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Hierarchical Sandwich-like Structure of Ultrafine N-Rich Porous Carbon Nanospheres Grown on Graphene Sheets as High-Rate Long-Life Anode Materials for Lithium Ion Batteries

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Abstract

A novel sandwich-like, graphene-based porous nitrogen-doped carbon (PNCs@Gr) material is prepared through facile pyrolysis of zeolitic imidazolate framework (ZIF-8) nanoparticles *in situ* grown on graphene oxide (GO) (ZIF-8@GO), and is evaluated as anode in lithium ion battery cell for the first time. It is found that the sandwich-like nanostructured PNCs@Gr exhibits remarkable capacities, outstanding rate performance and cycling stability exceeding carbon-based anode materials reported in literature. In addition to an extremely high initial capacity of 1378 mAh g⁻¹ at 100 mA g⁻¹, this PNCs@Gr electrode can be cycled at high specific currents of 500 and 1000 mA g⁻¹ with very stable reversible capacities of 1070 and 948 mAh g⁻¹ to 100 and 200 cycles, respectively. At an even higher specific current of 5000 mA g⁻¹, the electrode still delivers a reversible capacity of over 530 mAh g⁻¹ after 400 cycles, showing a capacity retention of as high as 84.4%. Such impressive electrochemical performance is ascribed to ideal combination of hierarchically porous structure, highly conductive graphene platform and high-level nitrogen doping in the sandwich-like PNCs@Gr electrode obtained via *in situ* synthesis.

Key words: N-doped carbon, graphene, sandwich-like nanostructure, anode materials, lithium ion batteries

Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used as energy storage devices for portable electronic devices.^{1,2} Nevertheless, the ever-increasing demands for emerging applications in portable electronics and electric vehicles (EVs) are pushing the research to develop LIBs with higher energy density and power density as well as longer cycling life. Graphite, the most commonly used commercial anode material, suffers from some disadvantages such as low theoretical capacity of 372 mAh g⁻¹ and distinctly poorer electrochemical performances at higher charge-discharge rates, which is far from satisfactory for meeting the needs of high-energy high-power LIBs.^{3,4} Thus, it is imperative to explore alternative carbon-based anode materials with enhanced Li-ion storage capacity, better rate capability, longer cycle life, as well as low cost and the potential for industrial scale production.

To develop high-performance carbon-based anode materials for new-generation LIBs, one strategy is to design and synthesize a novel nanostructure with the following features: (i) High specific surface area with a large number of available active sites to facilitate Li-ion storage capacity,^{5,6,7} (ii) high porosity for enhanced Li-ion transport, thereby leading to improved rate capability,^{8,9,10} (iii) excellent electrical conductivity and structural stability for rapid charge transfer with prolonged cycle life,^{11,12} (iv) heteroatom N or S doping to manipulate electronic and electrochemical properties and increase number of available active sites for Li-ion storage.^{13,14,15} To achieve these important properties, many new carbonaceous anode materials with various nanostructures have been evaluated for lithium storage and demonstrated significantly improved performance compared to commercial graphite anodes, such as heteroatom-doped graphene sheets,¹⁶ micro/nanoporous carbon,¹⁷ hollow carbon spheres,¹⁸ carbon nanofibers,¹⁹ and carbon nanobeads.²⁰ In spite of these efforts, few have sought to satisfy all the aforementioned features simultaneously since most carbonaceous materials have low electrical conductivity and poor structural stability when cycled at high charge/discharge rates as well as limited active sites for effective Li-ion storage. Therefore, the lithium storage capability and rate performance of carbonaceous anodes still need improvements. To manipulate their electrical conductivity and increase available active sites for lithium storage, the incorporation of nitrogen into carbon has proven to be an effective way to significantly enhance both electrical conductivity and electrochemical reactivity of carbon-based anode materials, resulting in improved performance in LIBs and other energy applications.^{36, 37} However, the synthesis of N-rich carbonaceous nanostructures reported previously usually involve tedious processes such as complex chemical reactions, chemical vapor deposition (CVD),²¹ thermal annealing with ammonia,²² and/or various templated-based approaches, which are expensive and time-consuming, and thus limit their practical applications for industrial scale production.

Because of these trade-offs, design and synthesis of highly porous N-rich carbonaceous anode materials with superior electrical conductivity remain a big challenge.

