Uniform Pomegranate-Like Nanoclusters Organized by Ultrafine Transition Metal Oxide@Nitrogen-Doped Carbon Subunits with Enhanced Lithium Storage Properties

Bingqiu Liu, Qi Zhang, Zhanshuang Jin, Lingyu Zhang, Lu Li,* Zhigang Gao, Chungang Wang,* Haiming Xie, and Zhongmin Su*

Uniform pomegranate-like nanoclusters (NCs) organized by ultrafine transition metal oxide@nitrogen-doped carbon (TMO@N–C) subunits (diameter = 4 nm) are prepared on a large scale for the first time through a facile, novel, and one-pot approach. Taking pomegranate-like Fe$_3$O$_4$@N–C NCs as an example, this unique structure provides short Li$^+$/electron diffusion pathways for electrochemical reactions, structural stability during cycling, and high electrical conductivity, leading to superior electrochemical performance. The resulting pomegranate-like Fe$_3$O$_4$@N–C NCs possess a high specific capacity (1204.3 mA h g$^{-1}$ at 0.5 A g$^{-1}$ over 100 cycles), a stable cycle life (1063.0 mA h g$^{-1}$ at 1 A g$^{-1}$, 98.4% retention after 1000 cycles), and excellent rate capacities (606.0 mA h g$^{-1}$ at 10 A g$^{-1}$, 92.0% retention; 417.1 mA h g$^{-1}$ at 20 A g$^{-1}$, 91.7% retention after 1000 cycles).

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used as a high-performance power source to fulfill the demands for electric/hybrid vehicles and energy storage devices because of the advantages of high energy density, long lifespan, and environmental friendliness.[1–9] To meet the increasing requirements for high-performance LIBs, intensive efforts have been devoted for superior electrode materials by replacing conventional graphite with transition metal oxides (TMOs), such as Fe$_3$O$_4$, Mn$_3$O$_4$, NiO, and ZnO.[10–15] TMOs have drawn particular attention due to their high theoretical reversible capacity, low cost, high abundance, and nontoxicity.[16–23] However, they suffer from poor cyclability and low rate capacity, which are caused by the drastic volume change during the charge–discharge cycling and low electric conductivity.[24–26] Thus, it is highly desirable to design and synthesize TMO-based anodes with high specific capacity and excellent stable cycling property.

Recently, adopting carbon coating has drawn considerable attention for increasing the electrical conductivity and enhancing the stability of the electrode materials as elastic buffer supports upon cycling to improve the electrochemical performance.[27–31] Even through the volume changes may be effectively controlled by flexible substrates, this strategy is still limited in improving specific capacity and rate performance. Nanoengineering of ultrafine nanostucture (ultrafine nanoparticles or ultrafine nanosized subunits) has become the most powerful mean to tackle above challenge because they can increase the electrode–electrolyte contact area, lower the absolute volume change, and shorten the distance for lithium-ion diffusion within the particles.[32,33] For instance, 3D mesoporous Co$_3$O$_4$ networks composed of small Co$_3$O$_4$ nanoparticles (5–10 nm) synthesized by Naqin Zhao exhibit high specific capacity (1033 mA h g$^{-1}$ at 0.1 A g$^{-1}$) and remarkable rate capability.[34] Furthermore, robust and favorable ultrafine secondary nanoparticles would effectively accommodate the severe volume variation upon cycling and prevent self-aggregation of the ultrafine nanoscale subunits, thus leading to improved capacity retention and rate capability. For example, polydopamine-coated SnO$_2$ nanocrystals comprising SnO$_2$ nanoparticles (diameter = 5 nm) developed by Lin and co-workers display excellent rate capability.[35] Nevertheless, the existing synthetic methods can only fabricate the ultrafine nanoparticles with exposed or mosaic structure which have disadvantages of inevitable aggregation and unstable nanostructure during long-term cycling; moreover, they are unsuitable for large-scale production. Hence, it is a great challenge to design and synthesize ultrafine carbon coating TMO subunit through a facile and one-pot method on a large scale.

