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Title: Microspheres self-assembled by anti-site defect-less nanocrystal-LiFePO4@C/rGO to achieve both high-rate capability and high tap density for Li-ion batteries

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COMMUNICATION

Microspheres self-assembled by anti-site defect-less nanocrystal-LiFePO$_4$@C/rGO to achieve both high-rate capability and high tap density for Li-ion batteries


Abstract: LiFePO$_4$@C/rGO hierarchical microspheres with superior electrochemical activity and high tap density were first synthesized using a Fe$^{3+}$-based single inorganic precursor (LiFePO$_4$@RF/GO) obtained from a template-free self-assembly synthesis, following with direct calcination. The synthesis process requires no physical mixing step. The phase transformation pathway from tavorite LiFePO$_4$ upon calcination was determined by the in situ high temperature XRD technique. Benefitted from the unique structure of the material, these microspheres can be densely packed together, giving a high tap density of 1.3 g cm$^{-3}$, and simultaneously, the defectless LiFePO$_4$ primary nanocrystals modified with highly conductive surface carbon layer and ultrathin rGO provide good electronic and ionic kinetics for fast electron/Li$^+$ ion transport.

Lithium-ion batteries (LIBs), as one important technology for electric energy storage, have revolutionally extend the battery life of portable electronic devices (e.g. smart phones, wearable devices, and laptop computers), and now stand as a promising up and storage system of electric energy storage. [1-3] To date, olivine (e.g. LiFePO$_4$), layer-type (e.g. LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$), and spinel (e.g. LiMn$_2$O$_4$) electrode materials are the three mostly used cathodes for high power LIBs. [1, 4] Among them, LiFePO$_4$ is more stable in thermodynamics and reaction kinetics than the other two owing to the presence of a robust polyanionic framework. [5-7] Moreover, LiFePO$_4$ prevails in terms of natural abundance, cost, and environmental friendliness. The major issue to this material is the negative transport kinetics in both Li$^+$ ion diffusion and electron delivery. Size tailoring, in conjunction with surface carbon (i.e. graphitic carbon, graphene, etc) coatings to form LiFePO$_4$/C nanocomposite is acknowledged as a technology of choice to alleviate this issue effectively. [8-9] However, when the particle size of LiFePO$_4$/C is decreased down to nanoscale, thermodynamic instability and high risk of side reactions with the organic electrolyte become into new hazards needed to be faced with. [10] In addition, the processability and tap density (less than 1.0 g cm$^{-3}$) of the powders also require improvements when it comes to a practical point of view. [11] For that, small LiFePO$_4$/C nanoparticles assembled into hierarchical architectures, ideally with a microsphere morphology, would naturally become more easily free-flowing and can be densely packed together, giving a higher tap density and hence a higher volumetric energy density. [12-14]

Hydrothermal and solvothermal synthesis technologies or a combination of them are the methods commonly used to create LiFePO$_4$/C microsphere with hierarchical architectures, the vast majority of which, however, required the use of instable and costly ferrous iron (Fe$^{2+}$) salts as the raw material, and simultaneously a reducing agent and/or inert gas to avoid the oxidation of Fe$^{2+}$ ions during reactions. [15, 16] On top of that, most attempts to develop new routes, especially through ferric iron (Fe$^{3+}$) based approaches, focused either on the “one-pot synthesis” or “in-situ carbon coating”, rather than considering both two concepts together. [12-14] Thus exploring a simpler synthesis scheme to produce LiFePO$_4$/C microspheres with ideal structural features will be of great interest.

In this communication, reduced GO-modified LiFePO$_4$/C (i.e. LiFePO$_4$@C/rGO) hierarchical microspheres were synthesized for the first time by a one-pot mixed-solvothermal process to form a ferric three-component precursor of LiFePO$_4$OH@RF/GO, followed by direct calcination at high temperature, during which tedious physical mixing and grinding step can be totally avoided. The final LiFePO$_4$@C/rGO microspheres created can be densely packed together, giving a high tap density of 1.3 g cm$^{-3}$, and simultaneously, the small primary LiFePO$_4$ nanoparticles (65 nm), in conjunction with the integrated carbonous conductive network can provide an adequate electrochemically available surface for enhancing the high-rate capability. The phase transformation mechanism from tavorite LiFePO$_4$OH to the olivine LiFePO$_4$ upon calcination was also determined by the in situ high temperature X-ray diffraction (XRD).