Porous metal organic frameworks (MOFs), as an emerging family of crystalline inorganic-organic hybrid materials, have been widely studied for gas separation,²³ sensors,²⁴ catalysis,²⁵ and drug delivery,²⁶ due to their high porosity and large surface area. Recently, MOFs have attracted much interest for the applications in LIBs and have proved to be promising precursors for constructing various nanostructured electrodes. For example, Yue et al. reported cubic mesoporous Co-ZnO@C via pyrolysis of Co-doped MOF-5, showing a specific capacity of 725 mAh g⁻¹ after 50 cycles at 100 mA g⁻¹.²⁷ Han et al. used direct carbonization at 800°C under inert atmosphere to fabricate ZIF-8@chitosan composites, which exhibit a reversible capacity of 750 mAh g⁻¹ after 50 cycles at 50 mA g⁻¹.²⁸ More recently, Hou et al. reported a Co₃O₄/N-doped carbon hybrid with dodecahedrons structure that delivers 892 mAh g⁻¹ after 100 cycles at 100 mA g⁻¹.²⁹ Nevertheless, due to the unavoidable breakdown inside the crystalline MOFs and relatively large crystal size ranging from 200 to 500 nm, these MOFs-derived N-doped carbon matrices still suffer from low electronic conductivity and poor structural stability, and thus result in significant capacity fading upon long-term cycling in LIBs.

Herein, to achieve novel carbonaceous anode material with all the merits of hierarchically porous structure, superior excellent conductivity and high-level nitrogen doping, we report a facile *in situ* synthesis strategy to prepare sandwich-like, graphene-based porous nitrogen-doped carbons (PNCs@Gr) through direct pyrolysis of zeolitic imidazolate framework (ZIF-8) nanoparticles grown on graphene oxide (GO) (ZIF-8@GO), for application as a high-performance anode material in LIBs for the first time. We select the prototypical ZIF-8 (Zn(MeIM)₂, MeIM= 2-methylimidazolate) with a high N content of ~34 wt% with extremely high specific surface area (~1700 m² g⁻¹) and large porosity as a suitable carbon precursor to yield *in situ* N-doped porous carbon, and GO serves as a structure-directing agent and potential platform for the growth and stabilization of ZIF-8 network.³⁰ Due to the insufficient functional groups on the GO surface, the amide carbonyl groups of poly(vinylpyrrolidone) (PVP) are used to enrich the functional groups of GO, which might coordinate with Zn ions and facilitate the uniform nucleation of ZIF-8 on the surface of GO. During subsequent carbonization process, ZIF-8 nanoparticles are transformed to N-rich porous carbon nanospheres, meanwhile GO is thermally reduced to highly conductive graphene. Finally, the sandwich-like PNCs@Gr nanostructure with high porosity, superior electrical conductivity and rich nitrogen content is successfully synthesized and will thus boost electrochemical performance in LIBs, due to synergic effects of the highly desirable properties. As a result, the sandwich-like PNCs@Gr electrode demonstrates remarkable capacities,

outstanding rate performances and cycling stability that are among the best results of carbon-based anode materials.

Results and Discussion.

Figure 1 presents a schematic showing the facile and scalable route for synthesizing PNCs@Gr in this work. First, GO is modified with PVP in the solution, followed by adding zinc nitrate and 2-methylimidazole separately, for *in situ* growth of ZIF-8 nanoparticles on GO. Next, the sandwich-like ZIF-8@GO sheet is transformed into the PNCs@Gr by direct carbonization in N₂ atmosphere at 700°C. Both porous N-doped carbon nanoparticles and graphene sheets not only serve as highways for fast electron transport, but also offer minimum diffusive resistance for mass transport on large electrode/electrolyte interfaces for charge-transfer reaction. Therefore, it is expected that the sandwich-like, graphene-based PNCs@Gr nanostructure will boost the electrochemical performance in LIBs.