Along these lines, we develop a facile and novel one-pot approach for the first time to synthesize a series of highly uniform pomegranate-like TMO@nitrogen-doped carbon nanoclusters (TMO@N–C NCs) with a large scale production, which are composed of numerous ultrafine TMO@N–C subunits (diameter = 4 nm). This approach has been demonstrated to synthesize various pomegranate-like TMO@N–C NCs, including simple oxides such as Fe$_3$O$_4$, Mn$_3$O$_4$, NiO, and ZnO. Taking pomegranate-like Fe$_3$O$_4$@N–C NCs as an example, the pomegranate-like Fe$_3$O$_4$@N–C NCs with this unique nanostructure show excellent cycle stability and superior rate capacity.
while evaluated as anode materials for LIBs, which exhibit high specific reversible capacity (1204.3 mA h g$^{-1}$), ultra-high rate capability (606.0 and 417.1 mA h g$^{-1}$ at 10 and 20 A g$^{-1}$, respectively), and long cycling capability (98.4% specific reversible capacity retention from the 2nd to 1000th cycles at 1 A g$^{-1}$).

2. Results and Discussion

Figure 1A illustrates the preparation of this unique pomegranate-like Fe$_3$O$_4@$N–C NC with a relatively simple process. First, an aqueous solution of polyacrylic acid (PAA), ammonium hydroxide, and isopropyl alcohol (IPA) were added into deionized water to form the PAA-NH$_4$ nanospheres (NSs), which have a network structure assembled by the PAA chains binding.[36] Subsequently, Fe(OH)$_3$ was deposited into the network of the PAA-NH$_4$ NS through the Fe$^{2+}$ hydrolysis under the alkaline conditions to obtain the Fe(OH)$_3$/PAA-NH$_4$ NSs under the alkaline conditions. As shown in Figure 1C, the Fe(OH)$_3$/PAA-NH$_4$ NSs are highly dispersible in solution because of the electrostatic repulsion of the carboxyl groups. Then, the pomegranate-like Fe$_3$O$_4@$N–C NCs were obtained by calcination at 500 °C for 4 h. The morphology of the pomegranate-like Fe$_3$O$_4@$N–C NCs can be perfectly preserved after calcination without any obvious cracking and each NC has a rough surface (Figure 1D). The high-resolution TEM (HRTEM) image in Figure 1E shows the single pomegranate-like Fe$_3$O$_4@$N–C NC organized by a large amount of ultrafine Fe$_3$O$_4@$N–C subunits. The inset of Figure 1E under an atmosphere of argon to carbonize the PAA-NH$_4$ shell and converted Fe(OH)$_3$ to Fe$_3$O$_4$ due to the carbothermic reduction to afford pomegranate-like Fe$_3$O$_4@$N–C NC.

Figure 1B shows the transmission electron microscopy (TEM) image of monodisperse PAA-NH$_4$ NSs with a uniform size of ≈90 nm via a facile method in an IPA/water system. Subsequently, FeCl$_2$·4H$_2$O was added into the as-synthesized PAA-NH$_4$ NSs to obtain Fe(OH)$_3$/PAA-NH$_4$ NSs under the alkaline conditions. As shown in Figure 1C, the Fe(OH)$_3$/PAA-NH$_4$ NSs are highly dispersible in solution because of the electrostatic repulsion of the carboxyl groups. Then, the pomegranate-like Fe$_3$O$_4@$N–C NCs were obtained by calcination at 500 °C for 4 h. The morphology of the pomegranate-like Fe$_3$O$_4@$N–C NCs can be perfectly preserved after calcination without any obvious cracking and each NC has a rough surface (Figure 1D). The high-resolution TEM (HRTEM) image in Figure 1E shows the single pomegranate-like Fe$_3$O$_4@$N–C NC organized by a large amount of ultrafine Fe$_3$O$_4@$N–C subunits. The inset of Figure 1E under an atmosphere of argon to carbonize the PAA-NH$_4$ shell and converted Fe(OH)$_3$ to Fe$_3$O$_4$ due to the carbothermic reduction to afford pomegranate-like Fe$_3$O$_4@$N–C NC.

