Ultrathin Nitrogen-Doped Carbon Layer Uniformly Supported on Graphene Frameworks as Ultrahigh-Capacity Anode for Lithium-Ion Full Battery

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The designable structure with 3D structure, ultrathin 2D nanosheets, and heteroatom doping are considered as highly promising routes to improve the electrochemical performance of carbon materials as anodes for lithium-ion batteries. However, it remains a significant challenge to efficiently integrate 3D interconnected porous frameworks with 2D tunable heteroatom-doped ultrathin carbon layers to further boost the performance. Herein, a novel nanostructure consisting of a uniform ultrathin N-doped carbon layer in situ coated on a 3D graphene framework (NC@GF) through solvothermal self-assembly/polymerization and pyrolysis is reported. The NC@GF with the nanosheets thickness of 4.0 nm and N content of 4.13 at% exhibits an ultrahigh reversible capacity of 2018 mA h g\(^{-1}\) at 0.5 A g\(^{-1}\) and an ultrafast charge–discharge feature with a remarkable capacity of 340 mA h g\(^{-1}\) at an ultrahigh current density of 40 A g\(^{-1}\) and a superlong cycle life with a capacity retention of 93% after 10 000 cycles at 40 A g\(^{-1}\). More importantly, when coupled with LiFePO\(_4\) cathode, the fabricated lithium-ion full cells also exhibit high capacity and excellent rate and cycling performances, highlighting the practicability of this NC@GF.

1. Introduction

As developed for more than two decades, lithium-ion batteries (LIBs) have been utilized as the major power supplier for mobile electronic devices and electric vehicles since they offer the highest energy density in comparison to other commercial battery systems. The electrode materials are the central factors of LIBs and largely dictate their ultimate performance.[1–4] Graphite, the commercial anode material, cannot meet the increasing demands of rapidly developing LIB markets due to its low theoretical specific capacity (372 mA h g\(^{-1}\)) and poor rate capability.[5] To increase the energy and power densities of LIBs, great efforts have been devoted to develop various alternatives to graphite, among which nanostructured carbon materials have received intensive interest due to their high electrical conductivity, low cost, designable structure, and porosity, etc.[6,7] Particularly, 2D ultrathin layer structure can enhance Li-storage ability by bounding Li not only on both sides of nanosheets, but also on the edges, defects, and covalent sites of nanosheets, while the 3D porous network can provide multidimensional electron transport pathway and shorten ion diffusion distance to promote the electrochemical reaction throughout the entire electrode.[7–10] Meanwhile, the introduction of heteroatom (e.g., N, B, S, F, and P) has been considered as another versatile approach to tune the intrinsic molecular structure of carbon materials, which can create more active sites and increase the electrode/electrolyte affinity and thus improve the Li storage properties to different extent depending on the specific synthetic conditions.[11–17] Therefore, it is believed that construction of carbon anode materials, which integrate 3D interconnected porous frameworks with 2D ultrathin heteroatom-doped carbon layers, is a highly promising route to achieve superior electrochemical performance. However, the current 3D carbon materials are always with thick wall or cluster-like frameworks, which substantially limit the efficiency of mass transport and charge storage for LIB electrodes.[18–23]

Herein, we report the first synthesis of judiciously designed ultrathin N-doped carbon layer grown on 3D graphene frameworks (NC@GF) via controllable in situ polymerization of uniform polyimide layer on graphene surface and self-assembly of graphene into 3D network structure simultaneously followed by pyrolysis under different temperatures. The graphene skeletons are fully coated by ultrathin N-doped carbon shell in this process. The thickness and composition of the composite nanosheet can be well adjusted by the pyrolysis temperature, and the optimized NC@GF with the wall thickness of 4.0 nm and the N content of 4.13 at% exhibits an ultrahigh reversible...
capacity of 2018 mA h g\(^{-1}\) after 300 cycles, remarkable rate capability with a capacity of 340 mA h g\(^{-1}\) at 40 A g\(^{-1}\), and a superlong cycle life with a capacity retention of 93% after 10 000 cycles at 40 A g\(^{-1}\). To the best of our knowledge, these results represent the best performance among all reported carbon anode materials. Theoretical calculation provides fundamental insight into the correlation between N species and electrochemical performance, consistent with the experimental results. To demonstrate the practical application of our NC@GF, soft-packaged full cell is further assembled with NC@GF as anode and commercial LiFePO\(_4\) as the cathode, exhibiting a high capacity of 124 mA h g\(^{-1}\) operated between 2.2 and 3.7 V and excellent rate and cycling performance, which highlights the great potential of NC@GF as a promising LIB anode.

