and b) FESEM images at different magnifications of the porous NiFe_2O_4 hollow cubes. (c and d) TEM images of the porous NiFe_2O_4 hollow cubes. (e) HRTEM image showing the assembled nanoparticles of NiFe_2O_4 hollow cubes and (inset) FFT pattern of the marked region. (f) HRTEM image showing the lattice fringes of cubic NiFe_2O_4 . (g–i) Elemental mappings of the porous NiFe_2O_4 hollow cubes.

For other as-obtained samples, the XRD analysis (Figure 4) demonstrates the successful formation of ternary metal oxides.

Figure 4. XRD patterns of the CoFe_2O_4 and ZnFe_2O_4 hollow cubes.

Pure CoFe_2O_4 (cubic structure, JCPDS card no. 00-022-1086) and ZnFe_2O_4 (cubic structure, JCPDS card no. 00-022-1012) phases are formed without any other detectable impurities. FESEM images of CoFe_2O_4 (Figure 5a,b) and ZnFe_2O_4 (Figure 5d,e), reveal similar cube morphology with uniform sizes (about $1 \mu\text{m}$). Their hollow interiors can be readily formed, which are unambiguously disclosed by TEM images (Figure 5c for CoFe_2O_4 and Figure 5f for ZnFe_2O_4).

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

Figure 5. (a and b) FESEM images at different magnifications of the porous CoFe_2O_4 hollow cubes. (c) TEM image of the porous CoFe_2O_4 hollow cubes. (d and e) FESEM images at different magnifications of the porous ZnFe_2O_4 hollow cubes. (f) TEM image of the porous ZnFe_2O_4 hollow cubes.

voltage range of 0.005–3.0 V. The electrochemical behavior of NiFe_2O_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_2O_4 lattice.⁴⁹ 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.

The first three cycles of galvanostatic discharge–charge voltage profiles of the NiFe_2O_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_2O_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_2O_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_2O_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_2O_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.^{16,38} 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_2O_4 electrode after 100 cycles. When it is discharged at a high current density of 5.0 A g^{-1} , the NiFe_2O_4 electrode still maintains a capacity of 447 mA h g^{-1} after 100 cycles.

The ultrafast charging and discharging capability of the NiFe_2O_4 electrode was evaluated at various current densities, ranging from 0.1 to 8.0 A g^{-1} . As depicted in Figure 6d, NiFe_2O_4 electrode delivers a high capacity of 1189 mA h g^{-1} at

Figure 6. Electrochemical characterizations of the porous NiFe_2O_4 hollow cubes. (a) First three cyclic voltammetry (CV) curves of NiFe_2O_4 electrode at a scan rate of 0.2 mV s^{-1} . (b) Galvanostatic discharge–charge voltage profiles of the first three cycles at a current density of 0.1 A g^{-1} . (c) Cycling performance of the NiFe_2O_4 electrode for the first 100 cycles at current densities of 0.5, 1.0, and 5.0 A g^{-1} . (d) Rate capabilities of the electrodes at current densities from 0.1 to 8.0 A g^{-1} .

0.1 A⁻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 NiFe₂O₄ 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 CoFe₂O₄ and ZnFe₂O₄ hollow structures are also evaluated. Figure S2 (Supporting Information) gives the cycling performance of the CoFe₂O₄ and ZnFe₂O₄ electrodes at constant current densities of 1.0 and 5.0 A g⁻¹. The CoFe₂O₄ electrode shows a relatively stable cycling performance. During the 100th cycle, CoFe₂O₄ electrode and delivers a high capacity of 770 mA h g⁻¹ at 1.0 A g⁻¹ and manages to stabilize at 290 mA h g⁻¹ at 5.0 A g⁻¹. A more stable cycling performance is achieved by the ZnFe₂O₄ electrode. When the ZnFe₂O₄ 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 CoFe₂O₄ and ZnFe₂O₄ 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, CoFe₂O₄ and ZnFe₂O₄ 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 CoFe₂O₄ and ZnFe₂O₄ 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 NiFe₂O₄ (Supporting Information Figure S3a,d) and CoFe₂O₄ (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 ZnFe₂O₄ (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 AFe₂O₄ nanoarchitectures via MOF self-sacrificial template strategy. The successful synthesis of uniform NiFe₂O₄, ZnFe₂O₄, and CoFe₂O₄ hollow architectures manifests the versatility of this method. The well-defined hollow structured AFe₂O₄ cubes are hierarchically assembled by numerous nanoparticles. These distinguishing structural features make the ternary AFe₂O₄ viable in a wide range of applications. When the obtained NiFe₂O₄, ZnFe₂O₄, and CoFe₂O₄ 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 NiFe₂O₄, ZnFe₂O₄, and CoFe₂O₄, respectively, at a high current density of 8.0 A g⁻¹. NiFe₂O₄ 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 ZnFe₂O₄ and CoFe₂O₄, 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 CoFe₂O₄ and ZnFe₂O₄; FESEM images and XRD of NiFe₂O₄, CoFe₂O₄, and ZnFe₂O₄ electrodes after cycling. (PDF)

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Notes

The authors declare no competing financial interest.

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