Figure 2a and b show the X-ray diffraction (XRD) patterns of the as-prepared ZIF-8, ZIF-8@GO, bare PNCs and sandwich-like PNCs@Gr nanostructure. Before carbonization, all the main diffraction peaks can be assigned to crystalline ZIF-8 and no noticeable difference is observed between the XRD patterns of ZIF-8 and ZIF-8@GO, since the main peak of ZIF-8 (112) almost overlaps with the main peak (001) of GO at $2\theta = 12.5^\circ$. After carbonization, ZIF-8 and ZIF-8@GO transform to PNCs and PNCs@Gr. The XRD patterns change significantly with the main peak occurring at around 25° corresponding to the interplane (002) reflection of graphite carbon. The broad low-intensity peaks imply that the PNCs and PNCs@Gr possess low degree of graphitization, which is consistent with previous reports.^{31,32} It is also worth noting that typical Zn peaks are not found in the XRD patterns of both PNCs and PNCs@Gr without aqueous acid washing, indicating that carbon-reduced Zn metal with low melting point (419.5°C) may have been vaporized away during the carbonization at 700°C, which is in good agreement with previous observation.^{33,34,35} Figure S1 shows the thermo-gravimetric analysis (TGA) result of pristine ZIF-8 sample. It can be seen that the ZIF-8 sample starts decomposition at around 550 °C, indicating a high thermal stability, which is beneficial for being a carbonization precursor, since high-temperature vaporization can be avoided, thereby improving the yield of final products. Raman spectrum of the ZIF-8@GO and sandwich-like PNCs@Gr structures reveal two distinct peaks at 1352 and 1590 cm⁻¹, corresponding to D band and G band of graphitic carbon materials. Notably, the I_D/I_G value of PNCs@Gr (I_D/I_G=0.99) is higher than ZIF-8@GO (I_D/I_G=0.94), demonstrating the formation of abundant defects and disordered carbon during the carbonization process.

The electrochemical performance of carbon-based anode materials in LIBs highly depends on the type and content of doped nitrogen in the carbonaceous materials, which can be analyzed by X-ray

photoelectron spectroscopy (XPS) as shown in Figure 2d-e. After carbonization, N 1s spectrum can be deconvoluted into three different peaks, pyridinic N (398.3 ± 0.2 eV), pyrrolic N (399.8 ± 0.2 eV) and quaternary N (400.8 ± 0.3 eV). It has been reported that N-doping can enhance electronic conductivity of carbon-based materials and facilitate charge transfer at the interface, which are highly desirable for electrodes in LIBs.³⁶ Furthermore, it is believed that the presence of N atoms introduces more defects in carbon and thus offers more available active sites for Li-ion storage.³⁷

To further examine the porous structure of bare PNCs and PNCs@Gr, N₂ adsorption-desorption isotherms were measured to determine the surface area and pore size distribution (PSD). As shown in Figure 2e, bare PNCs exhibit a type-I isotherm with a slight step over the relative pressure from 0.9 to 1.0, revealing a large portion of micropores, probably due to the inheritance of highly porous ZIF-8. Nevertheless, the sandwich-like PNCs@Gr shows a type-IV curve with a pronounced hysteresis loop. The high N₂ adsorption at the relative low pressure reveals the high microporosity, while the hysteresis loop indicates some portion of mesopores exist within the sandwich-like structure. The mesopores may originate from the evaporation of Zn during the carbonization process and are likely stacked between sandwich-like PNCs@Gr. Figure 2f shows the pore size distribution (PSD) of sandwich-like PNCs@Gr, revealing both micropores peaked at 0.77 and 1.40 nm and small mesopores peaked at 3.05 and 3.80 nm on the basis of the Density Functional Theory (DFT) method. The appropriate proportion of micropores guarantees its high SSA and mesopores are preferable for electrolyte penetration and lithium ion transport, and thus are extremely beneficial for both high energy density and high rate performance in LIBs. Furthermore, thanks to the abundant micro- and mesopores, the specific surface area (SSA) of PNCs@Gr reaches as high as $872 \text{ m}^2 \text{ g}^{-1}$, while that of bare PNCs is only $508 \text{ m}^2 \text{ g}^{-1}$, as revealed by the Brunauer-Emmett-Teller (BET) measurements. Owing to the severe restacking of graphene sheets, the pristine rGO or graphene obtained via thermal annealing of GO proves to possess low SSA of below $100 \text{ m}^2 \text{ g}^{-1}$,^{31,38} which is much lower than theoretical SSA value ($2630 \text{ m}^2 \text{ g}^{-1}$) of graphene without any overlap of sheets. Therefore, such a significant improvement in the SSA of sandwich-like PNCs@Gr is mainly attributed to synergic effects of components in this hybrid, whereas the likely agglomeration of PNCs and severe restacking of graphene sheets can be effectively addressed by this hierarchical nanostructure design. The larger surface area of PNCs@Gr is anticipated to offer more active sites for lithium ion storage, likely resulting in higher capacity and enhanced rate capability compared to bare PNCs.