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As schematically illustrated by Figure 1, the synthesis started with a one-step mixed-solvothermal process that proceeded at a designated temperature of 180 °C under mechanical stirring. The process involved the addition of a methanol solution containing formaldehyde to an aqueous solution containing Li⁺, Fe³⁺, PO₄³⁻, resorcinol and GO. Detail structure information and morphology of the GO are shown in Figure S1-S4. Here, the methanol acted as a chelating agent to disrupt the screening of charges by the water due to its relatively lower polarity. In other words, the methanol with a low dielectric constant can promote the electrostatic attraction between the negative phosphate groups and the positive Li⁺ and Fe³⁺ ions in the solution to establish stable ionic bonds. 

Along with the crystallization of LiFePO₄OH nanocrystals at an elevated temperature, the resorcinol added reacted with formaldehyde simultaneously to form the resorcinol-formaldehyde (RF) resin by a catalytic polymerization process. The RF resin coated in situ on the surface of LiFePO₄OH nanoparticles, separating them from each other to avoid continuous crystal growth, and linking them together via the polymer network to assemble the hierarchical microspheres. As thus, contact-induced growth of formed LiFePO₄OH nanoparticles was regulated by the surface RF resin coverage during reaction. Detailed polymerization mechanism between resorcinol and formaldehyde can be described by Figure S5. 

Moreover, the GO nanosheets with abundant hydroxyl and/or carboxyl groups anchored onto the LiFePO₄OH@RF composite through an electrostatic interaction and/or host-guest binding behavior, forming a three-component composite. 

Note that the RF resin is more chemically stable under such a high temperature than other organics such as sucrose, glucose, etc., which remained highly polyfunctional during the whole reaction and was capable of maintaining the strong chemical interactions with both LiFePO₄OH nanoparticles and GO nanosheets. Heat treatment in Ar/H₂ atmosphere led to the conversion of LiFePO₄OH@RF/GO into the final LiFePO₄@C/rGO composite microspheres. During the calcination process, the isolated nanoparticles of single inorganic favorite LiFePO₄OH crystallized into olivine LiFePO₄ nanocrystals, and meanwhile the surface RF resin and GO were converted into a highly conductive carbon shells network and large rGO nanosheets, respectively, and in situ restricted the growth of primary LiFePO₄ nanocrystals and the secondary microspheres.

As suggested by the XRD pattern of LiFePO₄OH@RF/GO (Figure 2A), all the Bragg reflections can be well indexed to the standard triclinic structure of favorite LiFePO₄OH (JCPDS No. 41-1376) without other discernible phases. The broad diffraction peaks of the XRD pattern presage a small particle size of the material. On the basis of Scherrer’s formula (d=0.89 λ/βcosθ), the mean size of primary LiFePO₄OH crystals can be estimated to be ~30 nm. A lack of GO and RF polymer characteristic signals can be explained by the lower content and the disordered state of the materials, respectively. The successful loading of RF resin on the LiFePO₄OH crystals was synthetically verified by the Fourier transform infrared spectroscopy (FTIR), HRTEM and TEM-energy dispersive spectroscopy (TEM-EDS) as illustrated in Figure S6-S8. A yellowish-brown appearance of the final LiFePO₄OH@RF/GO composite material suggests a slight pyrolysis of the RF polymer contained. Typical SEM images, given in Figure 2C, reveal that the LiFePO₄OH@RF/GO material shows a regular microsphere morphology with a mean particle size of 2.2 μm in diameter (Figure S9), on which a large number of ultrathin GO nanosheets with lateral size up to several micrometers can be clearly observed. At a higher magnification (inset in Figure 2C), one can notice the microspheres are composed of densely aggregated nanoparticles with tens of nanometers in size, in good agreement with the above XRD analysis, confirming the hierarchical architecture characteristic of the LiFePO₄OH@RF/GO composite microspheres. It is believed that the RF polymer formed in situ on the surface of the LiFePO₄OH nanocrystals has restricted their grain growth effectively during the solvothermal process. Besides,