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reveals the lattice fringe with an interplanar spacing of 0.25 nm, corresponding to the (311) plane of Fe₃O₄. Figure 1F exhibits scanning electron microscope (SEM) images of the pomegranate-like Fe₃O₄@N–C NCs, these NCs show highly uniform spherical morphology with an average size of 90 nm. Specially, it can be seen in the Figure 1G that the NC is composed by many ultrafine subunits with the diameter of about 4 nm, which can provide short diffusion path of lithium ions during lithiation. Interestingly, after using acid solution to etch the inner Fe₃O₄ displayed in Figure S2A,B (Supporting Information), we found that the morphology of the acid-etched pure carbon NCs is unchanged compared with the pomegranate-like Fe₃O₄@N–C NCs, hypothesizing the nanostructure is composed of each ultrafine subunit with an N–C coating. For directly proving this unique nanostructure, TEM measurement of a single pure carbon NC was also carried out, as shown in Figure S2C (Supporting Information). Obviously, the acid-etched carbon NC is consistent with the ultrafine subunits shown in Figure S2C, (Supporting Information) with an average size of about 4 nm corresponding to the ultrafine Fe₃O₄ subunit of the nanostructure. The elemental mapping images of a single pomegranate-like Fe₃O₄@N–C NC shown in Figure 1H–L demonstrate that the C (red), N (orange), O (yellow), and Fe (green) are uniformly distributed in the pomegranate-like Fe₃O₄@N–C NCs. Generally, the yield per single synthesis run depends on the amount of precursor used in the synthesis process. In current case (1.1 g of FeCl₂·4H₂O), about 0.7 g of pomegranate-like Fe₃O₄@N–C NCs can be successfully fabricated per single synthesis run as shown in Figure S1 (Supporting Information).

More importantly, such strategy is versatile and can be extended to prepare other pomegranate-like TMO@N–C NCs. Figure 2 shows TEM and SEM images of pomegranate-like Mn₃O₄@N–C NCs, NiO@N–C NCs, and ZnO@N–C NCs and their precursors prepared by the same approach, respectively. In comparison with the pomegranate-like Fe₃O₄@N–C NCs shown in Figure 1D,F,G, the similar pomegranate-like structures are clearly observed in all these cases. Figure 2C,H,M exhibit that the elements transition metals, C and N are uniformly distributed in all these samples, which are similar to pomegranate-like Fe₃O₄@N–C NCs. X-ray diffraction (XRD) patterns (Figure S3, Supporting Information) show that the identified peaks can be indexed to Mn₃O₄ (JCPDS Card No. 80-0382), NiO (JCPDS Card No. 44-1159), and ZnO (JCPDS Card No. 36-1451).

X-ray photoelectron spectrum (XPS) was employed to clarify the composition of the pomegranate-like Fe₃O₄@N–C NCs. The survey XPS (Figure 3A) confirms the presence of Fe, O, C, and N in the sample. The sub-XPS spectrum for Fe 2p (Figure 3B) exhibits two peaks at 710.7 and 724.1 eV, which are assigned to Fe 2p₃/2 and Fe 2p₁/2, respectively, and consistent with the standard XPS spectrum for Fe₃O₄. Additionally, the peaks at 712.1 and 725.3 eV belong to Fe 2p₃/2 and Fe 2p₁/2 of Fe⁺, as well as 710.2 and 723.4 eV, correspond to Fe 2p₃/2 and Fe 2p₁/2 of Fe²⁺, respectively. The XPS peak of N 1s (Figure 3C) is fitted by the peaks centered at binding energies of 398.9 and 400.0 eV, belonging to pyridinic and pyrrolic N, respectively. To determine the phase composition and crystalline structure of the composites, XRD measurement was performed. Figure 3D shows the XRD pattern of the pomegranate-like Fe₃O₄@N–C NCs. All of the identified peaks can be indexed to the face-centered cubic structure (JCPDS Card No. 04-0894).
Card No. 65-3107), indicating that Fe(OH)₃/PAA-NH₄ was converted to Fe₃O₄ due to the carbothermic reduction between the PAA-derived carbon and Fe(OH)₃. The XRD pattern reveals no obvious peaks corresponding to graphite, demonstrating that the carbon is not well crystallized. The carbon resulting from carbonization of PAA is in an amorphous state because of the absence of peaks corresponding to graphite in the XRD pattern. To verify the graphitization degree of the carbon phase in pomegranate-like Fe₃O₄@N–C NCs, Raman spectrum was measured. As shown in Figure 3E, two peaks at 1340 and 1587 cm⁻¹ are assigned to the D and G bands of carbon respectively. The value of the intensity ratio of the D and G bands (I_D/I_G) is used as an index to estimate the graphitization degree. Here, the I_D/I_G ratio is about 0.82, suggesting low crystallinity of the carbon in the sample. This kind of carbon possesses more Li storage sites than graphitic carbon, leading to increase its capacity. In order to quantify the mass content of carbon in pomegranate-like Fe₃O₄@N–C NCs, thermogravimetric analysis (TGA) was carried out. As shown in Figure 3F, when heated from room temperature to 800 °C in air, a major weight loss takes place between 300 and 400 °C, giving rise to an observed weight loss of 8 w% for pomegranate-like Fe₃O₄@N–C NCs.