Figure 3 displays SEM images of bare PNCs, ZIF-8@GO and sandwich-like PNCs@Gr. As shown in Figure 3a and b, bare PNCs consist of numerous nanoparticles (~150 nm in diameter) with rough surfaces and severe agglomeration is also observed, which is confirmed by TEM observation in Figure

S3. Interestingly, Figure 3c and d reveal that ZIF-8@GO sample preserves the sheet-like morphology of micrometer-sized GO, in which polyhedron-like ZIF-8 nanoparticles with an average diameter of approximately 150 nm are homogeneously grown on the GO surface. As shown in Figure 3e and f, the PNCs@Gr sample demonstrates that the sheet-like morphology is well preserved after direct carbonization of ZIF-8@GO at 700°C and the multilayer stacking feature is also observed in Figure S4. In addition, it is important to note that most of PNCs in the composite of PNCs@Gr are composed of ultrafine nanoparticles (~20 nm) due to the partial decomposition of ZIF-8 during the carbonization process. The composition of sandwich-like PNCs@Gr nanostructure is further analyzed by energy dispersive spectroscopy (EDS) elemental mapping. As shown in Figure 4a-d, C, N and O elements are homogeneously distributed, suggesting that the PNCs derived from ZIF-8 are dispersed uniformly on the graphene sheet, and thus form a sandwich-like nanostructure. In addition, the PNCs@Gr sample contains 28.4 wt% nitrogen, which is much higher than those of previously reported N-doped carbonaceous materials for LIBs. For instance, a chemical activation of Ppy nanofiber webs using KOH at 650°C was used to obtain N-doped CNFWs with a N content of ~10 wt%.⁵

TEM characterization is also performed for better visualization of ZIF-8@GO and PNCs@Gr, as shown in Figure 5. It can be seen in Figure 5a and b (TEM images of ZIF-8@GO at different magnifications) that ZIF-8 nanoparticles are homogeneously grown on the surface of GO, which is in good accordance with the SEM results. In addition, the HR-TEM image of ZIF-8@GO in Figure 5c reveals a very small area of exposed GO at the edges, confirms the existence of GO in the sample and the sandwich-like structure of ZIF-8@GO. After carbonization, Figure 5d-e reveal that PNCs@Gr displays apparently porous feature and preserve the sandwich-like morphology of ZIF-8@GO. The inset of Figure 5d shows the corresponding selected area electron diffraction (SAED), indicating the amorphous nature of PNCs@Gr, which is supported by the XRD result above. Finally, the HRTEM image in Figure 5f confirms the existence of graphene in the composite.

To evaluate the as-prepared bare PNCs and sandwich-like PNCs@Gr samples as anode materials for LIBs, various electrochemical measurements are carried out, as presented in Figure 6. The cycling performances of both PNCs and PNCs@Gr are evaluated over a range of 0.01-3.0 V *versus* Li/Li⁺. To activate the electrodes, a specific current of 100 mA g⁻¹ is initially used for the first three cycles during the cycling performance. As shown in Figure 6a-b, the PNCs@Gr anode shows an outstanding cycling stability with a high reversible capacity. At a specific current of 500 mA g⁻¹, the PNCs@Gr anode maintains a capacity of as high as 1070 mAh g⁻¹ after 100 cycles, which is much higher than that of bare PNCs (441 mAh g⁻¹), showing a significant improvement of capacity by 629 mAh g⁻¹. Even at a higher specific current of 1 A g⁻¹, the PNCs@Gr can still deliver a high capacity of 948 mAh g⁻¹ after 200