2. Results and Discussion

The strategy for synthesis of NC@GF is illustrated in Scheme 1. First, graphene oxide (GO) and pyromellitic dianhydride (PMDA) was dispersed in N-methyl pyrrolidone (NMP) by sonication. After the addition of 2,6-diaminoanthraquinone (DAAQ), the polyimide (PI) was in situ polymerized on the graphene surface after solvothermal treatment, which led to the simultaneous reduction and self-assembly of GO into 3D porous structure. The PMDA and DAAQ were both aromatic structure and could be uniformly absorbed on the graphene surface by \(\pi-\pi\) interactions. Then PI with the aromatic backbone can be further in situ polymerized on both sides of graphene surface as the shell layers. PI@GF with a 3D architecture was obtained after freeze-drying. Finally, the PI@GF monolith was heated at 500, 600, and 700 °C for 2 h under N\(_2\) atmosphere, giving rise to NC@GF-T, where \(T\) represents the annealing temperature. For comparison, pure PI was produced by the same method without involving GO, and the NC-GF-mix was obtained by calcinating the mixture of PI and graphene at 600 °C. Additionally, pure GF without PI was prepared by similar treatment involving only GO.

The morphology and microstructure of the as-obtained PI@GF, PI, and NC@GF-T were first investigated via scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) (Figure 1; Figure S1, Supporting Information). As presented in Figure 1a–c and Figure S1a (Supporting Information), highly interconnected 3D frameworks with pore sizes ranging from sub-micrometers to several micrometers are visible in the resultant PI@GF and NC@GF-T samples. In addition, both SEM and TEM images revealed that the in situ grown PI layer was fully and homogeneously coated on the graphene framework surface because of the strong \(\pi-\pi\) interaction between graphene and the monomers as well as the polymer (Figure S1b–h, Supporting Information). No free porous polymer particles or naked graphene sheets were seen in either the TEM or SEM images. This further suggested that, as expected, most of the monomers had been polymerized on the surface of graphene sheets. The PI sample without the graphene template exhibited large flower-like particle structure similar to a previous report (Figure S1i,j, Supporting Information). After pyrolysis of PI@GF at different high temperatures from 500, 600, to 700 °C, the carbon layers became thinner and flatter gradually (Figure 1d–I). The high-resolution TEM (HRTEM) images showed the oriented multilayer domains at the edge of the layer with an adjacent interlayer distance of ≈0.34 nm (Figure 1j–l). This observation was consistent with the \(d\)-spacing of the (002) crystal plane of bulk graphite. The element mapping images further supported the homogeneous distribution of nitrogen on these hybrid layers (Figure 2a–l). Furthermore, the AFM characterizations demonstrate that the wall thicknesses of as-prepared NC@GF-500, NC@GF-600, and NC@GF-700 were adjusted to be only ≈5.1, 4.0, and 2.1 nm, respectively, significantly thinner than pristine PI@GF (6.5 nm) and thicker than graphene (< 1 nm) (Figure 2m–o; Figures S1d and S2, Supporting Information). These results

Scheme 1. Schematic illustration of the controllable synthesis route for NC@GF. a) In situ polymerization of polyimide by PMDA and DAAQ on the GO surface and self-assembly of GO by solvothermal treatment. b) The pyrolysis of PI@GF at 500, 600, and 700 °C.
Figure 1. Microstructural characterization of NC@GF-500, NC@GF-600, and NC@GF-700: a–f) SEM images, g–i) TEM images, and j–l) HRTEM images of a,d,g,j) NC@GF-500, b,e,h,k) NC@GF-600, and c,f,i,l) NC@GF-700.

