

Supplementary Information

Nitrogen doped Carbon Honeycomb-like Structure Assembled by Mesoporous Nanosheets with Superior Performance in Lithium-Ion Batteries

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1. Experiment Section

1.1 Regents and equipment

All starting materials were purchased from Sigma-Aldrich and used without any purification. The composition and phase of the as-prepared products were acquired by the powder X-ray diffraction (XRD) pattern using a Bruker D8 diffractometer with CuK α radiation ($\lambda=1.5418 \text{ \AA}$) at room temperature. The morphology and crystal structure of as-prepared products were observed by scanning electron microscopy (Hitachi SU-8010 field emission SEM), and transmission electron microscopy (FEI Tecnai G20). All TEM samples were prepared by depositing a drop of diluted suspensions in ethanol on a carbon film coated copper grid. Thermogravimetric analysis (TGA) was carried on a TGA-Q500 thermoanalyzer with a heating rate of 10 °C/min under nitrogen atmosphere. The gas sorption isotherms were measured on an autosorp-IQ instrument from Quantachrome Instruments Corporation (Boynton Beach, Florida USA).

1.2 Synthesis of N-rich MOFs

In a typical synthesis,^[1] A mixture of Co(OAc) $_2$ ·4H $_2$ O (24.9 mg, 0.1 mmol), diimpym (21.8 mg, 0.1 mmol), and H $_2$ npta (21.1g, 0.1 mmol) were placed into a 25 mL Teflon reactor in the presence of 2 mL methanol-water ($v:v = 1:1$) and 50 μ L 0.1 M NaOH, which was sealed and heated to 120 °C. The temperature was held for 3000 mins, and then the reactant mixture was cooled at a rate of 0.1 °C min $^{-1}$ to room temperature, forming prismatic black crystals of **1** (yield, 70%). IR (solid KBr pellet): $\nu = 3121$ (w), 1626 (m), 1585 (s), 1533(m), 1484 (m), 1348 (m), 1330 (m), 1313 (m), 1274 (w), 1231 (m), 1142 (w), 1102 (w), 1063 (s), 992 (m), 939 (w), 917 (w), 860 (m), 786 (m), 728 (s), 646 (s), 614 (m), 543 (w), 518 (w), 486 (m) cm $^{-1}$. Elemental analysis calcd (%) for C $_{18}$ H $_{11}$ CoN $_7$ O $_6$: C 45.02, H 2.31, N 20.42; found: C 45.12, H 2.51, N 19.91.

1.3 Synthesis of porous Co $_3$ O $_4$ /N-C

Co $_3$ O $_4$ /N-C composite was synthesized via calcination of the obtained N-rich MOF at 500°C for 2 h in a N $_2$ condition with a slow heating rate of 0.5 °C·min $^{-1}$.^[1] The resulting powder was black in color.

1.4 Synthesis of Nitrogen doped carbon honeycomb-like structure assembled by mesoporous nanosheets

NCH was synthesized by a one-step etching process by use HCl as the etchant. Typically, 10 mg as-prepared porous $\text{Co}_3\text{O}_4/\text{N-C}$ was added to 8 mL H_2O and 2 mL HCl mixed solution and, then transferred to 25 mL Teflon-lined autoclave and heated at 150 °C for 6 h. After the autoclave cooled to room temperature naturally, samples were collected by centrifugation, thoroughly washed with distilled water 5-6 times, and dried at 60 °C. The method of directly etching N rich MOFs was similar as the obtained NCH. The difference was directly using N rich MOF as an etched substance.

1.5 Synthesis of Co_3O_4 by recovering etching solution (strategy 1)

The remaining liquid after etching was directly transferred to 25 mL teflon-lined autoclave in batches and heated at 200 °C for 10 h, then calcined the obtained products at 500 °C for 2 h.

1.6 Synthesis of N rich MOFs by recovering etching solution (strategy 2)

Taking 5 mL remaining liquid added in 5 mL methanol to form the mixture. 4,6-di(1H-imidazol-1-yl)pyrimidine (0.05 mmol), 5-nitroisophthalic acid (0.05 mmol) and 50 mL 0.1 M NaOH were added into above mixture. Then the mixture were placed into a 25 mL Teflon reactor and heated to 120 °C for 3000 mins. The products were collected as microcrystalline sample.

