Supporting Information

$sp^2/sp^3$ Hybridized Carbon as an Anode with Extra Li-Ion Storage Capacity:
Construction and Origin

Zongjing Lu, Denglei Gao, Ding Yi, Yijun Yang, Xi Wang,* and Jianmian Yao*
Experimental Procedures

Chemicals

All chemicals used in this study were of analytical grade and used directly without further purification. Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O) and commercial multiwalled carbon nanotube (MWCNT) were purchased from Aladdin. 2-methylimidazole was supplied by Innochem. Methanol was obtained from Beijing Chemical Plant. Moreover, separator (Celgard 2400) was purchased from Hoechst Celanese.

Materials synthesis

**Preparation of ZIF-67.** In a typical preparation, 350 mg Co(NO$_3$)$_2$·6H$_2$O was added into 30 mL of methanol and stirred for 30 min at room temperature to produce a pink solution. Simultaneously, 765 mg 2-methylimidazole was also dissolved in 30 mL methanol to form a colorless solution. Subsequently, the pink solution was instantly poured into the colorless solution under constant stirring. The whole mixed solution was thoroughly mixed and kept still at room temperature for 24 h to get the purple precipitates at room temperature. The as-obtained precipitates were collected by centrifugation, washed three times with ethanol, and finally dried under vacuum at 80 °C for 12 h.

**Synthesis of N-DF.** The as-prepared purple ZIF-67 powders were heated to 700 °C with a heating rate of 5 °C min$^{-1}$ in a tube furnace and maintained for 2 h under an Ar/H$_2$ gas flow (10% H$_2$). Finally, the black product, N-DF, was obtained.

Characterization methods

The morphology and structure of the as-prepared products were characterized by scanning electron microscope (SEM, JSM-7001F) and transmission electron microscopy (TEM, JEM-2100F). X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima III instrument with a Cu Kα radiation source ($\lambda = 1.5406$ Å) to analyze the phase composition of the samples as above mentioned. X-ray photoelectron spectroscopy (XPS) was acquired on an ESCALAB 250Xi instrument. Raman spectra were measured by using Horiba Jovin Yvon T64000 Raman
spectroscope ($\lambda_{ex} = 532$ nm). Thermogravimetric analysis (TGA)/differential thermal analysis (DTA) from 25 °C to 800 °C was carried out on EXSTAR TG/DTA STK-6300 with a heating rate of 5 °C min$^{-1}$ in air or nitrogen. The Brunauer-Emmett-Teller surface and nitrogen adsorption-desorption isotherms of the products were collected by using a Quantachrome Autosorb-IQ2 system at 77 K.

**Construction of N-DF nanobattery device**

*In situ* transmission electron microscopy (TEM) observations were conducted in a JEOL-2100F equipped with a PicoFemto Company TEM-STM holder. The as-prepared N-DF particles adhered to the gold rod as the working electrode. Similarly, a small piece of lithium foil was also attached to a tungsten wire as a reference and counter electrode. The gold rod and tungsten wire were installed on the corresponding position of the TEM–STM holder, respectively. The lithiation process was performed on a negative bias in the range of -3 to 0 V vs the metallic Li to the working electrode.

**Electrochemical characterizations**

The LIBs with N-DF anode were assembled as CR2025-type coin cells in an argon-filled glovebox. The mass ratio of active materials(N-DF), Super P, and polyvinylidene fluoride (PVDF) was 8:1:1, which were homogeneously suspended in N-methyl-pyrrolidone. The resulting slurry was directly coated onto a copper foil. The foil was dried at 80 °C in a vacuum oven for 12 h to form the working electrode with an average loading mass of active materials about 1.0 mg cm$^{-2}$. The dried foil was further stamped into some disks with a diameter of 14 mm. The coin cells were assembled in an argon-filled glovebox. The electrolyte was consisted of 1M LiPF$_6$ in the ethyl carbonate (EC) and diethyl carbonate (DEC) (EC/DEC = 1:1, v/v). The Li metal was collected as the counter and reference electrode. A polypropylene film (Celgard 2400, Hoechst Celanese) was collected as the separator, respectively. The galvanostatic charge-discharge tests were performed on a battery tester (CT200TA) in a
potential window of 0.01-3 V. Cyclic voltammetry (CV) was carried out between 0.01 and 3.0 V on the electrochemical workstations (CHI760E).