Figure 2. a–l) TEM images and the corresponding elemental mapping images: C, N, and O distribution in the square region in panels (a–c). m–o) AFM images of NC@GF-500, NC@GF-600 and NC@GF-700.
unambiguously validated that the ultrathin N-doped carbon layers had been successfully introduced on both sides of graphene sheets.

To gain further insight into the crystalline structures and compositional features of PI@GF and NC@GF-T, Fourier transform infrared (FTIR) spectrum and X-ray diffraction (XRD) patterns (Figures S3 and S4, Supporting Information) have been performed. The peaks at 1650 cm\(^{-1}\) in PI@GF was the symmetric stretching vibration of C=O bonds, which was shifted from 1770 cm\(^{-1}\) in PMDA, demonstrating the existence of imide bond. The peak at 1334 cm\(^{-1}\) in PI@GF was the stretching vibration of the C–N bond, indicating the PMDA and DAAQ units were connected by the C–N bond.\(^{[26]}\) For NC@GF-T samples, all of the strong peaks of C=O (1650 cm\(^{-1}\)) disappeared, indicating that the polymer had been carbonized. In XRD patterns, there were series of strong peaks of PI@GF, demonstrating the formation of crystalline polyimide in PI@GF. For NC@GF-T, the previous strong peaks in PI@GF disappeared, while a broad peak appeared at about 26°, corresponding to the low degree of graphitization (002) peak. These results indicated the successful conversion of the polyimide layers to carbon layers by the annealing process. It can be further demonstrated by Raman spectra of the NC@GF-T with visible D and G bands at about 1330 and 1600 cm\(^{-1}\), respectively (Figure S5, Supporting Information). The decreased \(I_D/I_G\) values of NC@GF-500 (\(I_D/I_G = 0.99\)), NC@GF-600 (\(I_D/I_G = 0.93\)), and NC@GF-700 (\(I_D/I_G = 0.93\)) compared with that of GF (\(I_D/I_G = 1.04\)) suggested that all NC@GF-T were with an amorphous carbon.\(^{[20]}\) The contents of graphene in NC@GF-500, NC@GF-600, NC@GF-700 were 41%, 48%, and 50%, respectively, which was determined by the thermogravimetric analysis (Figure S6, Supporting Information).

The chemical nature of the NC@GF-500, NC@GF-600, and NC@GF-700 was further investigated by X-ray photoelectron spectroscopy (XPS, Figure 3a; Figure S7, Supporting Information). The N contents of NC@GF-500, NC@GF-600, and NC@GF-700 were calculated to be 5.73, 4.13, and 3.10 at%, respectively. The N 1s spectra of NC@GF-500, NC@GF-600, and NC@GF-700 can be fitted to three peaks at \(\approx 398.9\), \(\approx 400.2\), \(\approx 401.0\) eV, corresponding to the pyridinic nitrogen (N1), pyrrolic nitrogen (N2), graphitic nitrogen (N3), respectively. Apparently, these peaks vary with the annealing temperature. As for three

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Figure 3. a) High-resolution N 1s XPS spectra of NC@GF-500, NC@GF-600, and NC@GF-700, respectively. b) Summary of the different nitrogen levels in NC@GF-500, NC@GF-600, and NC@GF-700, respectively. c) DFT calculations of relative energies (eV) of the reduced forms without and with Li coordination based on the neutral form.
NC@GF-T samples, the percentages of pyrrolic N, pyridinic N, and graphitic N in total N were 55.1%, 20.6%, and 25.3% for NC@GF-500; 29.3%, 30.5%, and 40.2% for NC@GF-600; and 28.7%, 23.6%, and 47.5% for NC@GF-700, respectively (Figure 3b). Such tunable levels of N-bonding configurations in NC@GF-T electrodes provide a precious opportunity to understand experimentally the essential effect of N-doping on the electrochemical performances for lithium storage.

