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COMMUNICATION

Template-free construction of hollow ZnFe$_2$O$_4$ nanotubes coated with nano-carbon layer as a competitive anode for Li-ion batteries

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One-dimensional hollow ZnFe$_2$O$_4$ nanotubes coated with ultrathin nano-carbon layer are delicately designed and fabricated via a facile template-free strategy, and exhibit superior rate behaviors and long-term cycle stability as an anode for Li-ion batteries.

Over the past decades, Li-ion batteries (LIBs) attracted enormous attentions owing to their high energy density and remarkable power density. Typically, the graphite has been widely utilized in commercial productions as a low-cost anode material for LIBs, however, it cannot fully meet the increasingly harsh requirements for higher-energy-density electrochemical devices owing to its lower theoretical capacity (~372 mAh g$^{-1}$). It, therefore, has become greatly imperative to explore more promising anode materials with higher rate capacity along with superb cycling stability.

Recently, binary ZnFe$_2$O$_4$ (ZFO) emerges as an attractive anode candidate thanks to its high specific capacity of ~1072 mAh g$^{-1}$ originating from both conversion reaction and alloying mechanism, and cost efficiency/environmental friendliness of both elemental Zn and Fe. While, its serious volume effect during charge/discharge process and modest electronic conductivity still should be efficiently addressed for further commercial applications. Appealingly, numerous pioneering contributions reveal that the electrochemical lithium storage performance of ZnFe$_2$O$_4$ can be considerably improved by rational composition and/or structure design. In general, hollow structures, particularly, one-dimensional (1D) hollow nanotubular architecture with rapid electronic transport, can well alleviate the volumetric expansion/shrinkage during the repeated Li$^+$-insertion/extraction processes, which is conducive to improving structural stability. Besides this, the elegant hybridization with carbonaceous materials will efficiently enhance the charge conductivity, and surf-interface stability of electrode materials. Unfortunately, if each method mentioned above was employed alone, just limited improvement in electrochemical Li-storage properties could be achieved. As a result, the integrated avenues are always necessary to construct advanced ZFO-based hybrid anodes, especially via facile synthetic strategies that require no any special equipments and stringent preparation conditions. This is undoubtedly of great significance to broad and successful industrial applications.

Herein, we first reported a simple, template-free fabrication of hollow ZFO nanotubes (NTs) coated with nano-carbon coating layer (denoted as ZFO@C NTs) (more details in the experimental section, see ESI†), as schematically illustrated in Scheme 1. Specifically, the ZnFe-PVP nanofiber precursor was first electrospun at 25 °C, and further annealed in air at 500 °C for 5 h. The resulted ZFO NTs were further coated with the polydopamine (PDA). After annealed at 500 °C in N$_2$, the ZFO@C NTs were finally achieved. As expected, when employed as an anode for LIBs, the as-fabricated hollow ZFO@C NTs exhibited even better lithium-storage behaviors in terms of reversible capacities, rate performance and cycling stability, compared to its counterpart ZFO NTs, thanks to synergistic contributions from 1D hollow structure and ultrathin conductive carbon coating layer.

Scheme 1 Schematic illustration for template-free synthesis of ZFO@C NTs

The X-ray diffraction (XRD) analysis was conducted to determine the crystallographic phases of resulted ZFO and ZFO@C NTs. As shown in Fig. 1a, all the discernable diffraction peaks of the synthesized ZFO NTs (the lower), including not only peak positions but their relative intensities, can be perfectly indexed to the cubic spinel ZFO (ICPDS No. 22-1012) with space group of Fd-3m. As regards the ZFO@C NTs, the reflections (the upper) all remain the same as those of the ZFO...
NTs (the lower), indicating that the carbon coating has no obvious effect on the ZFO phase at all. One should note that the undetected representative signals for the C further verify amorphous nature of the conductive carbon in the hybrid NTs. Corresponding Raman spectrum (Fig. S2, EIS†) further evidences the existence of typical carbon with an I_G/I_D value (i.e., the areal ratio of G-band to D-band) of ~0.84.