1.7 Electrochemical measurements.

The working electrode was fabricated through squeezing a mixture of binder (Polyacrylic acid, 50%), superconductive carbon black, and active materials, which the mixture weight ratio is 10: 20: 70. The mass loading of the active material is 0.8 mg/cm^2 . Lithium was used as the reference and counter electrodes. 1 M LiPF_6 electrolyte dissolved in a mixture, which is composed with dimethyl carbonate (DMC), ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (volume ratio of 1:1:1). The LAND-CT2001A instrument was used to measure the cycle life and electrochemical capacity of the working electrode by the galvanostatic method at the charge and discharge current density of 100 - 2000 $\text{mA}\cdot\text{g}^{-1}$. The cut-off potential for charge/discharge was set at 0.01 and 3.0 V (vs. Li^+/Li). All electrochemical measurements were performed at ambient temperature.

1.8 Theoretical calculated method.

The first-principles calculations were based on the Vienna ab initio simulation package (VASP). The projected augmented wave (PAW) method was used to describe the electron-ion

interactions.

2 Experiment Results

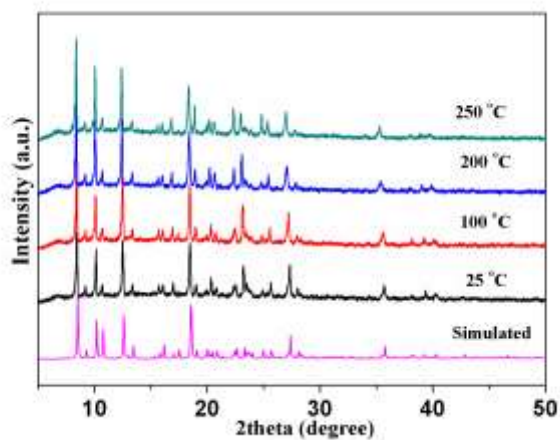


Fig. S1 The varied-temperature PXRD patterns of N-rich MOFs.

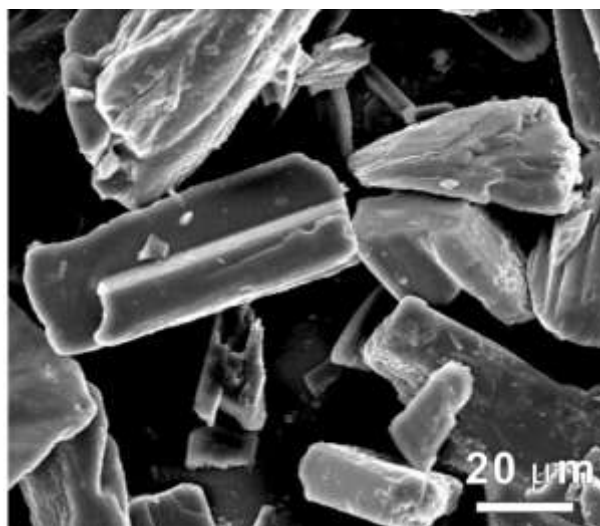


Fig. S2. SEM image of N-rich MOF.

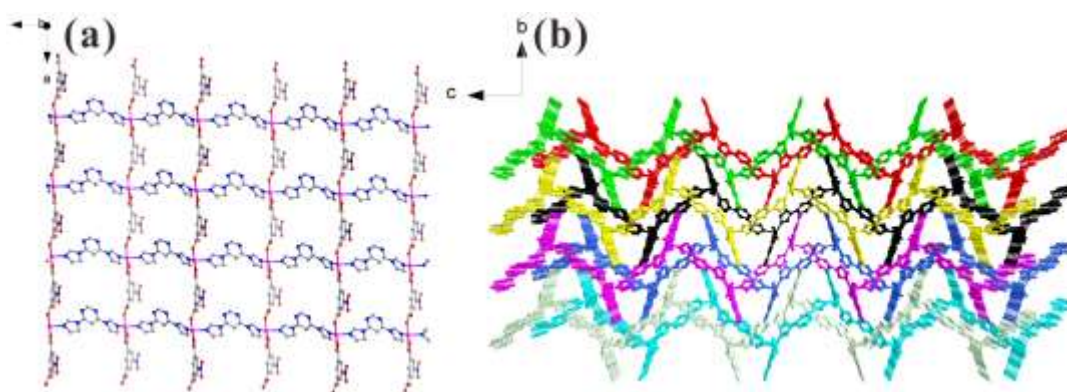


Fig. S3 (a) The single 2D layer of MOF, (b) the 2D+2D→2D interpenetrated layer structures. The individual layers are shown in different colors.