Figure 1. Schematic illustration for the synthesis process of LiFePO₄@C/rGO composite microspheres by using a three-component precursor (LiFePO₄OH@RF/GO) achieved from a template-free self-assembly approach (Step 1), followed by direct calcination at high temperature (Step 2).

Figure 2. (A) XRD powder patterns of LiFePO₄OH@RF/GO and LiFePO₄@C/rGO composite microspheres. (B) In situ high temperature XRD analysis of LiFePO₄OH@RF/GO microspheres under an inert atmosphere at controlled temperatures (25-700 °C, heating rate of 5 °C min⁻¹) with 15 minutes for each collection. Typical SEM images of (C) LiFePO₄OH@RF/GO and (D) LiFePO₄@C/rGO microspheres. Insets show corresponding HR-SEM images, and the scale bars are both 500 nm.
GO nanosheets with highly active negative groups (hydroxyl and carboxyl) chelated with positive Li\(^+\) and Fe\(^{3+}\) ions strongly, capable of depressing the secondary particle growth and also making the composite microspheres uniform in dimension.

Thermal heat treatment in an Ar/\(H_2\) (6 \%) atmosphere led to the conversion of LiFePO\(_4\)@RF/GO into LiFePO\(_4\)@C/rGO composite, as suggested by the XRD pattern (Figure 2A). The entire diffraction peaks of LiFePO\(_4\)@C/rGO material match well with the standard orthorhombic structure of LiFePO\(_4\) (JCPDS No. 81-1173). X-ray photoelectron spectroscopy (XPS) spectra were also analyzed to check for the oxidation state of iron species in the surface-near region (depth of <5 nm), as shown in Figure S10, which confirmed the iron species in LiFePO\(_4\)@C/rGO composite are all at a Fe (II) oxidation state.\(^{20}\) The mean particle size of LiFePO\(_4\) nanocrystals was estimated to be 65 nm by Scherrer’s formula. Given the fact that the LiFePO\(_4\) and its precursor (LiFePO\(_4\)@RF) were comparable in particle dimension, the surface residual carbon derived from the RF polymer in situ coated should have effectively restricted the particle growth of LiFePO\(_4\) crystals during heat treatment. Morphology details of LiFePO\(_4\)@C/rGO were illustrated by the SEM images (Figure 2D and Figure S11), from which we can observe the material remained the hierarchical microsphere morphology as LiFePO\(_4\)@RF/GO. It is interesting to note that part of the rGO nanosheet seems to embed into the interior of the microsphere, while the rest wraps around the exterior surface. Integrating large rGO nanosheets in such a manner can help to establish a continuous and robust conductive network, which extended from the external to the inside of the LiFePO\(_4\)/C microspheres and even between the microspherical particles, thus alleviating the polarization of electrode. \(N_2\) adsorption/desorption isotherm of LiFePO\(_4\)@C/rGO composite microspheres (Figure 3A) appears to be a type IV curve with a large type H2 hysteresis loop, typical characteristic of \(N_2\) molecular adsorption in mesoporous materials. Calculated from the adsorption isotherm, the Brunauer-Emmett-Teller (BET) surface area is determined to be 30.5 m\(^2\) g\(^{-1}\). Such high internal surface area and mesoporous structure would, we believe, not only allow a better penetration of electrolyte to facilitate the Li\(^+\) ion diffusion but also a better electrons transport in the interior of LiFePO\(_4\)@C/rGO microspheres, ultimately enhancing the rate capability for lithium ion insertion/deinsertion reaction. SEM-energy dispersive spectroscopy (SEM-EDS) mapping images of an individual LiFePO\(_4\)@C/rGO composite microsphere (shown in Figure S12) indicate a uniform distribution of Fe, P, O and C elements in the spherical scanning region. The sheet-like feature in the mapping just peculiar to the C element at the edges of the microspheres was attributable to the surface rGO nanosheets, indicating a complete reduction of GO upon heat treatment. Further investigation by TEM image, shown in Figure S13, indicates some typical discrete nanoparticles of LiFePO\(_4\)@C/rGO microspheres obtained by grinding centre around 65 nm in size, in good agreement with the above XRD result. High resolution TEM (HRTEM) image (Figure S14) reveals the visible lattice fringes correspond to a spacing of 0.25 nm (marked by a pair of parallel red lines in the crystalline region), which matches well with the expected spacing of the (131) plane of olivine-type LiFePO\(_4\), indicating the observed nanoparticles is single-phase LiFePO\(_4\) and highly crystalline. The LiFePO\(_4\) nanocrystal was coated by a layer of amorphous carbon with a typical thickness of ~2.0 nm.