To investigate the surface area and the pore size distribution of the pomegranate-like Fe₃O₄@N–C NCs, nitrogen adsorption–desorption was measured. As shown in Figure S4 (Supporting Information), a typical type IV curve with a hysteresis loop within the relative pressure range of 0.8–0.95 implies the existence of mesopore structures formed by the surface carbon layers. Based on that, the Brunauer–Emmett–Teller specific surface area and the total pore volume of the nanostructures are calculated to be 165.533 m² g⁻¹ and 0.411 cm³ g⁻¹, respectively, which are quite high values for pomegranate-like Fe₃O₄@N–C NCs. Besides, the pore size distribution (see the inset of Figure S4 in the Supporting Information) shows that the most probable pore size in the pomegranate-like Fe₃O₄@N–C NCs is centered at around 2.5 nm. Such a mesoporous pomegranate-like Fe₃O₄@N–C NCs with a high specific surface area can endow large electrode–electrolyte contact area and accommodate the volume expansion during the Li⁺ insertion and extraction process, resulting in high specific capacity and excellent cycling stability.

For deeply understanding the advantages of this unique nanostructure, the electrochemical properties of the pomegranate-like Fe₃O₄@N–C NCs are compared with those of core–shell Fe₃O₄@N–C composite prepared under the same conditions. Figure S5A (Supporting Information) shows the representative TEM image of the as-synthesized spherical Fe₂O₃ NSs with a uniform size of ≈85 nm and without aggregation. Figure S5B (Supporting Information) shows TEM image of core–shell Fe₃O₄@N–C NSs with a relatively narrow size distribution, uniform shape, and a mean diameter of about 90 nm. The high-magnification TEM image (see the inset of Figure S5B in the Supporting Information) exhibits that the carbon shells are uniform and continuous with a thickness of about 3 nm. The XRD patterns of pure Fe₂O₃ and core–shell Fe₃O₄@N–C NSs are shown in Figure S6 (Supporting Information). All peaks of pure Fe₂O₃ and core–shell Fe₃O₄@N–C NSs are in good agreement with those of α-Fe₂O₃ (JCPDS Card No. 33-0664), and after calcinating at 500 °C for 4 h, all of the identified peaks of the core–shell Fe₃O₄@N–C can be attributed to Fe₃O₄ (JCPDS Card No. 65-3107), that is, the Fe₂O₃ phase was completely converted to Fe₃O₄ at 500 °C during carbonization under argon atmosphere. TGA was also carried out for core–shell Fe₃O₄@N–C NSs to quantify the mass content of carbon. As shown in Figure S7 (Supporting Information), the content of carbon can be calculated to be about 8.2 wt%, indicating that the carbon contents of the two samples are almost the same.

The charge–discharge curves of the pomegranate-like Fe₃O₄@N–C NCs for various cycles in the voltage range...
of 0.01–3.00 V at a constant current density of 0.5 A g⁻¹ are shown in Figure 4A. In the first cycle, the pomegranate-like Fe₃O₄@N–C NCs show a high initial discharge capacity of 1626.8 mA h g⁻¹ and a charge capacity of 1295.5 mA h g⁻¹. The large irreversible capacity loss of 331.3 mA h g⁻¹ may be mainly attributed to irreversible processes such as the formation of a solid electrolyte interface (SEI layer) and amorphous Li₂O, which are quite common to the most anode materials. After the first cycle, the sample exhibits a high discharge capacity of 1204.3 mA h g⁻¹ retained even after 100th cycle, which is still much higher than the theoretical value of Fe₃O₄ (~928 mA h g⁻¹). The extra discharge capacity of the pomegranate-like Fe₃O₄@N–C NCs might be attributed to the reasons as follows: (1) it has been reported that smaller particle size of the transition oxide favored higher capacitive contributions in the total charge storage. [39] Thus, the probable reason might be due to the ultrafine diameter of the Fe₃O₄ nanoparticles (diameter = 2.5 nm) in the pomegranate-like Fe₃O₄@N–C NCs, which lead to high specific capacity; (2) the large surface area of the pomegranate-like Fe₃O₄@N–C NCs (165.533 m² g⁻¹) benefits the surface adsorption/desorption of lithium ions; (3) the extra lithium intercalation sites are created within the carbon shell during the annealing process. A mechanism for carbon with a defected structure holding extra lithium ions has been proposed by Li et al. [40]