**Computational methods**

All the calculations were based on density functional theory (DFT) by using the Vienna ab initio Simulation Package (VASP). The generalized gradient approximation was used for the exchange-correlation functional with the Perdew-Burke-Ernzerhof (PBE) parameterization. Considering the weak interlayered Van der Waals (VdW) interaction, empirical dispersion corrections proposed by Grimme (DFT-D3) were used for geometry optimization. We first built a periodical supercell (5×5) with a vacuum space of 15 Å in the z-direction, and a 4×4×3 Monkhorst-Pack mesh grid for special k-points was set up for Brillouin zone integration. The xyz-direction lattice constant of positive curvature graphene is 25×25×15 Å, and a 2×2×1 Monkhorst-Pack mesh grid for Brillouin zone integration. The negative curvature graphene (a=b=30 Å and c=20 Å for lattice parameters) was used with 1×1×1 Monkhorst-Pack sampling k-points. An energy cutoff of 400 eV was used for plane-wave basis sets. The convergence thresholds were set to 10⁻⁵ eV and 0.01 eV/Å for energy and force. We calculate the adsorption energy per Li atom ($E_{ad}$) as following:

$$E_{ad} = \frac{(E_{total} - E_h - zE_L)}{z}$$

where $E_{total}$, $E_h$ and $E_L$ represent the energy of graphene with Lithium adsorption, graphene without Lithium adsorption and one lithium atom, respectively; $z$ is the number of Li atoms.
Results and discussion

Synthesis mechanism of N-DF

During the pyrolysis process, the reduced gas streams play a critical role to break the coordination bonds between the metal ion and organic ligands, and then the metallic Co nanoparticles are formed preferentially on the surface of the ZIF-67 precursor. According to the bottom-up chemical synthesis approach, organic residuals of 2-methylimidazole as basic units are continually decomposed on the surface of the metallic Co nanoparticles catalyst.\textsuperscript{4-6} Simultaneously, the inside-out growth of interconnected N-doped carbon nanotubes (N-CNTs) generates some inner hollow voids.\textsuperscript{7,8}

Analysis of XRD patterns

The XRD patterns of N-DF and commercial MWCNT are illustrated in Figure 2a. A small broad peak of N-DF at about 24.9° is attributed to the (002) plane of carbon materials, which confirms the disorder of the graphitic layers. The peak value is at a lower angle than that of MWCNT (26.2°), implying the larger interlayer spacing of the graphitic layer for N-DF. The other three peaks of N-DF at about 44.2°, 51.4° and 76.1° are assigned to the (111), (200), and (220) lattice planes of cubic Co (JCPDS card #15-0806), respectively.\textsuperscript{9}

Analysis of Raman spectra

As can be seen from Raman spectra (Figure 2b), two broad peaks of N-DF appear at about 1334 cm\textsuperscript{-1} and 1595 cm\textsuperscript{-1}, which are indexed to the D and G bands, respectively. G band is known as a characteristic feature of the graphitic layers, while D band arises from carbon and nitrogen defects. Compared with the G band of MWCNT (1582 cm\textsuperscript{-1}), the corresponding band of N-DF exhibits blue-shifted, owning to nitrogen doping.\textsuperscript{10} The intensity ratio of two peaks (I_D/I_G) is related to the degree of the structural disorder in graphitic carbon lattice.\textsuperscript{11,12} The relative I_D/I_G intensity for N-DF is larger than that for MWCNT (1.06 vs. 1.01), indicating that the degree of disorder for N-DF is higher.
Rate capability