Generally speaking, the kinetic barrier for Li\(^+\) ions to diffuse through such a thin carbon layer can be totally neglected in contrast to other diffusion kinetic limitations upon cycling.\(^{21, 22}\) The mass fraction of carbon contained was determined by the CHN elemental analysis to be ~6 wt. %. Detailed structure information on the surface residual carbon was further verified by the Raman spectroscopy (Figure S15).\(^{12, 21, 23}\) Typically, an increase in the peak intensity ratio (I\(_{D}/I_{G}\)) in Raman is an indicator of a greater degree of ordering for graphitic materials.\(^{12, 21, 23}\) According to the fitting result, the I\(_{D}/I_{G}\) value of LiFePO\(_4\)@C/rGO was estimated to be 0.82, which is similar to or higher than those of most LiFePO\(_4\)/C modified with other types of semi-graphitized carbon.\(^{12, 23}\) implying the residual carbon pyrolyzed from the RF polymer and GO is more graphitized, capable of providing a better electric transfer around LiFePO\(_4\) nanoparticles. Moreover, a lack of LiFePO\(_4\) Raman response in the range of 600-1100 cm\(^{-1}\) illustrates that the carbon coating on the LiFePO\(_4\) nanoparticles is fairly complete.\(^{12, 21}\) In view of the one-dimensional (1D) Li\(^+\) diffusion pathway in the LiFePO\(_4\) framework, a thorough surface modification with a layer of highly graphitized carbon can enable the electrons to reach all the positions where Li\(^+\) intercalation takes place, leading to a higher rate capability.\(^{21, 24}\)

A Fe\(_2\) site anti-defect, namely Fe\(^{2+}\) ion occupying the Li\(^+\) site, is commonly observed in LiFePO\(_4\) crystals, and it has been proven unfavorable due to the blocking of the Li\(^+\) ions diffusion pathway.\(^{21, 25, 26}\) The content of Fe\(_2\) defects in LiFePO\(_4\) can be easily identified by FTIR spectroscopy. Theoretically, the absorption peak concerning to the P-O symmetric stretching vibration of PO\(_4\) tetrahedron in Fe\(_2\) defect-free LiFePO\(_4\) should emerge at 957 cm\(^{-1}\), and it shifts towards a higher wavenumber with the number of Fe\(_2\) anti-defect defects increasing.\(^{21, 25, 26}\) For LiFePO\(_4\)@C/rGO, the characteristic peak was measured to appear at 960 cm\(^{-1}\) (shown in Figure 3B), that is, close to the theoretical value of Fe\(_2\) defect-free LiFePO\(_4\), illustrating a very small number of Fe\(_2\) defects in the LiFePO\(_4\)@C/rGO material. To identify the cause of the extremely low defect population, the phase transformation mechanism of LiFePO\(_4\)@RF/GO was further studied. Figure 2B lists the in situ high temperature XRD data showing a detailed evolution from LiFePO\(_4\)@RF/GO to LiFePO\(_4\)@C/rGO during temperature ramping. Clearly, the triclinic LiFePO\(_4\) degraded starting at 400 °C and lasted until about 500 °C with the appearance of a new crystalline phase.