To better understand the effect of the N species on the electrochemical performance, the redox properties of these three N species were estimated using density functional theory (DFT) calculation (Figure 3c; Tables S1–S10, Supporting Information). The lowest-unoccupied molecular orbital energy level of the pyridinic N (−1.742 eV) was lower than those of pyrrolic N (−1.611 eV) and graphitic N (−1.646 eV), indicating favorable electron reduction of pyridinic nitrogen compared to pyrrolic nitrogen and graphitic N. The reduction of pyridinic N (E_red = 14.43 eV) and graphitic N (E_red = 11.12 eV) was energetically more favorable than those of pyrrolic N (E_red = 32.02 eV). The pyridinic N (−14.72 eV), graphitic N (−11.05 eV), and pyrrolic N (−17.06 eV) all enjoyed the stabilization by Li coordination. As the net energy change, pyridinic N (−0.28 eV) was lower than those of graphitic N (0.07 eV) and pyrrolic N (14.94 eV), leading to the highest activity for association of Li atoms.

To explore the electrochemical properties of NC@GF-T as anode for LIBs, the cyclic voltammogram (CV) curves of NC@GF-T were measured at a scan rate of 0.1 mV s⁻¹ ranging from 0.01 to 3.0 V versus Li/Li⁺ by using 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1) as the electrolyte at room temperature (Figure 4a; Figure S8a,b, Supporting Information). All of the NC@GF-T showed similar CV curves. Thus, the results of NC@GF-600 were discussed here as a typical example. Notably, for the first discharge cycle, a strong peak was observed at ≈0.6 V, which was usually attributed to the side reactions on the electrode surface due to the solid–electrolyte interphase (SEI) film.[10] Additionally, the intensity of this peak during the first cycle was much stronger than the intensity during the following cycles, indicating the occurrence of some irreversible reactions and the formation of an SEI film. From the second cycle forward, it was important to note that the CV curves were almost overlapped, indicating the stable and superior reversibility of NC@GF. The discharge/charge profiles of the first five cycles for the NC@GF-T electrodes at a current density of 0.5 A g⁻¹ between 0.01 and 3.0 V were further shown in Figure 4b and in Figure S8c,d (Supporting Information). For all samples, the presence of a plateau at ≈0.6 V in the first discharge cycle was attributed to the formation of SEI layer on the electrode surfaces. Surprisingly, the reversible capacities of NC@GF-600 in the first five cycles were much higher than that of NC@GF-500 and NC@GF-700, corresponding to much more active electrochemical reaction. According to the aforementioned XPS analysis, both the N content and species were responsible for the electrochemical reaction. Though with highest N content, the NC@GF-500 did not show the most active electrochemical reaction, for the reason that 500 °C was not optimal temperature for the carbonization of PI. In this case, most N atoms existed as pyrolic nitrogen by XPS analysis, which was not beneficial for Li storage. For NC@GF-600, with 4.13 at% total N contents and the highest pyridinic nitrogen contents, the discharge capacity were significantly improved, while NC@GF-700 with the least total N contents showed the lowest electrochemical activity. The initial coulombic efficiency of NC@GF-600 (60.1%) was low because of the formation of the SEI film, but still greater than the efficiency reported for many N-doped carbon materials,[14,20] suggesting that the newly prepared NC@GF-600, with the high pyridinic N content, hold great promise as novel anode materials for LIBs.