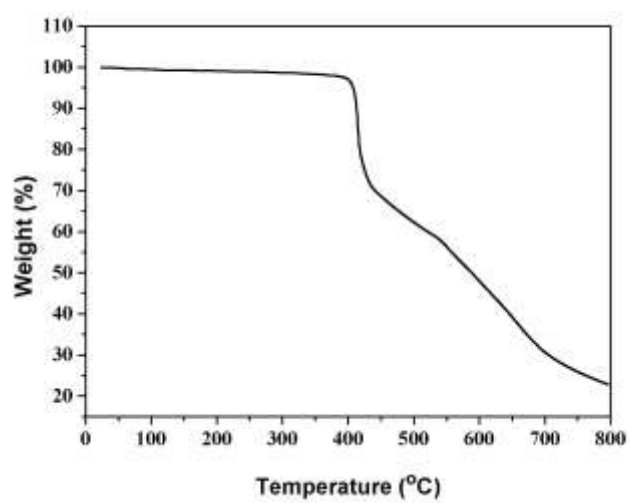


Fig. S4. TGA curve of N-rich MOF.

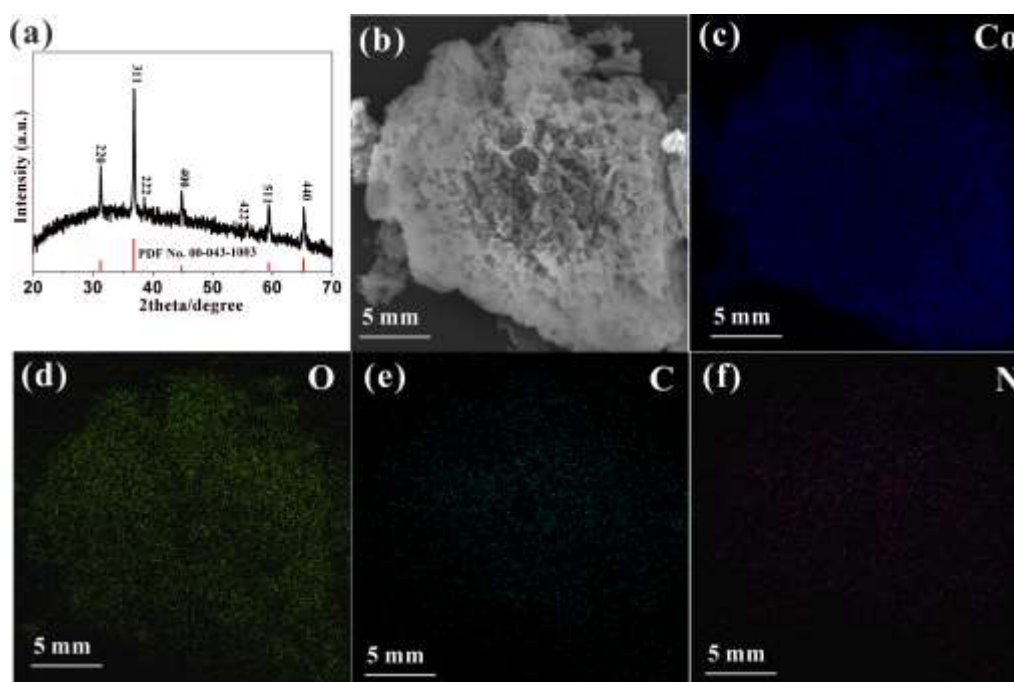


Fig. S5. (a) XRD pattern of Co₃O₄/N-C, (b) SEM image of a typical Co₃O₄/N-C sample, (c) Co elements mapping, (d) O elements mapping, (e) C elements mapping, (f) N elements mapping.

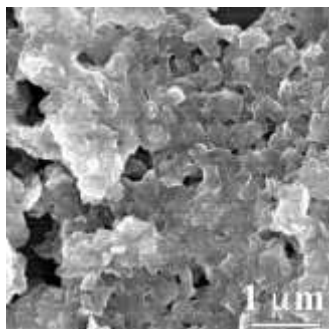


Fig. S6 the SEM image of N rich MOFs after acid etching.

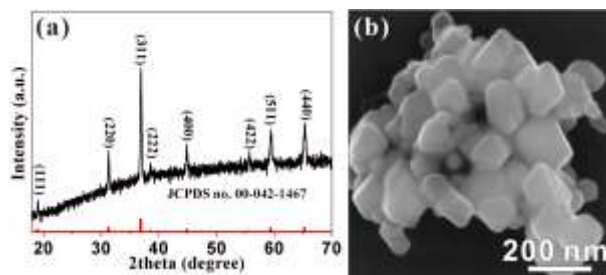


Fig. S7 (a) XRD pattern and (b) the SEM image of recovered products.