cycles, which is approximately 97.7% of the 4th cycle, while the capacity of bare PNCs is only 291 mAh g⁻¹. More importantly, when the specific current is increased to 5 A g⁻¹, the sandwich-like PNCs@Gr nanostructure retains a capacity of 530 mAh g⁻¹ after 400 cycles, demonstrating a capacity retention of as high as 84.4%. In addition, as shown in Figure 6d, during the long-time cycling, the columbic efficiency of PNCs@Gr is above 99% (except for the initial few cycles), demonstrating its good electrochemical reversibility. It is noted that electrochemical performances of PNCs@Gr exceed most previously reported carbon-based materials^{16,18,39,40,41,42,43,44,45,46} and recently reported MOF-derived anode materials for LIBs, as compared in Table S1 and S2.^{27,28,29,47,48,49,50,51,52} Such remarkable improvements of specific capacity and long-term cycling stability are attributed to the following factors. First, in the sandwich-like PNCs@Gr nanostructure, highly desirable combination of micro- and mesopores and ultrafine carbon nanospheres (~20 nm) embedded on the graphene surface offer larger surface area (872 m² g⁻¹) in comparison with bare PNCs (508 m² g⁻¹), and thus not only lead to sufficient electrode/electrolyte interface to effectively absorb lithium ions, but also promote rapid charge-transfer reaction. Second, the highly conductive, mechanically strong and flexible graphene not only enhance electronic conductivity of the whole electrode, but also help reduce agglomeration and collapse of structure upon long-term cycling, resulting in excellent structural stability and superior cycling performance. Finally, the high-level nitrogen doping is believed to further enhance both electronic properties and electrochemical reactivity of PNCs@Gr electrode via introducing defects and more available active sites for lithium storage.

Notably, the PNCs@Gr anode also shows superior rate capability at various specific currents ranging from 100 to 6000 mA g⁻¹. Figure S6 shows the initial three cycles of the PNCs@Gr electrode at a specific current of 100 mA g⁻¹ from the rate performance testing. The charge/discharge profiles are consistent with those previously reported for N-doped carbonaceous anodes for LIBs.^{5,16} A large irreversible capacity loss is observed, attributing to the formation of the SEI film and decomposition of the electrolyte. These results are consistent with the CV results in Figure S5, in which the cathodic peaks are present in the first cycle but disappearing in the 2nd and 3rd cycles. As shown in Figure 6e, the reversible capacities of PNCs@Gr are 1378, 1228, 1070, 984, 915, 854 and 647 mAh g⁻¹ at 100, 200, 400, 600, 800, 2000 and 4000 mA g⁻¹, respectively. Even at an extremely high specific current of 6000 mA g⁻¹, the reversible capacity is still as high as 412 mAh g⁻¹. More importantly, when the specific current returns back to 100 mA g⁻¹, the specific capacity can be recovered to 1432 mAh g⁻¹, indicating its excellent reaction reversibility and cycling stability. The corresponding charge/discharge curves of the PNCs@Gr electrode cycled at various rates are also displayed in Figure S7. However, bare PNCs anode shows much lower reversible capacities of 797, 692, 550, 508, 451, 421, 277 and 123 mAh g⁻¹

when cycled at 100, 200, 400, 600, 800, 2000, 4000 and 6000 mA g⁻¹, respectively. The superior rate performance of the sandwich-like PNCs@Gr electrode is ascribed to its hierarchical nanostructure, in which graphene significantly improves electrical conductivity of the electrode, and ultrafine carbon nanospheres offer shorter transport length of lithium ions and better stability when cycled at higher charge/discharge rates, thereby resulting in considerable improvement in rate capability compared to bare PNCs. Therefore, it can be concluded that the PNCs@Gr anode exhibits superior rate capability, significantly improved cycling stability and reversible capacity compared to bare PNCs.

To further understand the origin of superior rate capability of sandwich-like PNCs@Gr anode, electrochemical impedance spectra (EIS) is performed to investigate the processes occurring at the electrode/electrolyte interfaces and Li-ion intercalation/deintercalation within electrode materials in the battery cells. As shown in Figure 6f, the Nyquist plots of bare PNCs and PNCs@Gr are composed of a depressed semicircle in the medium-frequency region followed by a slanted line in the low-frequency region. It is observed that the electrode of sandwich-like PNCs@Gr nanostructure shows much lower charge transfer resistance of 30 Ω compared to that of bare PNCs (100 Ω), indicating much faster charge transfer at the electrode/electrolyte interface. Cyclic voltammetry (CV) curves of bare PNCs and sandwich-like PNCs@Gr electrode are also recorded in the voltage range of 0.01 - 3.0 V vs. Li/Li⁺ at a scan rate of 0.1 mVs⁻¹, as shown in Figure S5. Both bare PNCs and PNCs@Gr display typical CV curves of carbonaceous anode materials. However, it should be noted that the redox peaks from the PNCs@Gr electrode show higher corresponding specific current than that of bare PNCs, probably attributed to the enhanced electrical conductivity and electrochemical reactivity of the electrode, which is supported by the EIS results above.