In the galvanostatic discharge–charge cycling measurements at a current density of 0.5 A g⁻¹ (Figure 4c; Figure S7, Supporting Information), the initial reversibility capacities of NC@GF-500, NC@GF-600, and NC@GF-700 were 986, 1528, and 487 mA h g⁻¹, respectively, significantly higher than that of GF (343 mA h g⁻¹) and NC@GF-mix (423 mA h g⁻¹) (Figure 4c; Figure S9a, Supporting Information). The cycling performance of NC@GF-600 was superior to that of other NC@GF-T, NC@GF-mix, and GF electrodes. The reversible capacity of NC@GF-600 remained at 1213 mA h g⁻¹ after 100 cycles. Starting from the 100th cycle, the reversible capacity of NC@GF-600 was gradually increased to 1418 mA h g⁻¹ after 200 cycles. In comparison, the capacity of NC@GF-500 gradually increased to 921 mA h g⁻¹ after 100 cycles and then remained at 1211 mA h g⁻¹ after 200 cycles. The capacity of NC@GF-700 electrodes could also be maintained at about 568 mA h g⁻¹ after 200 cycles. In contrast, the NC@GF-mix and GF were decreased to 283 and 191 mA h g⁻¹ after 100 cycles, respectively. Interestingly, both NC@GF-500 and NC@GF-600 presented a slight but continuous increase of the capacity after 100 cycles, even the capacity of NC@GF-600 can reach a record high value of 2018 mA h g⁻¹ at the 300th cycle. Such an activation phenomenon was attributed to the delayed wetting of the electrolytes into the N-doped carbon layers.[27] The reversible formation and decomposition process of an organic polymeric/gel-like film on the interface of carbon shell layer also provided amounts of interfacial storage sites for excess Li through the “pseudocapacitance type behavior.”[28] Among three samples, CN@GF-700 with the least of N content showed the lowest capacity (≈560 mA h g⁻¹). Because of the highest graphitic N species in this composite, the lithiation/delithiation process in the composite was very stable and similar to graphite anode. Furthermore, the carbon nitride (2D sheets of tri-s-triazine connected via tertiary amines)–graphene framework (carbon nitride-GF) composites were also prepared to probe the effect of the different N species in composites on the lithium storage behavior (Figure S9b,c, Supporting Information).[20] The capacity of the composite was stable at 650 mA h g⁻¹ after 100 cycles at the current density of 500 mA g⁻¹ (Figure S9d, Supporting Information). These results indicated that the N-doped carbon with the triazine rings can also serve as anode electrode for LIBs. In addition, the capacity of NC@GF-600 was higher than carbon nitride-GF indicating that the pyridinic nitrogen might be more electrochemical active than the triazine rings.

In addition to the excellent cycling stability, the NC@GF-600 electrode also manifested excellent rate capability (Figure 4d), yielding capacities of 2470, 863, 486, and 340 mA h g⁻¹ at current densities of 0.1, 1, 10, and 40 A g⁻¹, respectively. Such a large capacity (340 mA h g⁻¹) at ultrahigh current density (40 A g⁻¹) has rarely been achieved for previous carbon anode materials and makes the NC@GF-600 extremely promising superfast
an electrode material. Notably, a large capacity of 1764 mA h g\(^{-1}\) for NC@GF-600 electrode was restored when the current density returned to 0.1 A g\(^{-1}\). These results were in sharp contrast to those of NC@GF-500 and NC@GF-700, which showed continuous capacity decrease during the ten cycles at each current density and decay to 244 and 169 mA h g\(^{-1}\) respectively, at a high current density of 40 A g\(^{-1}\). Furthermore, NC@GF-600 even showed a combination of superior rate capability and long-term cycling stability (Figure 4e). After activation at 0.5 A g\(^{-1}\) in the first 120 cycles, the galvanostatic charge–discharge test involving 10 000 cycles was carried out at a current density of 40 A g\(^{-1}\) which was seldom seen in the previous reports. The capacity was increased from 319 to 400 mA h g\(^{-1}\) after 4000 cycles at 40 A g\(^{-1}\), and the reversible capacity was kept at 298 mA h g\(^{-1}\) in the following cycles. In addition, the coulombic efficiency of NC@GF-600 always retained nearly 100%, further indicating its excellent reversibility. It is worth noting that the electrochemical performance of NC@GF-600 is superior to all carbon anode materials to the best of our knowledge including graphene/carbon-based nanostructures and most metal oxide/sulfide anode materials (Tables S11–S13, Supporting Information).