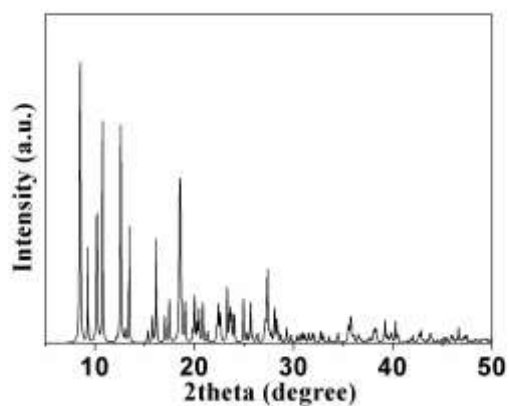


Fig. S8 XRD pattern of N rich MOFs obtained by reusing cobalt ions in remaining liquid.

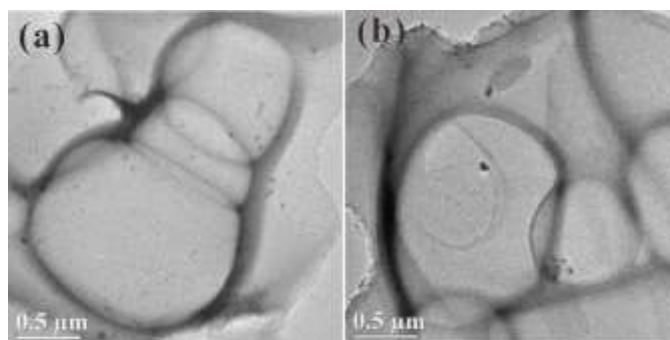


Fig. S9 TEM images of NCH.

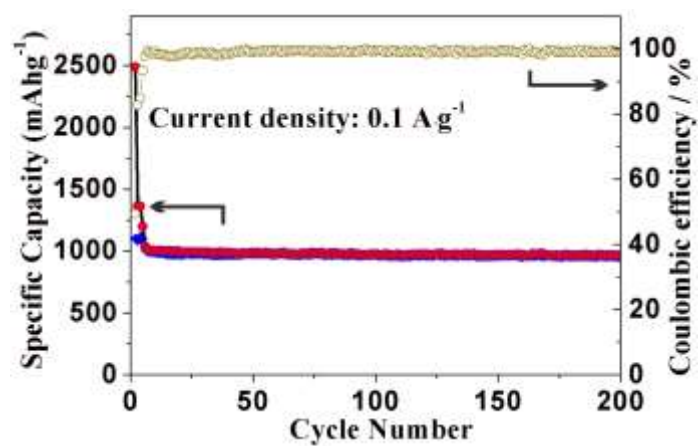


Fig. S10 the cycle performance and corresponding coulombic efficiency curves of NCH at a current density of 0.1 mA g⁻¹.

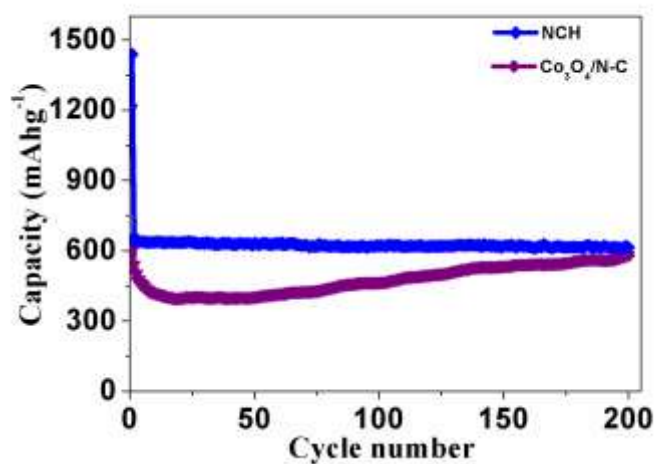


Fig. S11. Cycle performance of NCH and Co₃O₄/N-C tested at the same current density 1 A·g⁻¹.