The super high capacity, excellent cycling stability and superior rate capability of sandwich-like PNCs@Gr nanostructure can be attributed to their novel morphology and high-level nitrogen doping. In its synthesis, *in situ* growth of ultrafine carbon nanoparticles with highly porous structure effectively reduce the agglomeration phenomenon compared to bare PNCs, and thus leads to sufficient electrode/electrolyte interface and shorter transport length of Li ions, thereby promoting rapid charge-transfer reaction. On the other hand, highly conductive and mechanically strong graphene provides a continuous pathway for electron transport and stabilizes the structure upon long-term cycling. In addition, it is believed that the high-level N-doping in PNCs@Gr composite can further enhance its electronic conductivity and electrochemical reactivity, which is beneficial for its electrochemical performances in LIBs.

In conclusion, a sandwich-like, graphene-based porous nitrogen-doped carbons (PNCs@Gr) has been fabricated through direct pyrolysis of zeolitic imidazolate framework (ZIF-8) nanoparticles *in situ*

grown on graphene oxide (GO) (ZIF-8@GO), for application as a promising anode material in LIBs. When tested in battery cells, the sandwich-like nanostructure demonstrates significantly improved capacity, better cycling stability and rate capability compared to bare PNCs. The outstanding electrochemical performances of PNCs@Gr anode can be ascribed to the novel sandwich-like nanostructure and high-level N-doping in the composite. Thus PNCs@Gr demonstrates to be a promising alternative anode material with great potential in high-energy high-power LIBs. In addition, the obtained sandwich-like PNCs@Gr may also be applicable for supercapacitors and other fields.

Experimental Section.

Material Synthesis. All chemical reagents in this work were of analytical grade and were used without further purification.

Synthesis of ZIF-8. ZIF-8 crystals were prepared by mixing 0.81 g of 2-methylimidazole with 25 ml of methanol. After the solid is totally dissolved in the solvent, 0.7 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 25 ml of methanol was added to the solution. The mixture was stirred for 5 h. Solid was collected by centrifuging the mixture at 3000 rpm for 10 min and washed with methanol for at least three times. The collected solid was dried at 75°C overnight before using.

Synthesis of ZIF-8@GO. One gram of GO solution (8 mg mL^{-1}) was dispersed in methanol solution containing 50 mg of PVP, by sonication and stirring. Then 5 ml of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of methanol solution and 5 ml of 2-methylimidazole were separately added into GO/PVP solution (40 ml) and sonicated for 4 h. The mixture was kept at room temperature for 5 h and then the product was collected by centrifuging at 3000 rpm for 10 min and washed with methanol for at least three times. After freeze drying, the product (ZIF-8@GO) was obtained.

Synthesis of PNCs@Gr. The as-synthesized ZIF-8@GO was heated at 700 °C for 5 h under N_2 atmosphere using a heating rate of 2°C min^{-1} . For comparison purpose, bare PNCs was synthesized by direct carbonization of the as-synthesized ZIF-8 under the same condition.

Material characterizations. The crystal structure of the obtained powders was investigated by x-ray diffraction (XRD) using a Rigaku MiniFlex X-ray diffractometer with $\text{Cu K}\alpha$ radiation. XRD Data was collected in the range of $0^\circ \leq 2\theta \leq 80^\circ$ at a scan rate of 2 θ /min at room temperature. The Morphology of the samples was observed using field emission scanning electron microscopy (FE-SEM) on a FEI Quanta 3D FEG FIB/SEM dual beam system. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were captured to investigate the crystal structure and core-shell structure of the samples using a JEM-2010 instrument microscope at an acceleration voltage of 200 kV. XPS analysis was performed by X-ray photoelectron spectroscopy with an AXIS 165 spectrometer and a

twin-anode AlK α (1486.6 eV) X-ray source. Thermogravimetric (TG) analysis was performed on an SII STA7300 analyzer at a heating rate of 1 °C min⁻¹ in N₂. Gas sorption analyses were conducted using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with extra-high pure gases.