To verify the excellent electrochemical performance of NC@GF-600 compared to NC@GF-500 and NC@GF-700 electrodes, the AC impedance was measured subsequently. The Nyquist plots (Figure S8, Supporting Information) showed that the diameter of the semicircle for NC@GF-600 electrodes in the high-medium frequency region was smaller than other samples, indicating lower contact and charge-transfer impedances of NC@GF-600 compared to NC@GF-500 and NC@GF-700.
The equivalent circuit of the studied system was presented in Figure S9 (Supporting Information) to illustrate the internal resistance of the test battery according to literature. For NC@GF-600 electrodes, the values of the charge-transfer resistance ($R_{ct}$) and ohmic resistance ($R_{f}$) were 50.32 and 0.01 Ω, respectively, which are significantly lower than those of NC@GF-500 (60.24 and 0.03 Ω) and NC@GF-700 (69.95 and 0.02 Ω). This result confirmed that the 3D graphene framework coupled with ultrathin carbon-coating layer containing high-level pyridinic N should be responsible for the high conductivity of NC@GF-600 and thus greatly enhance the rapid electron/ion transportation during the electrochemical lithium insertion/extraction reaction.

Associated with the structural and compositional analysis of NC@GF-T as discussed above, it is reasonable to believe that such prominent electrochemical performances of NC@GF-600 could be attributed to the following factors: (i) the ultrathin N-doped carbon layer on both sides of graphene can greatly promote the charge transfer by modulating the electronic and full utilization of active sites to realize the rapid and complete Li storage; (ii) the highest pyridinic nitrogen level among the three NC@GF-T samples creates more active sites for lithium storage; (iii) unique structure in 3D architecture can not only provide multidimensional interconnected pathway for electron transport, but also enable the facile access of electrolyte and thus the fast transport of lithium ions, satisfying the kinetics demands of high-power lithium ion batteries; (iv) the high electrical conductivity of graphene frameworks within each carbon layer can act as mini-current collectors homogeneously dispersed in the electrode.

The ultrahigh capacity, excellent cycling stability, and remarkable rate capability of the NC@GF-600 half-cell encourage us to further measure its performance as anode in a full cell. A full lithium-ion battery was fabricated using the LiFePO$_4$ (LFP) as cathode and NC@GF-600 as anode. The voltage profile of the LFP cathode and NC@GF-600 anode versus Li was shown in Figure 5a. The LFP cathode exhibited a reversible capacity of 150 mA h g$^{-1}$ and a flat voltage plateau of 3.5 V versus Li, while the NC@GF-600 anode operates reversibly with continuous, plateau-free charge–discharge curves with the capacity of about 1250 mA h g$^{-1}$. On the basis of the results from half-cells, the lower and the upper cut-off voltages were set to 2.2 and 3.7 V, respectively, which are highly favorable for practical application. The full cell delivered a high capacity of 124 mA h g$^{-1}$ and an impressive energy density of 322 Wh kg$^{-1}$ at a current rate of 50 mA g$^{-1}$, indicating high utilization of NC@GF-600 (the capacity is calculated based on the total mass of both cathode and anode) (Figure 5b). In the following cycles, the full cell displayed a good capacity retention of 87% after 100 cycles, which is much better than most other graphene-based or carbon-based full cells (Table S14, Supporting Information). Even at a high current density of 200 mA g$^{-1}$, the capacity remained 83 mA h g$^{-1}$ after 200 cycles with a coulombic efficiency of 100%, demonstrating a superior stability (Figure 5c). NC@GF-600 also showed a remarkable rate performance exhibiting a capacity of 82 mA h g$^{-1}$ and energy density of 213 Wh kg$^{-1}$ up to 500 mA g$^{-1}$ current density (Figure 5d). To demonstrate the practical application of NC@GF-600, the soft-packaged of NC@GF-600/LFP full cell, as shown in Figure 5e,f, can drive the “LIB” light-emitting-diodes (LED) plate and color touch screen.

Figure 5. Electrochemical characteristic of the NC@GF-600/LFP full cell and its practical application. a) Charge–discharge voltage profiles of the single electrodes: NC@GF-600 anode (down curve) at 500 mA g$^{-1}$ and the LFP cathode (up curve) at 50 mA g$^{-1}$ versus Li. b) Charge–discharge voltage profiles of NC@GF-600/LFP full cell at 50 mA g$^{-1}$ and 200 mA g$^{-1}$. c) Cycling performance and d) rate performance of the full cell between 2.2 and 3.7 V. e,f) Photographs of the pouch-type full battery and its application in lightening “LIB” LED and color touch screen.
screen for a long time. This result indicated that our strategy of employing the 3D NC@GF with 2D N-doped nanosheets’ structure is promising to develop a high-performance anode material for LIBs.