**Figure 3.** (A) Typical \(N_2\) absorption-desorption isotherms of the LiFePO\(_4\)@C/rGO microspheres with a large type H2 hysteresis loop, typical characteristic of mesopore structure. (B) Typical FTIR spectrum of the LiFePO\(_4\)@C/rGO microspheres recorded in the wavenumber region of 400–1200 cm\(^{-1}\).
associated with single orthorhombic LiFePO₄. Thereafter, the degree of crystallization of the LiFePO₄ increased gradually as the temperature increased. It thus follows that the phase transformation pathway upon heat treatment from LiFePO₄OH to LiFePO₄ obeyed a local crystal to crystal phase transformation model, which is believed better for depressing the formation of Feₓ₂ super-anti-site defects in LiFePO₄ by avoiding the complex crystallographic phase transition and long-range solid-solid mass transfer process upon crystallization.

Remarkable rate capability and cycle stability are desirable features for high power LIBs. Galvanostatic charge/discharge performance of LiFePO₄/C/rGO microspheres are shown in Figure 4A. Here, 1 C rate corresponds to a current density of 170 mA g⁻¹. Notably, at a low rate of 0.2 C, the material discharged to a capacity of 157.2 mAh g⁻¹, that is, close to its estimated theoretical value (159.8 mAh g⁻¹) calculated by considering a well-defined mixture of active LiFePO₄ and the surface residual carbon (~6 wt. %). The material still delivered reversible capacities of 146.7, 139.8, 127.5, and 112.4 mAh g⁻¹ at intermediate rates of 1 C, 2 C, 5 C, and 10 C, respectively, and remained relatively flat voltage plateaus at all rates. A flatter potential plateau during the charge/discharge process for LiFePO₄/C/rGO indicates a less pseudocapacitive contribution from surface/interfacial lithium storage. [26] Even at high rates of 30 C and 60 C tested, LiFePO₄/C/rGO can still release stable discharge capacities of 86.5 and 60.8 mAh g⁻¹. After the incremental rate test up to 60 C rate, the reversible capacities almost restored to the initial values of 109.3 and 157 mAh g⁻¹ successively when the discharging rate was changed back to 10 C and 0.2 C, as shown in Figure 4B, illustrating the capacity decay at high rates is majorly due to the electrode polarization associated with diffusion-limited transfer of Li⁺ ion across the two-phase interface, rather than the structure instability of LiFePO₄/C/rGO material. [21] From a topological point of view, the superior electrochemical performance of LiFePO₄/C/rGO can be derived from the unique hierarchical composite structure of LiFePO₄OH@RF/GO precursor, which was formed from fully sealing RF resin polymer "shells" with a spherical 3D-connected network and single-source inorganic LiFePO₄ "cores" where the ideal elements of Li, Fe, P, and O are evenly distributed at the atomic level, thus capable of minimizing the formation of undesired impurities and Feₓ₂ lattice defects for the LiFePO₄ obtained owing to the absence of complex crystallographic phase transition and long-range solid-solid mass transfer process upon crystallization. [21, 27] In addition, the ultrathin rGO nanosheets anchored on the surface can establish a continuous and robust conductive network for inter-particle electrical connection to lower the soft contact impedance. [19, 28]

