A nitrogen-rich graphdiyne containing hexaazatrinaphthylene

for high-performance lithium-ion batteries

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Supporting Information

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1. Supporting Methods

1.1. General materials and methods

All chemicals were purchased commercially from Tansole. Unless otherwise stated, all reagents and solvents were used as received without further purification. **HATN-6Br** (compound **3**) and **HATN-6TIPS** (compound **4**) were synthesized according to procedures described in the reference literature. The copper foil was washed successively with 3 M HCl, deionized water, and acetone, then blown-dry under N₂ gas, prior to use in the fabrication of **HATN-GDY**.

¹H- and ¹³C- NMR spectra were performed on 400 MHz spectrometer (Bruker AVANCE NEO 400 Ascend) in the indicated solvents at room temperature. Chemical shifts were reported in δ (ppm) relative to TMS (δ =0). MALDI-TOF mass spectrometry analysis was performed on a Bruker Microflex-LRF mass spectrometer in positive ion.

Scanning electron microscope (SEM) images were collected using scanning electron microscope (JEOL, JSM-7500F) at an accelerating voltage of 5.0 kV. Transmission electron microscope (TEM) was performed on a JEM-2100 electron microscope with an accelerating voltage of 200 kV.

The UV-vis absorbance was measured by UV spectrometer (HITACHI, 4100).

The AFM images were recorded on Bruker Multimode 8 AFM with Nanoscope V controller.

XPS was performed on a Thermo Scientific ESCALab 250Xi instrument. The parameters were as follows: Al K α (1486.6 eV, 150 W) radiation was used as the X-ray

source, the vacuum degree of the chamber was 3.6×10^{-9} mbar and the scan range was $-10\sim1350$ eV. The spectra were analyzed using XPSPeak Software.

Raman spectra were investigated on HORIBA Raman spectrometer (LabRAM HR Evolution), with an excitation wavelength at 532 nm and a spot diameter of 1 μ m.

N₂ adsorption isotherms were measured up to 1 bar at 77 K using a Micrometrics ASAP 2460 surface area analyzer. Prior to measurements, samples (ca. 60 mg) were degassed for over 12 h at 120 °C. UHP grade N₂ and He were used throughout the adsorption experiments. Oil-free vacuum pumps and oil-free pressure regulators were used for measurements to prevent contamination of the samples during the degassing process and isotherm measurement.

The contact angle test was measured on SL200KS of Shanghai SoLon.

Abbreviations. Petroleum ether (PE), dichloromethane (DCM), N,Ndimethylformamide (DMF), tetrahydrofuran (THF), triethylamine (Et₃N), acetic acid (HOAc), bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh₃)₂Cl₂), triisopropylsilylacetylene (TIPS), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Atomic Force Microscope (AFM).

1.2 Synthesis

Compound 3: To a two-necked flask, 4,6-dibromo-benzene-1,2-diamine (compound 1)

(7.98 g, 30 mmol), cyclohexanehexone (compound **2**) (1.68 g, 10 mmol), 140 mL AcOH was added and heated up to 140 °C for 36 h. The solid precipitate was collected by centrifugation and further washed with water, ethanol, and acetone to give the compound **3** (7.29 g, 85%) as a greenish-yellow solid.

Compound 4: CuI (22 mg, 0.12 mmol) and compound 3 (1.715 g, 2 mmol) were added to the degassed solution of DMF (80 mL) and Et₃N (160 mL). Pd(PPh₃)₂Cl₂ (140 mg, 0.2 mmol) was then added to the mixture solution. At last, triisopropylsilylacetylene (TIPS, 5.37 mL, 24 mmol) was added dropwise to the mixture solution. Then, the reaction mixture was refluxed under an N₂ atmosphere at 120 °C for 36 h. After cooling to room temperature, the resulting mixture was diluted with DCM, washed with brine, dried over Na₂SO₄, and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/PE) 5:1; R_f (DCM /PE 2:1): 0.35)gave pure compound 4 (0.38 g, 26%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃): 8.84 (s, 1H), 1.21 (s, 21H); ¹³C NMR (100 MHz, CDCl₃): 143.96 (C), 135.54 (C), 142.71 (C), 128.96 (C), 104.29 (C), 100.81 (C), 18.78 (CH), 11.32 (CH₃). MALDI-TOF-MS m/z: [M+H]⁺ calcd. for C₉₀H₁₃₃N₆Si₆ 1467.600; found 1467.903.