3. Conclusions

In summary, artificial ultrathin N-doped carbon nanosheets coated on 3D graphene frameworks were successfully developed into affordable anodes for rechargeable LIBs with high energy density and long cycle life. It is anticipated that this protocol for the fabrication of novel and unique 3D structure, which integrates the distinctive features of a 3D porous structure, 2D nanosheets, and molecular-level controlled N-doping, will pave the way for the ongoing research in energy-related applications.

4. Experimental Section

**Samples Preparation:** GO was prepared from graphite flakes by a modified Hummer’s method.[35] The PI@GF was synthesized by a one-pot method. Typically, 43.6 mg of PMDA was dissolved into 6 mL of 1.5 mg mL\(^{-1}\) GO/NMP solution. The suspension was ultrasonicated for 10 min and 47.6 mg of DAAQ was added. Then the as-prepared suspension was transferred into a 30 mL Teflon-lined stainless steel autoclave for a solvothermal reaction at 180 °C for 12–24 h to form a 3D framework structure. After cooling naturally, the as-prepared sample dipped into deionized (DI) water for three times. Finally, the targeted PI@GF with a 3D architecture was obtained after freeze-drying. The NC@GF-500, NC@GF-600, and NC@GF-700 were carbonized at tunable temperatures of 500, 600, and 700 °C under \(N_2\) atmosphere for 2 h, respectively. The control polyimide was synthesized by the same condition without adding GO. GF was prepared by the hydrothermal reduction of GO at 180 °C for 12 h and freeze-drying, and the NC-GF-mix was attained from mixing the GF with polyimide and then carbonization at 600 °C under \(N_2\) atmosphere for 2 h.

Materials Characterization and Computational Details: SEM measurements were performed on a Zeiss Ultra-55 field emission scanning electron microscope. TEM studies were conducted on an FEI Tecnai G2 20TWIN electron microscope at an operating voltage of 200 kV. AFM observation measurements were performed using a scanning probe microscope (Multimode 8) water in tapping mode. XRD analysis was performed on Rigaku D/Max 2500 X-ray diffractometer using Cu Kα radiation (\(\lambda = 1.54 \text{ Å}\)) at a generator voltage of 40 kV and a generator current of 20 mA with a scanning speed of 5° min\(^{-1}\) from 10 to 80°. FTIR spectral measurements were performed using a Perkin-Elmer Paragon 1000 FTIR Spectrometer. Raman measurements were recorded on an Invia/Reflex Laser Micro-Raman spectroscopy (Horiba Jobin Yvon, French) with an excitation laser beam wavelength of 532 nm. XPS was measured by Thermo 250XI. DFT calculations were performed with the Gaussian 09 program. All geometry optimizations were carried out at the RB3LYP level of density functional theory with the 6-31G(d) basis set.

Electrochemical Measurements: Electrochemical experiments of half-cells were carried out in 2016 coin-type cells. The anode electrodes were prepared by mixing the hybrids, carbon black (Super-P), and poly(vinyl difluoride) (PVDF) with a weight ratio of 70:20:10 and pasting the mixture on pure copper foil (99.6%). Pure lithium foil was used as the counter electrode. The LFP cathode was prepared by mixing 80% LFP, 10 wt% Super-P, and 10 wt% PVDF dissolved in NMP to form slurry, which was then pasted on an Al foil. The anode electrode was precycled in half-cells and then assembled into full cells. The cathode capacity was limited, and the cathode-to-anode specific capacity loading ratio was 1:1.1. The full cells were tested using galvanostatic charge-discharge protocols on LANHE System at room temperature. Full cells were cycled within a voltage range from 2.2 to 3.7 V. The current density and the capacity for full cell test were calculated on the total weight of both electrodes.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

3D graphene frameworks, high-performance anodes, lithium-ion batteries, N-doped, ultrathin carbon layers

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