The rate capability of N-DF and MWCNT is investigated at different current densities (Figure 3d). In comparison, N-DF shows a much higher capacity than those of MNCNT at different current densities. Even at 2.0 A g\textsuperscript{-1}, N-DF still delivers a considerable capacity of 378 mAh g\textsuperscript{-1}, slightly higher than the theoretical capacity of graphite (372 mAh g\textsuperscript{-1}). Notably, the reversible capacity of N-DF recovers to 614 mAh·g\textsuperscript{-1} when the current density returns to 0.1 A·g\textsuperscript{-1}, demonstrating its excellent high-rate capability.

![Figure S1. XRD patterns of as-prepared ZIF-67 and simulated ZIF-67.](image)

![Figure S2. (a) SEM images of ZIF-67 dodecahedra and (b) the corresponding particle size distribution statistics of ZIF-67.](image)
Figure S3. (a) TGA of ZIF-67 dodecahedra in argon and TGA (blue)/ DTA (red) of the N-DF sample in air.

As shown in Figure S3b, the N-DF sample starts to burn at an extremely low temperature of $\sim 230 \, ^\circ C$. The maximum rate of mass loss occurs at $\sim 290^\circ C$, where a strong exothermic peak is observable in the DTA curve. In any case, this loss process corresponds to burning of carbon in the sample before 300 $^\circ C$, confirming that the entire sample consists of curved and individual graphene layers sparsely separated from each other. The burn temperature of N-DF is lower than the previous reports.\textsuperscript{13} This result may mainly depend on the catalytic effect of Co in the oxidation process and the adsorption oxygen activity of the curved graphite layers.\textsuperscript{14,15} Although it is not clear which of these two factors is the main factor to reduce the burn temperature, it can be determined that carbon atoms (resembling the dangling atoms at the graphene edge) in the curved graphite layers are considerably active and easily participate in a chemical reaction, as compared to the coplanar sp$^2$ hybridized carbon atoms.
Figure S4. (a) SEM images of as-obtained N-DF and (b) the corresponding particle size distribution statistics of N-DF. (c, d) High-magnification SEM images of N-DF.

Figure S5. High-resolution TEM image of the Co nanoparticle embedded into N-doped carbon nanotubes of N-DF.
Figure S6. (a, b) SEM images of commercial MWCNT; (c-f) TEM images of commercial MWCNT.

Figure S7. N$_2$ adsorption/desorption isotherms of N-DF (a) and MWCNT (b), the inset is corresponding BJH pore size distribution.

**Analysis of nitrogen adsorption/desorption isotherms**

The nitrogen adsorption/desorption isotherms of N-DF and MWCNT exhibit the characteristics of type II and type IV isotherms confirmed by the Brunauer-Emmett-Teller (BET) method (Figure S7). The N-DF samples display the specific surface area of 219.5 m$^2$ g$^{-1}$, slightly higher than that of MWCNT (170.5 m$^2$ g$^{-1}$). The pore size dispersion curve confirms that N-DF is mainly mesoporous structure centred at 3.39 nm. The high surface area and mesopores of N-DF could reduce the diffusion resistance of Li$^+$ and facilitate capacitive performance.
The presence of cobalt in the N-DF is particularly noted. Based on the limited probe depth (~5-10 nm) of XPS, the corresponding high-resolution Co 2p spectrum is fitted with two prominent peaks, readily attributed to Co 2p$^{1/2}$ at 780.2 eV and Co 2p$^{3/2}$ at 795.7 eV, respectively. The result of high-resolution Co 2p spectrum finds that only the characteristic peaks of metallic cobalt are identified (Figure S8), which displays that the cobalt on the surface of N-DF exists in the form of metallic cobalt, without the presence of other cobalt compounds. In addition, the cyclic voltammetry (CV) curves of N-DF have no peaks associated with the electrode reaction between other cobalt compounds and Li$^+$, suggesting that the cobalt on the bulk phase of N-DF presents only as metallic cobalt (Figure 3a). Thus, the cobalt of N-DF is completely reduced to metallic cobalt. The results of CV also have no peaks associated with the electrode reaction between metallic cobalt and Li$^+$, suggesting that Co nanoparticles of N-DF are an inert material for LIBs. Acid treatment experiments of N-DF were followed with 1 M H$_2$SO$_4$ or 1M HCl for 24 h to remove Co nanoparticles. However, these carbon-encased Co nanoparticles are inaccessible to reactants as they remain completely encapsulated within the graphitic carbon shell even after acid leaching, in agreement with the previous reports in the literature. Considering that metallic cobalt nanoparticles are inert materials for LIBs, there is residual metallic cobalt, and other ions may be introduced in acid treatment, the cobalt nanoparticles of N-DF are not treated.
**Figure S9.** (a) CV curves of MWCNT at a scan rate of 0.1 mV s$^{-1}$. (b) Galvanostatic discharge-charge profiles of the MWCNT at 0.1 A g$^{-1}$.