In our case, using N–C shell coating on Fe₃O₄ nanoparticles incorporates the desirable characteristics of Fe₃O₄ nanoparticles and N–C shell in the whole nanostructure, and a strong synergistic effect is realized. However, the initial discharge and charge capacities of the core–shell Fe₃O₄@N–C NSs are only 1281.7 and 806.7 mA h g⁻¹ at 0.5 A g⁻¹ (see Figure S9A in the Supporting Information), respectively, revealing that the ultrafine Fe₃O₄@N–C subunits of the pomegranate-like Fe₃O₄@N–C increase the capacities of the NC electrode cycled at 0.5 A g⁻¹ due to the shorter Li⁺ pathway than the core–shell Fe₃O₄@N–C. The cyclic voltammetry (CV) curves of the pomegranate-like Fe₃O₄@N–C NCs are shown in Figure S8 (Supporting Information). In the first cycle, a strong cathodic peak can be seen at about 0.72 V associated with the reduction of Fe₃O₄ to Fe and the formation of Li₂O. Such strong cathodic peak at 0.72 V is in good agreement with the plateau in the first discharge capacity–voltage in Figure 4A. The CV curves of the pomegranate-like Fe₃O₄@N–C NCs are stable and show good reversibility after the second cycle, which is consistent with its good cycling performance. The discharge–charge cycling performances of the pomegranate-like Fe₃O₄@N–C NCs and core–shell Fe₃O₄@N–C NSs over 100 cycles at a current density of 0.5 A g⁻¹ are illustrated in Figure 4B. The reversible discharge capacity of the core–shell Fe₃O₄@N–C NSs decreases from 973.3 to 826.8 mA h g⁻¹ after 100 cycles. Unlike the core–shell Fe₃O₄@N–C NSs, little capacity decay of the pomegranate-like Fe₃O₄@N–C NCs can be seen from the second cycle onward, and the discharge capacity slightly decreases from 1265.5 (the second discharge capacity) to 1204.3 mA h g⁻¹ over the 100 cycles with high average Coulombic efficiency, corresponding to 95.2% of the second-cycle discharge capacity, indicating that the pomegranate-like Fe₃O₄@N–C NCs display excellent cycle stability. Impedance measurements were performed to demonstrate electron transport and Li-ion diffusion at room temperature in the frequency range of 0.01 Hz to 100 kHz. The impedance spectra of pomegranate-like Fe₃O₄@N–C NCs and core–shell Fe₃O₄@N–C NSs over 100 cycles at a current density of 0.5 A g⁻¹ are shown in Figure 4C, which consist of a depressed semicircle in the high to medium frequency region and an inclined line in the low-frequency region.

**Figure 4.** Electrochemical performances of pomegranate-like Fe₃O₄@N–C NCs A) discharge–charge curves at 0.5 A g⁻¹ in the voltage range of 0.01–3.0 V, B) cyclic performance of pomegranate-like Fe₃O₄@N–C NCs and core–shell Fe₃O₄@N–C NSs at 0.5 A g⁻¹, C) Nyquist plots of the fresh cycle, 100th, 500th, and 1000th cycle in the frequency range of 100 kHz to 0.01 Hz, D) rate capability at different rates (increased from 0.5 to 20 A g⁻¹), and E) long cycling performances of pomegranate-like Fe₃O₄@N–C NCs at 1, 10, and 20 A g⁻¹.
The impedance data are analyzed using Z-view software by fitting to an equivalent electrical circuit (the inset of Figure 4C) composed of electrolyte ($R_e$) and charge transfer ($R_d$) resistances, a constant phase element (CPE) instead of pure capacitance (due to the depressed semicircle observed in the spectra), diffusional components like Warburg impedance ($W_i$) and the intercalation capacitance ($C_{int}$), similar to the circuit employed for other oxide electrodes. It can be seen that the pomegranate-like Fe$_3$O$_4$@N–C anode exhibits a lower value of $R_e$ of 53.4 Ω after 100 cycles, as compared to 115.7 Ω at the fresh cycle, implying that the charge transfer impedance decreases substantially compared to its fresh cycle. Especially, the value of $R_d$ after the 1000th cycle differs only slightly from the 500th cycle, demonstrating the good structure stability of the electrode. The total resistances of the core–shell Fe$_3$O$_4$@N–C NSs are all larger than that of the pomegranate-like Fe$_3$O$_4$@N–C electrode at various cycles (see Figure S9C in the Supporting Information). The result reveals that the ultrafine Fe$_3$O$_4$@N–C subunits promote the charge transfer, and thus improve the electrochemical performance.