Electrochemical Measurements. Electrochemical properties of the electrode materials were evaluated by integrating into 2032-type coin cells. Typically, the electrodes were prepared by uniformly coating a homogeneous slurry of 80 wt% active material powders, 10 wt% acetylene black (conductive carbon, Alfa Aesar, 99.5%), and 10 wt% polyvinylidene fluoride (PVDF, Alfa Aesar) binder in 1-methyl-3-pyrrolidone (NMP) solvent on copper foils and then dried in vacuum at 120°C for 24 h. Coin cells with lithium foil as counter electrode were assembled in an argon-filled glove box. The electrolyte was 1 M LiPF₆ dissolved in ethylene carbonate (EG), dimethyl carbonate (DMC) and diethyl carbonate (DEC) at a volumetric ratio of 1:1:1. The electrochemical performance of coin cells was tested at various C-rate regimes in the voltage range of 0.01-3.0 V vs. Li/Li⁺ by using an 8-channel battery analyzer (MTI Corporation). Cyclic voltammetric (CV) measurement was carried out on a CHI605C electrochemical analyzer at a scanning rate of 0.1 mV/s between 0.01 V and 3.0 V vs. Li/Li⁺. All electrochemical measurements were performed at room temperature.

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Supporting Information

TGA curves of pristine ZIF-8, TEM images of bare PNCs, detailed CV curves of both bare PNCs and sandwich-like PNCs@Gr electrodes, the initial three charge-discharge curves of PNCs@Gr at 100 mA g⁻¹, and the corresponding charge-discharge curves of PNCs@Gr cycled at various rates.

Figure Legends

Figure 1. Schematic illustration of the synthesis process of the sandwich-like PNCs@Gr nanostructure.

Figure 2. XRD patterns of (a) ZIF-8 and ZIF-8@GO before carbonization and (b) bare PNCs and sandwich-like PNCs@Gr nanostructure after carbonization. High-resolution spectrums of the N 1s XPS peaks of (c) ZIF-8 and (d) bare PNCs. (e) Nitrogen adsorption-desorption isotherms of bare PNCs and sandwich-like PNCs@Gr nanostructure. (f) Pore size distribution (PSD) of PNCs@Gr.

Figure 3. SEM images of (a, b) bare PNCs, (c, d) ZIF-8@GO and (e, f) sandwich-like PNCs@Gr nanostructure.

Figure 4. (a) SEM image of the sandwich-like PNCs@Gr nanostructure, and (b-e) corresponding element mapping results.

Figure 5. (a, b) TEM images of ZIF-8@GO at different magnifications, and (c) HRTEM image of ZIF-8@GO. (d, e) TEM images of the sandwich-like PNCs@Gr nanostructure at different magnifications, and (f) HRTEM image of PNCs@Gr.

Figure 6. Electrochemical characterizations of bare PNCs and sandwich-like PNCs@Gr electrodes. (a, b) Cycling test of bare PNCs and sandwich-like PNCs@Gr electrodes at 500 mA g^{-1} and 1 A g^{-1} , respectively. (c) Cycling performance of the sandwich-like PNCs@Gr electrode at 5 A g^{-1} for 400 cycles and (d) corresponding Columbic efficiency. (e) Rate capability of bare PNCs and sandwich-like PNCs@Gr electrodes cycled at various specific currents ranging from 100 mA g^{-1} to 6 A g^{-1} . (f) Nyquist plots of bare PNCs and sandwich-like PNCs@Gr electrodes.

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Figure 4. (a) SEM image of the sandwich-like PNCs@Gr nanostructure, and (b-e) corresponding elemental mapping results.

Figure 5. (a, b) TEM images of ZIF-8@GO at different magnifications, and (c) HRTEM image of ZIF-8@GO. (d, e) TEM images of the sandwich-like PNCs@Gr nanostructure at different magnifications, and (f) HRTEM image of PNCs@Gr.

Figure 6. Electrochemical characterizations of bare PNCs and sandwich-like PNCs@Gr electrodes. (a, b) Cycling test of bare PNCs and sandwich-like PNCs@Gr electrodes at 500 mA g⁻¹ and 1 A g⁻¹, respectively. (c) Cycling performance of the sandwich-like PNCs@Gr electrode at 5 A g⁻¹ for 400 cycles and (d) corresponding Columbic efficiency. (e) Rate capability of bare PNCs and sandwich-like PNCs@Gr electrodes cycled at various specific currents ranging from 100 mA g⁻¹ to 6 A g⁻¹. (f) Nyquist plots of bare PNCs and sandwich-like PNCs@Gr electrodes.

Supporting Information

Figure S1. TGA curve of the ZIF-8 sample which reveals decomposition occurs at around 550 °C, indicating a high thermal stability of pristine ZIF-8. The weight loss of pristine ZIF-8 from 550 to 1000 °C is mainly due to evaporation of Zn and transformation of organic linkers into porous carbon.

Figure S2. Raman Spectra of pristine ZIF-8, ZIF-8@GO and sandwich-like PNCs@Gr. Raman spectra of ZIF-8@GO and sandwich-like PNCs@Gr reveal two dominant peaks at 1352 and 1590 cm^{-1} , corresponding to D band and G band of graphitic carbon materials, which are absent in the Raman spectra of pristine ZIF-8. For ZIF-8@GO, the peaks marked by aster are from ZIF-8.

Figure S3. TEM images of bare PNCs prepared by direct carbonization of ZIF-8 sample, showing severe agglomeration of porous carbon nanospheres.

Figure S4. SEM image of the sandwich-like PNCs@Gr nanostructure with multilayer stacking feature.

Figure S5. Cyclic voltammetry curves of bare PNCs and sandwich-like PNCs@Gr samples at a scan rate of 0.1 mVs^{-1} .

Figure S6. Charge/discharge profiles of the sandwich-like PNCs@Gr electrode at 100 mA g⁻¹ (the initial three cycles from rate capability testing).

Figure S7. Charge/discharge profiles of the sandwich-like PNCs@Gr electrode cycled at various current densities.

Table S1. Comparisons between electrochemical performance of PNCs@Gr in the present work and those of previously reported carbonaceous anodes with various microstructures for applications in LIBs.

Anode materials	Current density (mA g ⁻¹)	Cycle number	Specific capacity (mAh g ⁻¹)	Ref.
PNCs@Gr	500	100	1070	Our work
	1000	200	948	
	5000	400	530	
N-doped graphene sheets	50	30	872	Ref.16. ACS Nano, 2011
Hollow carbon nanospheres (HCNS)	37	50	630	Ref.18. Adv. Energy Mater, 2011
Micro-sized porous carbon spheres	100	100	507	Ref.39. Nanoscale, 2015
N-rich porous carbon (OHC)	100	100	1178	Ref.40. J. Mater. Chem. A, 2015
	1000	100	591	
Porous carbon	100	70	660	Ref.41. Chem. Eur. J, 2015
Porous carbon microspheres (HPCM)	50	70	480	Ref.42. Carbon, 2015
CNT-CNF	100	70	1150	Ref.43. J. Am. Chem. Soc, 2013
N-doped graphene	50	50	1136	Ref.44. Electrochem. Acta, 2013
HN-CNT	100	100	397	Ref.45. J. Power Sources, 2012
PMC-650	100	100	1365	Ref.46. Energy Environ. Sci, 2013

Table S2. Comparisons between electrochemical performance of PNCs@Gr in the present work and those of recently reported MOF-derived anode materials for LIBs.

Anode materials	Current density (mA g ⁻¹)	Cycle number	Specific capacity (mAh g ⁻¹)	Ref.
PNCs@Gr	500	100	1070	Our work
	1000	200	948	
	5000	400	530	
Co-doped ZnO@C (CZO@C)	100	50	725	Ref. 27. ACS Appl. Mater. Interfaces, 2014
ZIF-8@chitosan	50	50	750	Ref.28. Chem.Commun, 2014
Co ₃ O ₄ /N-PC	100	100	892	Ref.29. Nano Energy, 2015
MWCNTs/Co ₃ O ₄	100	100	813	Ref.47. ACS Nano, 2015
ZnO@ZnO/C NRAs on carbon cloth	500	100	699	Ref.48. Adv. Mater, 2015
CuO nanostructure derived from Cu-MOF	100	40	538	Ref.49. Nano Energy, 2013
ZnO QDs@porous carbon	75	50	1200	Ref.50. J. Am. Chem. Soc, 2012
Spindle-like mesoporous Fe ₂ O ₃	200	50	911	Ref.51. Nano Lett, 2012
Porous TiO ₂ derived from MIL-125	840	200	155	Ref.52. Chem. Commun, 2015

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