Fig. 1 (a) XRD patterns, and XPS elemental (b) Fe 2p and (c) Zn 2p spectra of ZFO and ZFO@C NTs; (d) typical C 1s (the upper) and N 1s (the lower) spectra of ZFO@C NTs

In order to get more information about surface elemental compositions and corresponding oxidation states of the obtained two products, X-ray photoelectron spectroscopy (XPS) testing was performed. Fig. 1b comparatively shows the Fe 2p spectra and fitting curves of ZFO and ZFO@C NTs. Clearly, there is no significant difference in the bond energy (BE) between the two. The fitted peaks with BEs at ~711.4 and ~713.0 eV correspond to the characteristic peaks of Fe 2p1/2 in the tetrahedral (A-site) and octahedral (B-site), respectively, while those at ~719.6 and ~725.5 eV are related to the satellite peak and Fe 2p1/2, respectively, indicating the existence of Fe3+ in the ZFO phase.5,6,12 From the high-resolution Zn 2p spectra (Fig. 1c), the fitted peaks at BEs of ~1021.7 and ~1044.8 eV are ascribed to the Zn 2p3/2 and 2p1/2, respectively, confirming that the elemental Zn exists in the two samples in the form of Zn2+.5,6,15 Fig. 1d demonstrates the core-level XPS spectra of the C 1s (the upper) and N 1s (the lower) in the ZFO@C NTs. The presence of four types of carbon can be observed. To be specific, the peaks at ~284.5 and ~285.0 eV are assigned to carbons in the form of C-C (C1) and C-O (C2), along with another two peaks at ~286.2 and ~288.9 eV ascribed to the O-C (C3) and O=C-O (C4), respectively.12 The N (~4.1 at.%) shows two forms of N species, i.e., the quaternary N (~400.3 eV, N1, ~1.6 at.%) and pyridinic N (~398.7 eV, N2).6 As noted, the former favors for the enhanced electronic transport through the 1D ZFO@C NTs.6

Typical field emission scanning electron microscope (FESEM) observations (Fig. 2a-c) clearly visualize a typical porous tubular structure of ZFO NTs, which are constructed with many nanoscale subunits. There is no doubt that the porous structure will facilitate the following coating each ZFO nanograin uniformly by PDA. The hollow architecture of ZFO NTs is further confirmed evidently by transmission electron microscope (TEM) images (Fig. 2d, e). It can be seen from higher-magnification TEM micrograph (the inset in Fig. 2e) that the outer diameter of ZFO NTs is approximately 110 nm, along with a thin wall of ~12 nm in thickness. The unique ZFO NTs are typically composed of well-crystalline nano-dimensional particles with a diameter of ~7 nm and even less (Fig. 2f). From the high-resolution TEM (HRTEM) images (Fig. 2f, g), two sets of well-defined lattice fringes with spacings of 0.49 and 0.3 nm, corresponding to the (111) and (220) planes of the spinel ZFO, respectively, can be apparently discerned. The selected area electron diffraction (SAED) pattern with multiple concentric rings authenticates the polycrystalline feature of ZFO NTs (Fig. 2h). The template-free formation of the unique hollow ZFO NTs mainly depends upon the applied electropinning process. The easy volatilization of the involved ethanol solvent will result in the spontaneous outward movement of Zn2+/Fe2+ ions along the radial direction of the resultant ZnFe-PVP fibers. It is the concentration difference of metal ions that ensures the formation of NTs, along with the assistance of following calcination in air.15

Fig. 2 (a–c) FESEM, (d, e) TEM and (f, g) HRTEM images, and (h) SAED pattern of the ZFO NTs; (i) TEM, (j, k) HRTEM, (l) STEM and corresponding EDX elemental mapping images of the ZFO@C NTs

After subsequent carbon coating, the ZFO@C NTs well inherit the tubular structure of ZFO NTs (Fig. 2i). The enlarged TEM observation (Fig. 2j) shows that the surface of the ZFO NTs is covered evenly with an ultrathin nano-carbon layer with a thickness of about 3–4 nm. After the amorphous carbon coating, the lattice fringes with a spacing of 0.3 nm, corresponding to the (220) crystal plane of ZFO, are still distinct (Fig. 2k). The scanning TEM (STEM) and corresponding elemental energy-dispersive X-ray (EDX) mapping images (Fig. 2l).
21] explicitly corroborate the uniform distributions of Zn, Fe and O elements in ZFO@C NTs, along with the C species mainly distributed outside the ZFO NTs.