Compound **5**: Compound **4** (144.6 mg, 0.1 mmol) in 10 mL THF was added 1.0 mL tetrabutylammonium fluoride (TBAF, 1M in THF) under Ar at rt and stirred for 30 min. The colorless solution changed to black. The mixture was extracted with ethyl acetate(20 mL, three times). The combined organic layers were washed with brine and concentrated in vacuo to give compound **5** as a greenish-yellow grease.

HATN-GDY: Compound **5** (52.9 mg, 0.1 mmol) was dissolved in a mixture of DMF (10 mL) and anhydrous pyridine (15 mL). The prepared monomer solution was then slowly dropped into a pyridine solution (20 mL) containing three pieces of copper foils (length×width×thickness = $1.2 \text{ cm} \times 3.0 \text{ cm} \times 0.1 \text{ mm}$) under argon in 30 minutes. The reaction system was stirred gently at 80 °C for 3 days. It was observed that black films formed on the copper foils' surface. The copper foils were taken out and cleaned with acetone for 3 times to remove the residual monomers and oligomers on the surface. The **HATN-GDY** was obtained as the black films which were insoluble in common solvents.

1.3 High-resolution XPS spectra of N 1s of HATN-GDY.

For N 1s binding energy, two obvious peaks over 399.3 eV (HATN N) and 401.2 eV (protonated N) could be identified (Figure S4). The protonated N may be associated

with the partial protonation of **HATN** N by concentrated hydrochloric acid during the Cu foil etching process. It should be noted that the protonation of **HATN** in **HATN-GDY** should be limited to the surface. The signal at 401.2 eV for protonated N in the XPS spectrum is probably an overstatement of its actual content because XPS is more sensitive to the surface composition.

1.4 Electrochemical and electron properties measurements

Cyclic voltammetry measurement

The electrochemical performance was collected in CR2016-type coin cells, which were assembled in an argon-filled glove box with H₂O and O₂ level <0.1 ppm. The **HATN-GDY** grown in situ on copper foil is cut into 1 cm² and the film on one side is scraped off. Then put the electrode in a vacuum oven at 80 °C for 12 h. After that, transfer the electrode to the glove box to assemble the battery and the side with film is going to contact with separator. The mass loading of active substance are 0.25 mg for **HATN-GDY**. The mass loading of single electrode is the difference of before and after removing the film. Averaged from nine sets of data to get the final value involved in the calculation. after that used as working electrodes without adding any binders. A pure Li foil was used as the counter electrode, separated from the working electrode by a Celgard 2500 polymeric separator and a liquid electrolyte (ethylene carbonate, dimethylcarbonate, 1:1 by volume) with 1.0 M LiPF₆ for LIBs.

The assembled half cells were cycled between 0.005 and 3 V using the LAND CT2001A battery system. The CV measurements were performed on CHI760 electrochemical workstation. The EIS was conducted at a 5 mV ac oscillation amplitude

over frequency range of 100 kHz-0.1 Hz. Nyquist plots EIS measurements of the **HATN-GDY** composite electrodes before and after 100 cycles at the current density of 500 mA g⁻¹ in half-cells vs. Li-metal (Figure S8). The impedance measurements were conducted at open circuit potential. In the equivalent circuit, R_e represents the electrolyte resistance; R_s is the equivalent resistance of the SEI layer formed on the electrode; R_{ct} is the charge-transfer resistance; Z_w is the Warburg impedance; CPE represents the corresponding double-layer capacitance.