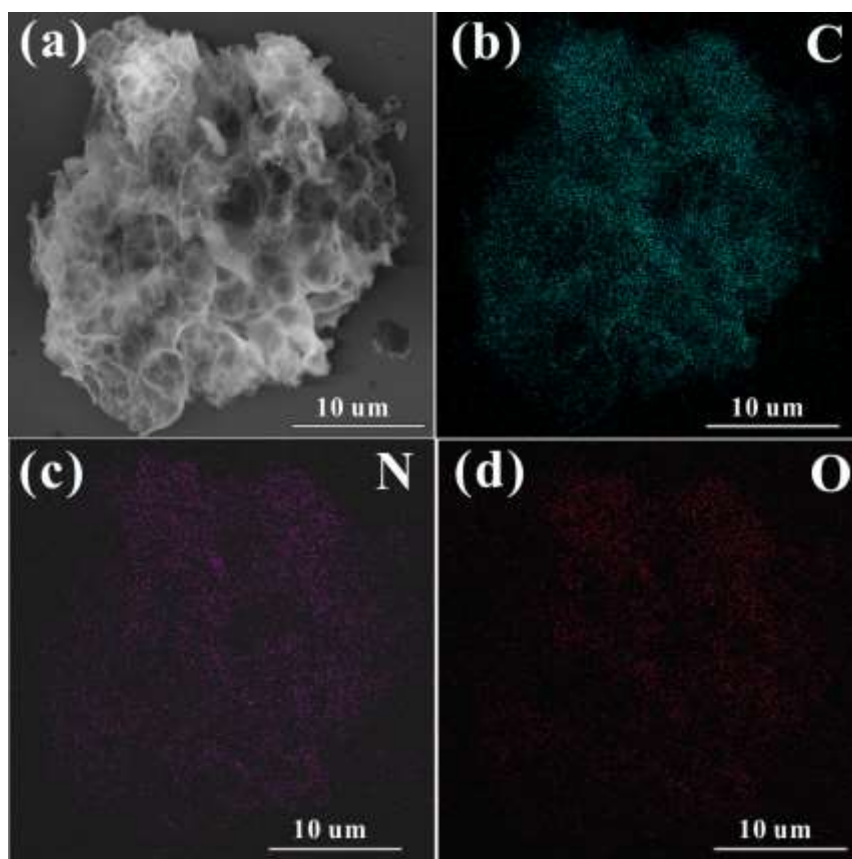


Fig. S12. (a) SEM image, (b-d) elements mapping of NCH sample after charge and discharge process.

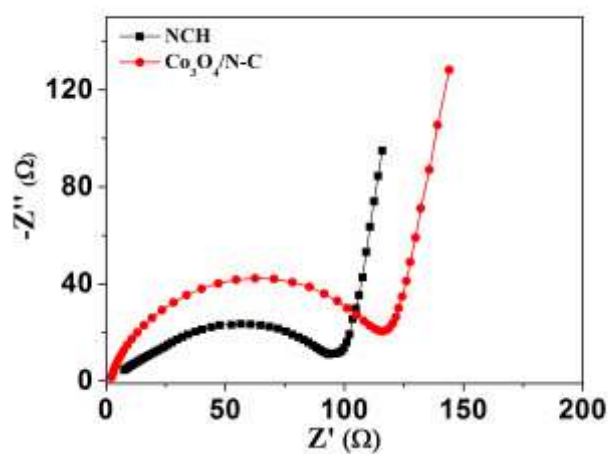


Fig. S13 Impedance spectra of NCH and $\text{Co}_3\text{O}_4/\text{N-C}$.