The rate performances of the pomegranate-like Fe$_3$O$_4$@N–C NCs and core–shell Fe$_3$O$_4$@N–C NSs are shown in Figure 4D, which is the key factor for practical application such as hybrid and pure electric vehicles during the lithium-ion insertion/ extraction processes. Of the two samples, the pomegranate-like Fe$_3$O$_4$@N–C NCs exhibit the better rate capability. The discharge capacities of the pomegranate-like Fe$_3$O$_4$@N–C NCs are 1206.3, 1053.1, 940.6, 750.0, 609.4, 496.9, and 412.5 mA h g$^{-1}$ at current densities of 0.5, 1, 2, 5, 10, 15, and 20 A g$^{-1}$, respectively. Remarkably, even at current density as high as 20 A g$^{-1}$, the materials can still deliver a reversible capacity of 412.5 mA h g$^{-1}$, which is much higher than the theoretical capacity of graphite (372 mA h g$^{-1}$). Moreover, the pomegranate-like Fe$_3$O$_4$@N–C NSs still exhibit 1209.1 mA h g$^{-1}$ when the current is restored to 0.5 A g$^{-1}$, corresponding to 98.7% of the initial capacity. To investigate the long cycling performance of the pomegranate-like Fe$_3$O$_4$@N–C NCs, we examine upon 1000 cycles at high current density (1, 10, and 20 A g$^{-1}$) shown in Figure 4E. Excellent cycling performance with a high stable capacity can be obtained from the pomegranate-like Fe$_3$O$_4$@N–C NCs. The initial discharge and charge capacities of the pomegranate-like Fe$_3$O$_4$@N–C NCs are up to 1633.3 and 1127.6 mA h g$^{-1}$ at 1 A g$^{-1}$, respectively. It can be seen that the capacity slightly declines at the first 50 cycles and then increases continuously and finally reaches a high specific capacity of 1063.0 mA h g$^{-1}$ after 1000 cycles, which is about 98.4% retention of the second capacity. Even at high current density of 10 and 20 A g$^{-1}$, the pomegranate-like Fe$_3$O$_4$@N–C NCs still deliver high discharge capacity of 606.0 and 417.1 mA h g$^{-1}$ after 1000 cycles, with a capacity retention of 92.0% and 91.7%, respectively, indicating high capacity and excellent capacity retention of the pomegranate-like Fe$_3$O$_4$@N–C NCs. The core–shell Fe$_3$O$_4$@N–C NSs electrode shows a very poor cycling performance that only delivers 261.5 mA h g$^{-1}$ after 1000 cycles at 20 A g$^{-1}$ (see Figure S9B in the Supporting Information). It is clear that the capacity fading of core–shell Fe$_3$O$_4$@N–C NSs is rather severe at a current density of 20 A g$^{-1}$, and the capacity after 1000 cycles declines to only 261.5 mA h g$^{-1}$, owing to the longer Li$^+$ pathway and the unstable core–shell nanostructure at relative high current density. The excellent electrochemical performance of the pomegranate-like Fe$_3$O$_4$@N–C NCs, especially the high capacity and excellent cycling stability available at high current density, should be attributed to the ultrafine subunits and the stable structure of carbon supports, increasing electrical conductivity and shortening Li$^+$/electron diffusion pathways during the repeated redox reaction. Scheme 1 shows the Li$^+$ diffusion pathways in the pomegranate-like Fe$_3$O$_4$@N–C NCs and core–shell Fe$_3$O$_4$@N–C NSs. The pomegranate-like Fe$_3$O$_4$@N–C NCs have the advantage of easy electrolyte penetration, and structural stability, and they dramatically shorten Li$^+$ diffusion pathway and facilitate Li$^+$ diffusion throughout the entire NC during cycling. Herein, the Li$^+$ diffusion pathway in the as-synthesized pomegranate-like Fe$_3$O$_4$@N–C NCs is only 2 nm, leading to its high specific capacity and excellent rate capability. The core–shell Fe$_3$O$_4$@N–C NSs, on the other hand, display longer Li$^+$ diffusion pathway with increasing depth below the surface of the NS.