To prove this, we synthesized LiFePO₄@C in an identical process except the addition of GO during the hydrothermal synthesis for comparison (Figure S16), whose rate performance was inferior to that of LiFePO₄@C/rGO (Figure S17). The good electronic and ionic kinetics of LiFePO₄@C/rGO were further supported by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses, as shown in Figure S18 and S19. The material was found to exhibit higher rate capability than those of the LiFePO₄/C microspherical samples reported in the references (shown in Figure S20), [12-15, 29-31] Although the performance of LiFePO₄/C/rGO at higher rates (>10 C) was slightly lower than that of the nanosized LiFePO₄/C reported by the previous studies, [21, 24] the LiFePO₄/C/rGO material achieved a tap density of 1.3 g cm⁻³, which is almost 30 % higher than that currently reported for carbon-coated irregular LiFePO₄ nanomaterials (≤1.0 g cm⁻³), thus better for volumetric energy density. Some micromized LiFePO₄/C [92, 33] had been reported to show a higher tap density (1.6 or even 1.9 g cm⁻³), but their rate capabilities are markedly lower than LiFePO₄@C/rGO due to the slow Li⁺ ion transport in the bulk (imposed by the larger primary particles). Therefore, it can be regarded the LiFePO₄/C/rGO composite microspheres provide a good compromise between tap density and rate capacity, giving a relatively high tap density and simultaneously a high rate capability.

The long-term cycling stability of obtained LiFePO₄/C/rGO microspheres was evaluated by continuous charge/discharge at 2 C rate for 300 cycles, and then at a high rate of 10 C for 700 cycles, as shown in Figure 4C. The capacity retention of the material is superior. Almost no capacity fading can be observed after cycling at 2 C for 300 cycles. When cycled at 10 C for another 700 cycles, the final capacity retention was higher than 95 %, equivalent to less than 0.007 % capacity loss per cycle. Corresponding coulombic efficiency as shown in the inset of Figure 4C stayed at about 100 %. In addition to the contributions of the stable LiFePO₄ nanocrystals, the robust spherical 3D conductive carbon network along with large rGO nanosheets formed in situ on the surface of LiFePO₄ particles are also supposed to play a critical role in the good cycling reversibility by relaxing the strain energy of the entire electrode upon Li⁺ ion insertion/extraction.

Conclusions

In summary, we have developed a unique method to create hierarchical LiFePO₄/C/rGO composite microspheres through a template-free self-assembly approach to form a Feₓ₂-based single-source inorganic precursor-LiFePO₄OH@RF/GO, followed
by direct calcination. Benefitted from the unique hierarchical architecture of the material, these microspheres can be densely packed together, giving a high tap density of 1.3 g cm$^{-3}$, and simultaneously, the defect-less LiFePO$_4$ primary nanocrystals modified with highly conductive surface carbon layer and ultrathin rGO provide good electronic and ionic kinetics, thus achieving superior electrochemical performance including good rate capability and cycling stability. The synthesis route we reported also has the advantages in simplicity, low cost, and environmental friendliness for scale-up and commercialization. We hope this work would enlighten a brand-new way to the mass production of microspherical LiFePO$_4$/C cathodes for high power LIBs.

**Experimental Section**

**Materials synthesis.** The graphene oxide (GO) was produced from natural graphite flakes (Sigma-Aldrich, <20 μm) by a modified Hummers method (Y. Xu, H. Bai, G. Lu, et al., J. Am. Chem. Soc., 2008, 130, 5856–5857; X. Yan, Y. Li, F. Du, et al., Nanoscale, 2014, 6, 4108-4116). GO-modified LiFePO$_4$/OH/RF (named as LiFePO$_4$/OH@RF/GO) hierarchical microspheres were synthesized by a one-pot mixed solvothermal method. Typically, 0.01 mol H$_3$PO$_4$, 0.02 mol lithium hydroxide monohydrate, 0.01 mol Fe(NO$_3$)$_3$$\cdot$9H$_2$O and 0.005 mol resorcinol were dissolved in 10 g of graphene oxide suspension (~2 mg mL$^{-1}$). Afterwards, 10 g of methanol solution containing 0.01 mol formaldehyde was added. The mixture solution was then transferred into an autoclave and heated at 180 °C for 6 h under argon gas atmosphere (2 atm). After being cooled down to the room temperature by water quench, the brown precipitate was collected by filtration, washed several times with deionized water, and dried for 6 h at 70 °C. rGO-modified LiFePO$_4$/C (LiFePO$_4$/OH@C/rGO) hierarchical composite microspheres were obtained by a subsequent calcination of the LiFePO$_4$/OH@RF/GO precursor at 700 °C for 6 h under an Ar/H$_2$(6 %) atmosphere. The synthesis of LiFePO$_4$/OH@RF was similar to that of LiFePO$_4$/OH@RF/GO except the addition of GO. LiFePO$_4$/OH@C was obtained by calcining LiFePO$_4$/OH@RF under the condition identical to the preparation of LiFePO$_4$/C/rGO.