**Figure S10.** (a, b) HRTEM images of different MWCNT. (c-f) HRTEM images of different N-CNTs exhibiting the nanoscale curved geometry structures of N-CNTs, where red and blue circles mark the concave and convex structures, respectively.
Figure S11. The optimized models of pyridinic-N and pyrrolic-N embedded into the carbon network from top and side views: (a) a single pyridinic -N or pyrrolic-N, zero curvature; (b) one pyridinic-N and pyrrolic-N, zero curvature; (c) three pyridinic, zero curvature (d) two pyridinic-N and one pyrrolic-N, zero curvature. The finite fragment structures of carbon are modeled with hydrogen atom terminations, as represented by the white ends of the ball and stick models.

Optimized structural model by the density functional theory (DFT) calculations: The optimized model of a single pyridinic-N or pyrrolic-N embedded into the carbon network displays in Figure S11a; this result suggests that a single pyrrolic-N embedded into the carbon network is unstable, while a single pyridinic-N is stable and the optimized model with zero curvature exhibits a flat structure; similarly, one pyridinic-N and one pyrrolic-N embedded into the network is also unstable and the optimized model presents zero curvature structure. (Figure S11b); as shown in Figure S11c, the optimized model of three pyridinic-N embedded into the carbon network displays a zero curvature structure; Although the optimized model of two
pyridinic-N and one pyrrolic-N shows that the nitrogen atoms is non-coplanar, the entire carbon network remains coplanar with a zero curvature structure (Figure S11d).

Figure S12. Top views and adsorption energies of a single Li atom adsorbed on the adjacent six-membered rings of polygon defects.

Figure S13. Side views and adsorption energies of different numbers of Li atom adsorbed on graphene with zero curvature (a₁-a₄), positive curvature structure (b₁-b₄) and negative curvature structure (c₁-c₄). With the exception of the periodic graphene structure, the finite fragment
structures are modeled with hydrogen atom terminations. White balls represent hydrogen atoms, gray balls represent carbon atoms, and purple balls represent Li atoms.

**Figure S14.** (a, b) CV curves of N-DF and MWCNT at different scan rates ranging from 0.2 to 3.0 mV s\(^{-1}\). (c) The corresponding linear relation of peak currents and scan rates. (d) CV curve with a capacitive fraction (pink) of MWCNT at 1.0 mV s\(^{-1}\).