To further demonstrate the excellent structure stability of the pomegranate-like Fe$_3$O$_4$@N–C NCs, TEM and SEM were analyzed in the delithiated and lithiated state after 1000 cycles at 1 A g$^{-1}$. As shown in Figure S10 (Supporting Information), it can be found that no obvious volume change can be observed in the lithiated state and the morphology of pomegranate-like Fe$_3$O$_4$@N–C composite structure remains well and highly dispersed, indicating the good structural stability of the pomegranate-like Fe$_3$O$_4$@N–C NCs in the process of
electrochemical cycles. Considering its excellent stability of the nanostructure, the pomegranate-like Fe$_3$O$_4@$N–C NCs are believed to become potential high performance anode materials for long cycle life and high-rate Li-ion batteries.

3. Conclusion

In summary, a facile and novel one-pot method has been developed to fabricate the pomegranate-like TMO@N–C NCs composed of numerous of ultrafine TMO@N–C subunits, which notably have a rather high yield. Taking pomegranate-like Fe$_3$O$_4@$N–C NCs as an example, compared with the core–shell Fe$_3$O$_4@$N–C NSs, these pomegranate-like Fe$_3$O$_4@$N–C NCs can provide short Li$^+$/electron diffusion pathways for electrochemical reactions, structural stability during cycling and high electrical conductivity, leading to superior electrochemical performance for Li-ion batteries. When evaluated as anodes for Li-ion batteries, the pomegranate-like Fe$_3$O$_4@$N–C NCs showed high discharge capacities of 1204.3 mAh g$^{-1}$ at 0.5 A g$^{-1}$ over 100 cycles (95.6% retention), 1063.0 mAh g$^{-1}$ at 1 A g$^{-1}$ (98.4% retention), 606.0 mAh g$^{-1}$ at 10 A g$^{-1}$ (92.0% retention) and 417.1 mAh g$^{-1}$ at 20 A g$^{-1}$ (91.7% retention) after 1000 cycles. Thus, the superior electrochemical performance of the obtained pomegranate-like Fe$_3$O$_4@$N–C NCs indicates that the integration of the pomegranate-like NCs composed of ultrafine subunits and the N–C coating is a feasible way to improve the electrochemical performance of next-generation Li-ion batteries. Furthermore, this strategy can be further applied for the preparation of other cathode and anode materials with this unique pomegranate-like nanostructure. The unique pomegranate-like nanostructure organized by ultrafine Fe$_3$O$_4@$N–C subunits in this work can have significant implications in developing next-generation-high-performance LIBs with great promises to promote the practical applications in energy storage devices.

4. Experimental Section

Materials: PAA ($M_w ≈ 1800$) was purchased from Sigma-Aldrich (USA). Ferrous chloride tetrahydrate (FeCl$_2$·4H$_2$O, 99.7%), manganese chloride tetrahydrate (MnCl$_2$·4H$_2$O, 99.0%), nickel chloride hexahydrate (NiCl$_2$·6H$_2$O, 98.0%), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, 99.0%), anhydrous ethanol, IPA, and aqueous ammonia solution were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd and used without further purification. Deionized water was used in all experiments. From the author.

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

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21573040 and 21603029), the National Science Foundation of China (21573040 and 21603029), the Natural Science Foundation of China (21573040 and 21603029), and the Natural Science Foundation of China (21573040 and 21603029).

Supporting Information is available from the Wiley Online Library or from the author.
Conflict of Interest
The authors declare no conflict of interest.

Keywords
high rate performance, lithium-ion batteries, nitrogen-doped carbon, pomegranate-like nanoclusters, ultrafine nanoparticites

Received: August 25, 2017
Revised: September 19, 2017
Published online:
