Hierarchical Sandwich-Like Structure of Ultrafine N-Rich Porous Carbon Nanospheres Grown on Graphene Sheets as Superior Lithium-Ion Battery Anodes

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ABSTRACT: A sandwich-like, graphene-based porous nitrogen-doped carbon (PNCs@Gr) has been prepared through facile pyrolysis of zeolitic imidazolate framework nanoparticles in situ grown on graphene oxide (GO) (ZIF-8@GO). Such sandwich-like nanostructure can be used as anode material in lithium ion batteries, exhibiting remarkable capacities, outstanding rate capability, and cycling performances that are some of the best results among carbonaceous electrode materials and exceed most metal oxide-based anode materials derived from metal organic frameworks (MOFs). Apart from a 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 a 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 an impressive electrochemical performance is ascribed to the ideal combination of hierarchically porous structure, a highly conductive graphene platform, and high-level nitrogen doping in the sandwich-like PNCs@Gr electrode obtained via in situ synthesis.

KEYWORDS: N-doped carbon, graphene, sandwich-like nanostructure, metal organic frameworks, lithium ion batteries

INTRODUCTION
Lithium-ion batteries (LIBs) have been commonly used as power sources in portable electronics.¹–³ Nevertheless, the ever-increasing demands for emerging applications in portable electronics and electric vehicles (EVs) are driving the development of LIBs with higher energy density and power density as well as longer cycling life. As one of the commercially available anode materials, graphite is the most common one but still exhibits some drawbacks such as a 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 electrode materials with highly reversible capacity, enhanced cycling stability, better rate performance, and the potential for industrial scale production.

To develop high-performance carbonaceous electrode materials for new-generation LIBs, one strategy is to design and synthesize a novel nanostructure with the following features: (i) large surface area with abundant active sites to...
facilitate Li-ion storage capacity,^5−7^ (ii) high porosity for enhanced charge transport, thereby resulting in improved rate capability,^8−10^ (iii) excellent structural stability and electronic conductivity to promote rapid charge transfer with prolonged cycle life,^11^ and (iv) heteroatom N or S doping to manipulate electronic and electrochemical properties and increase number of available active sites for Li-ion storage.\(^{13^\text{-}15}\) To achieve these, many new carbonaceous anode materials with various nanostructures have been evaluated for lithium storage and demonstrated notably improved battery performance compared to commercial graphite anodes, such as heteroatom-doped graphene sheets,\(^{12}\) micro/nanoporous carbon,\(^{16}\) hollow carbon spheres,\(^{17}\) carbon nanofibers,\(^{18}\) and carbon nanobeads.\(^{19}\)

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 improvement. By introducing more available active sites for lithium storage, incorporation of nitrogen into carbon has proven to significantly enhance both electronic conductivity and electrochemical reactivity of carbon-based anode materials, resulting in improved performance in LIBs and other energy applications.\(^{13^\text{-}15,35,36}\)

However, the synthesis of N-rich carbonaceous nanostructures reported previously usually involve tedious processes such as complex chemical reactions, chemical vapor deposition (CVD),\(^{20}\) thermal annealing with ammonia,\(^{21}\) and/or various template-based approaches, which are costly and tedious, and thus hamper 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.

Metal organic frameworks (MOFs) are a family of crystalline materials with inorganic–organic hybrid structure and have been widely studied for gas separation,\(^{22}\) sensors,\(^{23}\) catalysis,\(^{24}\) owing to their large pore volumes and extremely high specific surface areas. Recently, MOFs have attracted much interest for the applications in LIBs and have proven to be promising precursors for constructing various nanostructured electrodes.\(^{5^\text{-}8,25^\text{-}26}\) For instance, Yue et al. reported mesoporous Co-ZnO@C via pyrolysis of Co-doped MOF-5, showing a reversible capacity of 725 mAh g\(^{-1}\) after 50 cycles at a specific current of 100 mA g\(^{-1}\).\(^{26}\) Han et al. used direct carbonization at 800 °C under inert atmosphere to fabricate ZIF-8@chitosan composites, which exhibit a specific capacity of 750 mAh g\(^{-1}\) after 50 cycles at a specific current of 50 mA g\(^{-1}\).\(^{27}\) Hou et al. reported a CoO\(_2\)/N-doped carbon hybrid with dodecahedrons structure that delivers 892 mAh g\(^{-1}\) after 100 cycles at a specific current of 100 mA g\(^{-1}\).\(^{28}\) Nevertheless, due to the unavoidable breakdown inside the crystalline MOFs and relatively large crystal size ranging from 250 to 500 nm, these MOFs-derived N-doped carbon matrices still exhibit poor structural stability and low electronic conductivity, and thus result in significant capacity fading over prolonged cycling in LIBs.

Herein, to achieve a carbonaceous anode material with all the merits of hierarchically porous structure, superior excellent conductivity, and high-level nitrogen doping, we present an in situ synthesis approach to obtain sandwich-like, graphene-based porous nitrogen-doped carbons (PNCs@Gr) via facile pyrolysis of zeolitic imidazolate framework (ZIF-8) nanocrystals grown on graphene oxide (GO) (ZIF-8@GO), for application as a high-performance anode material in LIBs. We selected ZIF-8 as a suitable carbon precursor to yield in situ N-doped porous carbon due to its high N content of ~34 wt %, large porosity, and high specific surface area, and meanwhile GO serves as a structure-directing agent and potential platform for nucleation, growth, and stabilization of ZIF-8 nanocrystals. Due to insufficient surface functional groups of GO, the amide carbonyl groups of poly(vinylpyrrolidone) (PVP) can be utilized to enrich the functional groups of GO, which might be beneficial for the uniform growth of ZIF-8 nanocrystals on the GO sheet. During a 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, as well as cycling stability that are better than most carbonaceous anode materials reported previously.

## EXPERIMENTAL SECTION

### Preparation of ZIF-8

ZIF-8 crystals were synthesized by mixing 0.81 g of 2-methylimidazole with 25 mL of methanol. To this solution, 0.7 g of Zn(NO\(_3\))\(_2\)-6H\(_2\)O and 25 mL of methanol were added. Afterward, the mixed solution was stirred for 5 h. Finally, the solid was collected by centrifuging the mixture at 3000 rpm for 10 min, followed by washing with methanol for three times. The collected solid was dried at 75 °C overnight before using.

### Synthesis of ZIF-8@GO

The as-synthesized ZIF-8@GO was carried out based on a modified approach from literature.\(^{31}\) Typically, 1 g of the as-prepared graphene oxide solution (8 mg mL\(^{-1}\)) was dispersed in methanol solution containing 50 mg of PVP, by sonication and stirring. Then 5 mL of Zn(NO\(_3\))\(_2\)-6H\(_2\)O of methanol solution was first added into GO/PVP solution (40 mL) followed by adding 5 mL of 2-methylimidazole. Then the mixed solution was kept for 5 h at room temperature. Afterward, the product was collected by centrifuging at 3000 rpm for 10 min followed by washing with methanol three times. After freeze-drying, the final 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\(_2\) using a ramp rate of 2 °C/min. For comparison purposes, bare PNCs were prepared by facile pyrolysis of the as-synthesized ZIF-8 sample under the same condition.

### Material Characterizations

Powder X-ray diffraction (XRD) measurements were conducted using a Rigaku MiniFlex X-ray diffractometer with Cu K\(_\alpha\) radiation. XRD Data were collected in the range of 2° ≤ 2θ ≤ 90° at a scan rate of 2°/min. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were carried out using an FEI Quanta 3D FEG FIB/SEM dual beam system. The nanostructures of the samples were investigated by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) using a JEM-2010 instrument microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed using an AXIS 165 spectrometer and a twin-anode AlKa X-ray source. Thermogravimetric (TG) analysis was carried out using an STA7300 analyzer at a ramp rate of 1 °C/min under N\(_2\) atmosphere. Brunauer–Emmett–Teller (BET) measurements were carried out using Quantachrome Instruments Autosorb-iQ with extra-high pure gases. Raman spectroscopy was carried out with a confocal Raman system in air ambient environment (WITTEC alpha300 K) with 532 nm diodes laser.

### Electrochemical Measurements

The working electrodes in this work were studied by integrating into 2032-type coin cells for various electrochemical measurements at room temperature. Within the coin cells, the lithium foil works as the counter electrode, and all the coin...
Before carbonization, the main diffraction peaks of the as-synthesized samples, namely, ZIF-8, ZIF-8@GO, ZIF-8@PVP, and ZIF-8@Gr transformed into the PNCs@Gr by direct pyrolysis in N2 atmosphere at 700 °C. During this process, organic ligands (2-methylimidazolate) from ZIF-8 nanocrystals are carbonized, meanwhile part of the nitrogen species and the carbon-reduced zinc metal vaporize away due to instability of nitrogen species at high temperature and low melting point of zinc.\(^{30,31}\) Within this unique nanostructure, both porous N-doped carbon nanoparticles and graphene sheets not only serve as highways for fast electron transport, but also facilitate fast mass transport at electrode/electrolyte interfaces. Therefore, it is expected that the sandwich-like, graphene-based PNCs@Gr nanostructure will boost the electrochemical performance in LIBs.

In Figure 1, the synthetic route for preparing the sandwich-like PNCs@Gr nanostructure is schematically shown. First, GO is transformed into the PNCs@Gr by direct pyrolysis in N2 atmosphere at 700 °C. 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 (002) reflection of graphite. The broad low-intensity peaks imply that the PNCs and PNCs@Gr have low degree of graphitization, which is consistent with previous reports of other carbonaceous materials.\(^{30−34}\) It is also found that Zn diffusion peaks are not present in the XRD patterns of both PNCs and PNCs@Gr, indicating that carbon-reduced Zn metal with low melting point (419.5 °C) may have been vaporized away during the carbonization process at 700 °C. Figure S1 of the Supporting Information (SI) shows the thermogravimetric analysis (TGA) result of pristine ZIF-8 sample. It can be seen that the ZIF-8 sample starts to decompose at around 550 °C, indicating a good thermal stability, which is beneficial for being a suitable carbonization precursor, since severe vaporization at high temperature can be avoided, thereby improving the yield of final products. As shown in Figure S2, the Raman spectra of the ZIF-8@GO and sandwich-like PNCs@Gr structures reveal two characteristic peaks at 1352 and 1590 cm\(^{-1}\), which are attributed to the D band and G band of graphitic structure. 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.\(^{35}\)

The lithium storage properties of N-doped carbonaceous anode materials highly depend on the doped nitrogen type and doping amount. Therefore, X-ray photoelectron spectroscopy (XPS) measurements of pristine ZIF-8 and bare PNCs are performed. As can be seen in Figure 2c,d, after carbonization, the high-resolution spectrum of N 1s is deconvoluted into three different peaks, namely, pyridinic N (398.3 ± 0.2 eV), pyrrolic N (399.8 ± 0.2 eV), and quaternary N (400.8 ± 0.3 eV). This phenomenon indicates successful doping of nitrogen into the resultant porous carbon during the carbonization process of N-containing organic ligands, which is consistent with previous reports.\(^{31}\) According to the literature,\(^{32}\) the electronic conductivity of carbonaceous materials can be significantly improved by nitrogen doping, resulting in improved charge transfer at the interface, which are highly desirable for applications in LIBs.
electrodes in LIBs. Furthermore, it is believed that the presence of nitrogen dopants introduces more defects and thus offers more available active sites to enhance the Li-ion storage properties.

To further examine the porous structure of bare PNCs and PNCs@Gr, N$_2$ adsorption–desorption isotherms are performed to determine their specific surface area (SSA) and corresponding pore size distribution (PSD). As shown in Figure 2e, bare PNCs display a typical type-I isotherm showing 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 typical type-IV curve exhibiting a pronounced hysteresis loop. The high N$_2$ 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 likely stacking between sandwich-like PNCs@Gr. Figure 2f shows the pore size distribution (PSD) of sandwich-like PNCs@Gr, revealing both micropores are peaked at 0.77 and 1.40 nm and mesopores are peaked at 3.05 and 3.80 nm based on the Density Functional Theory (DFT) analysis. The appropriate proportion of micropores guarantees its high SSA and mesopores are preferable for electrolyte penetration and Li-ion transport, and thus are extremely favorable for both high

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 spectra 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.
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 m² g⁻¹, while that of bare PNCs is only 508 m² 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 m² g⁻¹, which is significantly lower than theoretical SSA value (2630 m² 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, thus leading to improved specific 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 (~200 nm in diameter) with rough surfaces and severe agglomeration is also observed. 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 nanocrystals are uniformly grown on the GO surface, and their average diameter is approximately 150 nm. 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. Moreover, it is observed that PNCs in the composite of PNCs@Gr are composed of ultrathin nanoparticles (~20 nm), likely owing to 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 revealed in Figure 4a–d, carbon, nitrogen, and oxygen 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. Furthermore, due to the evaporation of Zn during the carbonization process, we barely observe the Zn element distribution from elemental mapping results. In addition, the PNCs@Gr sample contains 21.5 wt % nitrogen, which is significantly higher than most of the previously reported N-doped carbonaceous materials in LIBs.5,16,40,44

TEM characterization was also performed for better visualization of ZIF-8@GO and PNCs@Gr, as displayed in Figure 5. As can be seen in Figure 5a and b (TEM images of ZIF-8@GO at different magnifications), ZIF-8 nanoparticles are homogeneously grown on GO sheets, which is in good agreement with the SEM observations. 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 reveals that PNCs@Gr displays an apparently porous feature and preserves 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 lithium storage properties of the as-prepared bare PNCs and sandwich-like PNCs@Gr samples, various electrochemical measurements are performed. Cyclic voltammetry (CV) curves of bare PNCs and sandwich-like PNCs@Gr electrode are recorded between 0.01 and 3.0 V vs Li/Li⁺, as shown in Figure 6. Both bare PNCs and PNCs@Gr display typical CV characteristics of carbon-based anodes. However, it should be noted that the redox peaks from the PNCs@Gr electrode show obviously higher specific current than that of bare PNCs, likely resulted from the enhanced electrical conductivity and electrochemical reactivity of the electrode.

The cycling performances of both PNCs and PNCs@Gr are also evaluated at specific currents of 500 mA g⁻¹ and 1 A g⁻¹, respectively. 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 revealed in Figure 7a,b, the PNCs@Gr anode shows an outstanding cycling performance and a high reversible capacity. At a specific current of 500 mA g\(^{-1}\), the PNCs@Gr maintains a much higher reversible capacity of 1070 mAh g\(^{-1}\) than that of bare PNCs (441 mAh g\(^{-1}\)) after 100 cycles, 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 remain a high reversible capacity of 948 mAh g\(^{-1}\) after 200 cycles, which is approximately 97.7% of the fourth cycle, while the capacity of bare PNCs is only 291 mAh g\(^{-1}\). More importantly, when the specific current reaches 5 A g\(^{-1}\), the sandwich-like PNCs@Gr nanostructure retains a specific 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 7d, upon prolonged cycling, the Columbic efficiency of PNCs@Gr is increased to above 99% after initial several cycles, demonstrating its excellent electrochemical reversibility. It is noted that electrochemical performances of PNCs@Gr exceed most previously reported carbon-based materials\(^{16,18,38-43}\) and recently reported MOF-derived anode materials for LIBs, as compared in Tables S1 and S2.\(^{16,18,27-29,39-51}\) 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, a highly desirable combination of micro- and mesopores and ultrafine carbon nanospheres (\(\sim 20 \text{ nm}\)) embedded on the graphene surface offer larger surface area (872 m\(^2\) g\(^{-1}\)) in comparison with bare PNCs (508 m\(^2\) g\(^{-1}\)), and thus not only result in large electrode/electrolyte interface to effectively store lithium ions, but also facilitate fast charge transfer. Second, the highly conductive, mechanically strong and flexible graphene not only improve 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 from 100 to 6000 mA g\(^{-1}\). As displayed in Figure 7e, the reversible capacities of PNCs@Gr are 1378, 1228, 1070, 984, 915, 854, and 647 mAh g\(^{-1}\) at 100, 200, 400, 600, 800, 1200, and 4000 mA g\(^{-1}\), respectively. Even at 6000 mA g\(^{-1}\), the reversible capacity of PNCs@Gr remains 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\(^{-1}\), demonstrating its outstanding reaction reversibility and cycling stability. However, the bare PNCs anode shows much lower reversible capacities of 797, 692, 550, 508, 451, 277, and 123 mAh g\(^{-1}\) when cycled at 100, 200, 400, 600, 800, 1200, 4000, and 6000 mA g\(^{-1}\), respectively. The superior rate capability of the sandwich-like PNCs@Gr electrode is ascribed to its hierarchical nanostructure, in which graphene significantly improves the electrical conductivity of the electrode, and ultrafine carbon nanospheres offer a 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 carried out to investigate electrochemical kinetics occurring at the electrode/electrolyte interfaces and Li-ion intercalation/deintercalation within electrode materials in the battery cells. As seen in Figure 7f, the Nyquist plots of bare PNCs and PNCs@Gr shows a slanted line in the low-frequency region and a depressed semicircle in the medium-frequency region.\(^{3}\) It is observed that the electrode of sandwich-like PNCs@Gr nanostructure shows a charge transfer resistance of 30 \(\Omega\), which is much lower than that of bare PNCs (100 \(\Omega\)), indicating a significantly enhanced charge transfer within the whole electrode.

Figure 8a shows the initial three cycles of the PNCs@Gr electrode at 100 mA g\(^{-1}\) from the rate performance testing. Typical charge/discharge profiles are consistent with N-doped carbonaceous anodes for LIBs.\(^{5,16}\) It is observed that a large irreversible capacity loss occurs in the initial cycle, attributed to the unavoidable decomposition of the electrolyte and formation of the solid-electrolyte interphase (SEI) film.\(^{7,15}\) Such observation is consistent with the CV results in Figure 6, in which the

**Figure 6.** Cyclic voltammetry curves of (a) sandwich-like PNCs@Gr and (b) bare PNCs at a scan rate of 0.1 mV s\(^{-1}\).
cathodic peaks disappear in the second and third cycles. The charge/discharge curves of the PNCs@Gr electrode cycled at various rates are also displayed in Figure 8b.

The super high capacity, significantly enhanced rate capability, and excellent cycling performance of sandwich-like PNCs@Gr nanostructure are ascribed to their novel nanostructure and desirable 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 fast Li-ion transport pathways, thereby promoting rapid charge transfer. Furthermore, highly conductive and mechanically strong graphene provides continuous electron-transport pathways 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.

■ CONCLUSIONS

A sandwich-like, graphene-based porous nitrogen-doped carbons (PNCs@Gr) has been fabricated through direct pyrolysis of zeolitic imidazolate framework (ZIF-8) nano-
particles 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 exhibits high reversible capacity, better cycling stability, and excellent rate capability, in comparison with bare PNCs. The outstanding electrochemical performances of PNCs@Gr anode can be attributed to its novel sandwich-like nanostructure and proper N-doping in the composite. Thus, PNCs@Gr demonstrates to be a promising alternative to commercial graphite anode with great potential in high-performance LIBs. In addition, the obtained sandwich-like PNCs@Gr may also be applicable for supercapacitors and other fields.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b01430.

TGA curve of ZIF-8 sample under N2; Raman spectra of ZIF-8, ZIF-8@GO, and PNCs@Gr; tables of cycling performances comparison between our work with other carbonaceous electrode materials and most of reported MOF-derived materials for LIBs, respectively (PDF)

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The authors declare no competing financial interest.

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