The entire stored charge of N-DF is contributed by two parts: the diffusion-controlled contribution from the Li\(^+\) insertion process and the surface-induced capacitive contribution. Generally, the contribution ratios of the two mechanisms can be qualitatively analyzed by the relationship between the peak current density \(i\) and scan rate\(v\)

\[
i = a v^b
\]

(1)
Where \( a \) and \( b \) are adjustable parameters and \( b \)-value can be obtained from the slope of \( \log(i) \) vs. \( \log(v) \) plot. The \( b \)-value gives a good indication of the contribution ratios of storage capacity. When the \( b \)-value is close to 0.5, the storage capacity is dominantly controlled by the diffusion-controlled process, whereas the \( b \)-value approaches 1.0, the storage capacity is dominated by the surface-induced capacitive process. The calculated \( b \)-value for the peak delithiation currents of N-DF is 0.73 in Figure S14c, suggesting that the capacity of N-DF originates from a mixed mechanism associated with the diffusion-controlled contribution and the surface-induced capacitive contribution. Additionally, MWCNT also exhibits a similar kinetic mechanism for the lithium storage (\( b=0.74 \)). Furthermore, the source of storage capacity can be quantitatively analyzed based on the following equation (2)

\[
i = k_1 v + k_2 v^{1/2}
\]  

(2)

Herein, \( k_1 v \) and \( k_2 v^{1/2} \) represent the diffusion-controlled contribution and capacitive contribution, respectively. The values of \( k_1 \) and \( k_2 \) are determined from the slope and intercept of the \( i/v^{1/2} \) versus \( v^{1/2} \) plots.
Table S1. Comparison of the extra capacity of present work with reported N-doped carbon materials for lithium ion storage: the theoretical capacities of graphite and graphene are 372 mAh g$^{-1}$ and 744 mAh g$^{-1}$, respectively; based on DFT calculation in the literature search,$^{16}$ the theoretical capacity of pyridinic nitrogen, pyrrolic nitrogen and graphitic nitrogen are 1262 and 1198 and 1087 mAh g$^{-1}$, respectively; in order to simplify the calculation process and reflect the extra capacity, the theoretical capacity of nitrogen species is calculated according to the maximum capacity (1262 mAh g$^{-1}$). In addition, the theoretical capacity of N-doped carbon materials calculated based on the mass fraction of carbon and nitrogen is almost the value as the theoretical capacity calculated by the atomic percentage of carbon and nitrogen. Therefore, in the calculation process, the mass fraction or atomic percentage provided by the literature is directly used to calculate the theoretical capacity. Hence, the equation of theoretical capacity of N-doped graphite and carbon nanotube (CNT): Theoretical capacity = (100% - N content)$ \times $ 372 mAh g$^{-1}$ + N content $ \times $ 1262 mAh g$^{-1}$; the equation of theoretical capacity of N-doped graphene: Theoretical capacity = (100% - N content)$ \times $744 mAh g$^{-1}$ + N content $ \times $ 1262 mAh g$^{-1}$; the extra capacity is calculated by the following equation: Extra capacity= Experimental capacity – Theoretical capacity.

| Samples                                      | N content (wt% or at%) | Theoretical capacity (mAh g$^{-1}$) | Experimental capacity (mAh g$^{-1}$) | Extra capacity (mAh g$^{-1}$) | Reference |
|----------------------------------------------|------------------------|-------------------------------------|--------------------------------------|-------------------------------|-----------|
| compact N-doped carbon (CNC)                 | 26.56                  | 608                                 | 1655                                 | 1047                          | 17        |
| N-doped carbon honeycomb-like structure (NCH)| 17                     | 523                                 | 951                                  | 428                           | 18        |
| N-doped hollow carbon nanospheres (NHCNSs)   | 16.6                   | 520                                 | 2053                                 | 1533                          | 19        |
| nitrogen atoms into carbon nanospheres (NHCNSs) | 14.51                 | 501                                 | 1091                                 | 590                           | 20        |
| nitrogen-doped carbon capsules (hN-CCs)      | 13.8                   | 495                                 | 1046                                 | 551                           | 21        |
| Graphite | porous bimetallic Co/Zn embedded N-doped carbon (Co-Zn/N-C) | 12.76 | 486 | 702 | 216 | 22 |
|----------|----------------------------------------------------------|-------|-----|-----|-----|----|
| protein derived mesoporous carbon (PMC)                 | 10.1  | 462 | 1780| 1318| 23 |
| nitrogen-deficient g-C₃N₄ (ND-g-C₃N₄)                    | 8.84  | 451 | 2753| 2302| 24 |
| branched N-doped graphitic tubular foam (BNG)             | 5.99  | 425 | 1049| 624 | 25 |
| hierarchical porous nitrogen-doped carbon nanosheets (HPNC-NS) | 4.7   | 414 | 1865| 1451| 26 |
| N-doped hard carbon nanoshells with tailored graphitic/defective degree (N-GCNs) | 1.4   | 384 | 1253| 869 | 27 |
| Co nanoparticles embedded in nitrogen-doped carbon nanocubes (Co/NCs) | -     | <1262 | 1375| >113| 9 |