In order to further study the pore structure and textural properties of the as-synthesized ZFO and ZFO@C NTs, nitrogen sorption tests were conducted accordingly. Typical N\textsubscript{2} sorption isotherms manifest that both curves can be classified as the type I-V with a H3 type hysteresis loop (Fig. S3a, EIST)\textsuperscript{2,6,11}, suggesting the mesoporous characteristics of ZFO and ZFO@C NTs, which can be supported well by their Barrett-Joyner-Halanda pore size distribution (PSD) plots (Fig. S3b, EIST). Especially, the PSD plot of the ZFO NTs distinctly shifts to the smaller size range after carbon coating, verifying that the PDA-derived carbon is also located in the inherent pores of the resultant porous ZFO NTs. As a result, the pore volume (~0.15 cm\textsuperscript{3} g\textsuperscript{-1}) and average pore size (~15.2 nm), smaller than those of ZFO NTs (Table S1, EIST\textsuperscript{1}), are obtained in the ZFO@C NTs. It consequently endows the ZFO@C NTs with a specific surface area of ~38.5 m\textsuperscript{2} g\textsuperscript{-1}, somewhat higher than ZFO NTs (~34.9 m\textsuperscript{2} g\textsuperscript{-1}). Such unique mesoporous nanotubular architecture will promote the electroactive sur/interfaces between electrode and electrolyte, and also provide enough space to accommodate huge volumetric change over repeated lithiation/delithiation processes, particularly at high rates.\textsuperscript{6,16,17}

### Fig. 3

Fig. 3 Electrochemical evaluation of ZFO and ZFO@C NTs: (a) The first discharge-charge plots (300 mA g\textsuperscript{-1}); (b) rate behaviors in the current range from 200 to 3200 mA g\textsuperscript{-1}; (c) discharge capacities and HRD files as a function of current density; and (d) cycling behaviors at 500 mA g\textsuperscript{-1}.