**Materials characterizations.** X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2550 diffractometer at 50 kV and 20 mA with Cu Ka radiation ($\lambda$=1.5418 Å). Fourier transform infrared spectrometer (FTIR) spectra were tested by a Bruker IFS-660/S spectrometer. X-ray photoelectron spectroscopy (XPS) tests were performed on an ESCA LAB MARK II spectrometer. Morphology details of the materials were examined by JEOL JSM-6700F scanning electron microscope (SEM) and JEOL JSM-3010 transmission electron microscopy (TEM). Nitrogen absorption-desorption isotherms were examined on a Micromeritics ASAP 2020M instrument. The specific surface areas were calculated by employing the Brunauer-Emmett-Teller (BET) equation. CHN analysis was carried out by an Elementar Vario MICRO cube analyzer. Raman spectrum was collected by a Renishaw inVia Raman microscope with 514.5 nm laser radiation and fitted using a Gaussian-Lorentzian model. Atomic force microscopy (AFM) images were obtained using a Bruker Dimension Icon scanning probe microscope. The tap density was measured from the method reported by Qian et al. (J. Phys. Chem. C 2010, 114, 3477-3482): a certain mass of the product was placed in a small measuring cylinder and tapped on for at least 5 min by hand. The measured volume of the tapped powder and its mass were used to calculate the tap density.

**Electrochemistry tests.** For the electrochemical test, 80 wt. % of active material, 10 wt. % of acetylene black (AB) and 10 wt. % of polyvinylidene fluoride (PVDF) were firstly mixed evenly with N-methyl-2-pyrrolidone (NMP). The blended slurry formed was then cast on an aluminum foil current collector. After being dried thoroughly in vacuum at 110 °C, the electrode sheet was tailored into disks of φ10 mm and assembled in CR2032 coin-type cells with lithium metal as counter electrode under an Ar-filled glovebox. The loading mass of active material in the electrode is ~2 mg (area of 0.785 cm$^2$). A mixed solution of ethylene carbonate (EC), ethylmethyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 by volume) containing 1 M LiPF$_6$ was used as electrolyte. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured on a Bio-Logic VSP electrochemical workstation. CV curves were recorded with increasing scanning rates from 0.2 to 5 mV s$^{-1}$ (2.5–4.1 V). EIS was collected at open circuit voltage (OCV) after three cycles of activation in the frequency range of 200 KHz-10 mHz (amplitude of 5 mV). All the electrochemical tests were performed at ambient temperature (~25 °C).

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**Keywords:** LiFePO$_4$/C/rGO • hierarchical microspheres • antidote defects • LiFePO$_4$/OH • lithium ion batteries

Microspheres self-assembled by anti-site defect-less nanocrystal-LiFePO$_4$@C/rGO to achieve both high-rate capability and high tap density for Li-ion batteries

The major merit of this work is to determine a unique method to synthesize hierarchical LiFePO$_4$@C/rGO composite microspheres with enhanced electrochemical activity and high tap density by using ferric iron-based single inorganic precursor (LiFePO$_4$OH@RF/GO) achieved by a template-free self-assembly synthesis, followed by direct calcination. The preparation process requires no physical mixing step and is proven effective in depressing the Fe anti-site defects in LiFePO$_4$ crystals.