| Carbon nanotube | N-enriched carbon/carbon nanotube composite (NEC/CNT) | 21.1 | 560 | 1050| 490 | 7 |
| N-doped core–sheath carbon nanotube films (N-CNT)        | 10.25 | 463 | 943 | 480 | 28 |
| hierarchical porous N-doped carbon (atc.PNC-750)         | 6     | 425 | 516 | 91  | 29 |
| N-doped carbon nanotubes (NCNTs)                         | 4.52  | 412 | 1814| 1402| 30 |
| N-doped hollow carbon nanotubes and carbon nanofibers (CNT–CNF) | 2.4   | 393 | 1920| 1527| 31 |
| N-doped carbon nanotubes (NCNTs)                         | 1.4   | 384 | 1150| 766 | 32 |

| Graphene | N-doped graphene analogous particles (N-C-800) | 17.72 | 836 | 2132| 1296| 33 |
| N-doped carbon/reduced graphene oxide (N-carbon/rGO)     | 15.4  | 824 | 1100| 276 | 34 |
| nitrogen doped porous graphene (NPG)                      | 12    | 806 | 900 | 94  | 35 |
| N-doped graphene                                          | 3.67  | 763 | 872 | 109 | 36 |
| highquality, nitrogen-doped, mesoporous graphene particles (HNMG) | 2.1   | 755 | 1138| 383 | 37 |
| nitrogen-doped graphene nanosheets (N-GNS)                | 2     | 754 | 900 | 146 | 38 |
Table S2. Theoretical capacity of N-DF for lithium storage: The oxygen element is ignored due to the source of oxygen being probably the absorbed oxygen from the air; Metallic cobalt are inert to react with Li$^+$ and therefore the theoretical capacity of metallic cobalt is 0 mAh g$^{-1}$; theoretical capacity of carbon is 372 mAh g$^{-1}$, based on graphite; the theoretical capacity of pyridinic nitrogen, pyrrolic nitrogen are respectively 1262 and 1198 mAh g$^{-1}$, based on DFT calculation in the literature search; the contents of each element including Co, carbon and nitrogen (pyridinic and pyrrolic nitrogen species) are based on the results of XPS measurement, consistent with the results of the element analysis. The equation of theoretical capacity of dodecahedral is listed as follows: Theoretical capacity = Metallic cobalt content $\times$ 0 mAh g$^{-1}$ + Carbon content $\times$ 372 mAh g$^{-1}$ + Pyridinic N content $\times$ 1262 mAh g$^{-1}$ + Pyrrolic N content $\times$ 1198 mAh g$^{-1}$.

| Samples | Metallic cobalt content | Carbon content | Pyridinic N Content | Pyrrolic N Content | Theoretical capacity (mAh g$^{-1}$) |
|---------|-------------------------|----------------|--------------------|-------------------|-----------------------------------|
| N-DF    | 0.1422                  | 0.8272         | 0.0129             | 0.0178            | 345                               |
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