Thanks to these attractive structural merits, as discussed above, our ZFO@C NTs can be highly anticipated as advanced anode for LIBs. A coin cell (CR2032) was assembled to evaluate the half-cell electrochemical behaviors of ZFO and ZFO@C NTs. The cyclic voltammetry (CV) curves of ZFO@C NTs were obtained in the voltage range of 0.01 – 3.0 V (vs. Li/Li\textsuperscript{+}) at a sweep rate of 0.1 mV s\textsuperscript{-1} (Fig. S4, EIST\textsuperscript{1}). Apparently, the shape of the first cycle is completely different from the subsequent cycles. In the 1st cycle, a weak cathodic peak around 0.89 V can be observed, followed by another intensive peak centered at 0.61 V. These peaks correspond to the structural transformation and redox reactions that occur during potential scanning, including the formation of Zn\textsuperscript{2+}/Fe\textsuperscript{0} and further reductive conversion into the Fe\textsuperscript{0}, Li\textsuperscript{2+} and Li\textsuperscript{0}.\textsuperscript{5,12-15} Over the anodic process, the broad peaks at ~1.61 and ~1.92 V correspond to the oxidation of Zn\textsuperscript{2+}/Fe\textsuperscript{0} into Zn\textsuperscript{2+}/Fe\textsuperscript{3+}. The overall-averaged curves of the 2nd and 3rd cycles suggest the identical yet highly reversible electrochemical reactions between Fe(III)/Zn(II) and Fe(0)/Zn(0).\textsuperscript{5,15-18} Remarkably, the ZFO@C NTs render large initial discharge/charge capacities of ~1176/~912 mAh g\textsuperscript{-1} at a current density of 300 mA g\textsuperscript{-1}, corresponding to an initial Coulombic efficiency (CE) of ~77.6%, as shown in Fig. 3a. By contrast, the ZFO NTs just obtain a discharge capacity of ~999 mAh g\textsuperscript{-1}, along with the 1st CE value of ~72.7%. The irreversible capacity loss should be mainly ascribed to the electrolyte decomposition and formation of the solid-electrolyte-interphase (SEI) layer.\textsuperscript{5-13,27} In the 2nd charge-discharge cycle (Fig. 3b, EIST\textsuperscript{1}), the CE value of the ZFO@C NTs rapid increases up to ~97.4%, still larger than the ZFO NTs (~97.1%).\textsuperscript{5} Fig. 3b displays the rate performance of ZFO and ZFO@C NTs under various current densities from 200 to 3200 mA g\textsuperscript{-1}. As the current density increases, the capacity of ZFO NTs decays significantly. Competitively, the ZFO@C NTs exhibit excellent rate behaviors with discharge specific capacities of ~904, ~836, ~763, ~664, and ~539 mAh g\textsuperscript{-1}, respectively, as collected in Fig. 3c, at current densities of 200, 400, 800, 1600 and 3200 mA g\textsuperscript{-1}. While, the ZFO NTs only obtain reversible capacities of ~813 and ~240 mAh g\textsuperscript{-1} at 200 and 3200 mA g\textsuperscript{-1}, respectively. Additionally, as the current density goes back to 100 mA g\textsuperscript{-1}, a capacity as large as ~1013 mAh g\textsuperscript{-1} still can be recovered for the ZFO@C NTs, even higher than that of ZFO NTs (~537 mAh g\textsuperscript{-1}) in the same case. Evidently, the capacities at each current density are all larger than, and/or comparable to other ZFO-C composites (the lower panel in Fig. 3c),\textsuperscript{10,14,19-26,28} even ZFO/conducting polymer composites,\textsuperscript{5,29,30} and ZFO nanostructures.\textsuperscript{31,32} It is worthy of stating that the ZFO@C NTs possess striking high-rate-dischargeability (HRD), which is defined as the ratio of the discharge capacity at certain current density to that at 200 mA g\textsuperscript{-1}. Obviously, the HRD of ZFO@C NTs remains as ~60%, much higher than ZFO NTs (~30%) at a larger current density of 3200 mA g\textsuperscript{-1}. This highlights the remarkable rate property of ZFO@C NTs for potential high-power application, which should be reasonably attributed to its smaller charge transfer resistance (Fig. S6, EIST\textsuperscript{1}). Furthermore, only a reversible discharge capacity of ~479.3 mAh g\textsuperscript{-1} can be maintained by ZFO NTs after 500 consecutive cycles at a current density of 500 mA g\textsuperscript{-1}. As a sharp contrast, the ZFO@C NTs demonstrate superior cycling performance with a retained discharge capacity of ~817.6 mAh g\textsuperscript{-1}, revealing its exceptional electrochemical stability. As seen from the TEM observation (Fig. S7, EIST\textsuperscript{1}), the cycled ZFO@C NTs anode well maintain the 1D hollow nano-tubular structure, proving its robust structural stability for better long-duration cycle life.

In summary, in the work, we firstly devised a bottom-up template-free method towards scalable fabrication of 1D ZFO NTs, and then coated them with the PDA-derived ultrathin nano-carbon layer to obtain the hollow ZFO@C NTs. The
underlying formation process of the hollow ZFO NTs was tentatively proposed here. Thanks to its unique 1D hollow mesoporous architecture, robust structural stability, and small charge-transfer resistance, the as-synthesized ZFO@C NTs electrode displayed remarkable electrochemical properties in terms of reversible capacity, rata behaviors and long-term cyclic lifespan, particularly at large current densities, when utilized as a competitive anode for LIBs. Our contribution here will provide better guidance for future rational design of hollow binary, and even ternary metal oxide NTs with conducting carbon coating for advanced LIBs and beyond.

Conflicts of interest
There are no conflicts to declare.

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