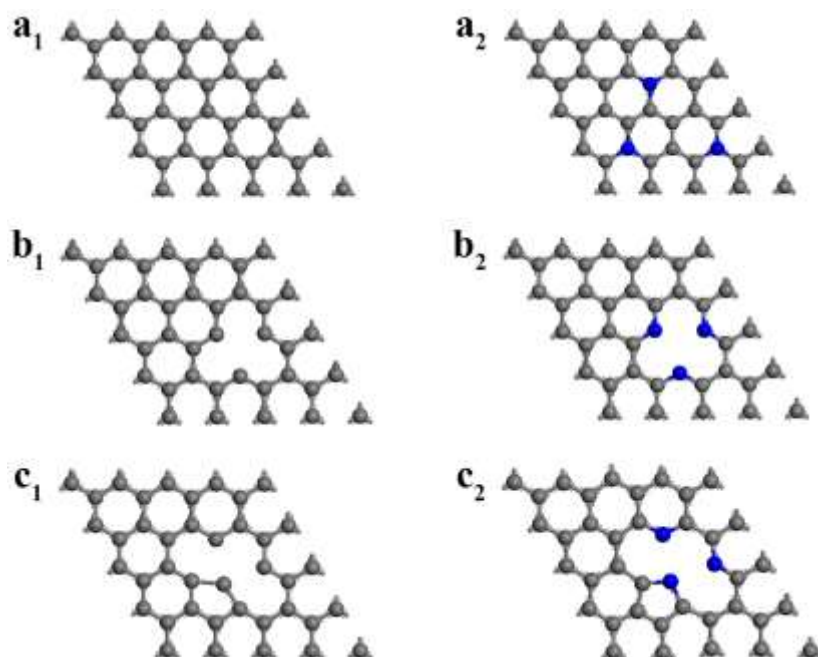


Fig. S14 Schematic of clean graphene with part of the defect (a₁-c₁), and three kinds of graphene (a₂) graphitic, (b₂) pyridinic and (c₂) pyrrolic graphene.

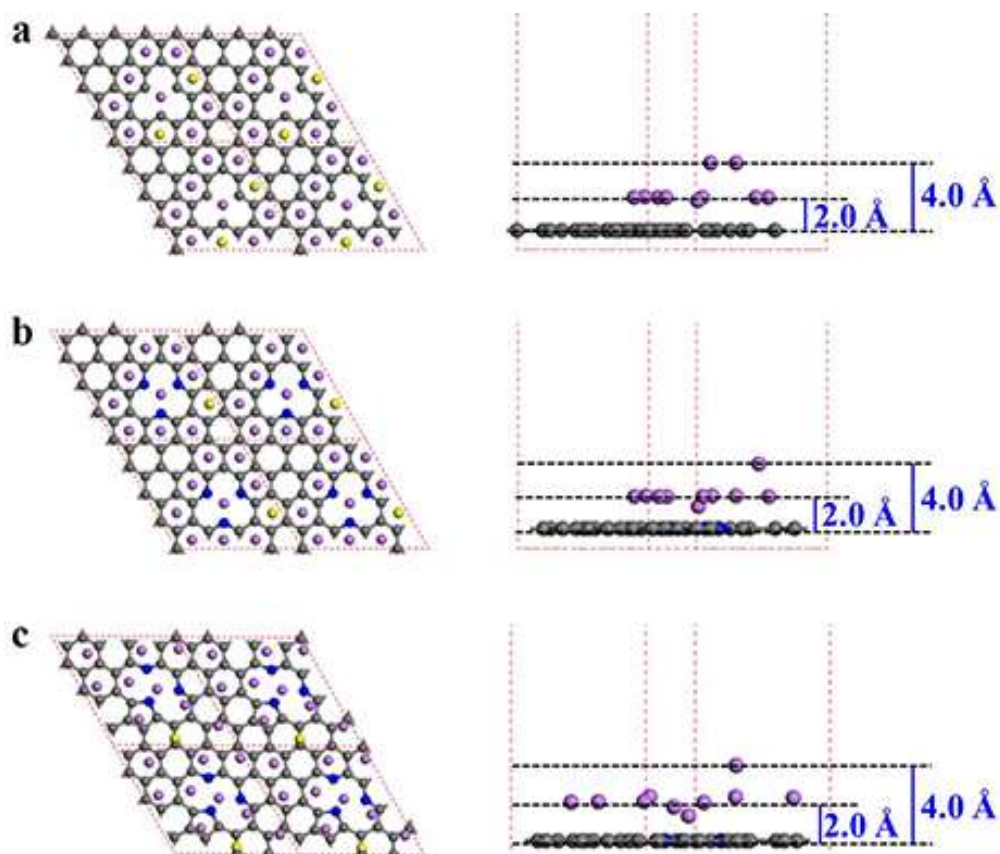


Fig. S15. Ten Li atoms adsorbed on three kinds of N doped graphene. (a) Graphene, (b) pyridinic, (c) pyrrolic. Li (pink); N (blue); C (gray).

Table S1 Comparison of the LIB performance for different electrodes.

Active material	Charging rate (mA·g ⁻¹)	Capacity retention (Capacity in mAh·g ⁻¹)	Cycle No
This work	1000	609	500
Hollow carbon nanospheres ^[2]	186	400	100
Porous carbon fiber ^[3]	186	400	45
Graphene nanosheets ^[4]	50	600	20
Folded structured graphene ^[5]	100	568	100
Nitrogen-doped porous graphene ^[6]	400	490	200
Nitrogen-doped graphene ^[7]	74	550	50
Nitrogen-doped carbon nanotube ^[8]	100	397	100
Nitrogen-doped graphene/graphite foam ^[9]	186	397	300

3 References:

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