Conductivity measurement.

The current-voltage (*I-V*) curve was tested using a computer-controlled Keithley 2400 sourcemeter. The artificial device was fabricated with the structure of Cu/**HATN-GDY**/Cu. The measurement was conducted at a bias voltage of -4 V to 4 V.

2. Supporting Figures and Legends

Fig. S1 ¹H NMR spectrum of compound 4.

Fig. S2 13 C NMR spectrum of compound 4.

Fig. S3 HR-MS spectrum of compound 4.

Fig. S4 High-resolution XPS spectra of N 1s of HATN-GDY.

Fig. S5 The current-voltage (*I-V*) curve of HATN-GDY. The linear equation of the fitting line is y = 6.3x, and R_2 is 0.9996.

Contact angle of water : 107.52°

Contact angle of electrolyte : 8.81°

Fig. S6 The contact angle test of **HATN-GDY** with deionized water/electrolyte (1.0 M LiPF₆ soluble in dimethyl carbonate and ethylene carbonate).

Fig. S7 The thermogravimetric analysis profiles of HATN-GDY.

Fig. S8 The cyclic voltammetry curves of HATN-GDY.

Fig. S9 The cyclic voltammetry curves of **HATN-GDY** electrodes at different scan rates of 0.1 to 5 mV/s.

Fig. S10 The pseudo-capacitive contribution in the total current of CV curve under 5 mV/s.

Fig. S11 Fitting curves of the relationship between peak current and scanning rate.

Fig. S12 (a) Nyquist plots of **HATN-GDY** based electrode before and after 100 cycles at a current density of 500 mA g⁻¹. (b) The corresponding fitting parameters. The equivalent circuits of **HATN-GDY**-based electrode before and after 100 cycles are shown in (c) and (d).

Fig. S13 The charge-discharge plots of a HATN-GDY based electrode under various current density.

Fig. S14 The initial three galvanostatic charge-discharge curves based on HATN-GDY under 0.05 A g^{-1} .

Fig. S15 The cycle performance of HATN-GDY at 0.2 A g⁻¹.

Fig. S16 The cycle performance of HATN-GDY at 0.5 A g⁻¹.

Fig. S17 The cycle performance of HATN-GDY at 2 A g⁻¹.

Fig. S18 The FT-IR spectra before HATN-GDY electrode and after 500 cycles at a current density of 500 mA g^{-1} .

| Electrode | Capacity | Discharge rate | Cyclic stability | Ref. |
|------------------------------|-----------------|--------------------|------------------|-----------|
| | $(mA h g^{-1})$ | (mA g^{-1} or C) | (cycles) | |
| HATN-GDY | 2139 | 50 | 200 | This work |
| HATN-GDY | 1205 | 200 | 230 | This work |
| HATN-GDY | 952 | 500 | 730 | This work |
| HATN-GDY | 480 | 2000 | 5000 | This work |
| S-GDY | 675 | 500 | 120 | 2 |
| S-GDY | 423 | 1000 | 100 | 2 |
| GDY-NW | 908 | 50 | / | 3 |
| GDY-NW | 526 | 1000 | 1000 | 3 |
| PQ-GDY | 570 | 200 | 800 | 4 |
| N-GDY | 785 | 200 | 200 | 5 |
| N-GDY | 761 | 500 | 400 | 5 |
| N-GDY | 510 | 2000 | 1000 | 5 |
| TiO ₂ @graphdiyne | 432.4 | 1000 | 300 | 6 |
| H1F1-GDY | 2050 | 50 | 50 | 7 |
| 3DGDY | 610 | 50 | 200 | 8 |
| 3DGDY | 250 | 500 | 400 | 8 |
| F-GDY | 1674 | 50 | 150 | 9 |
| OSPC | 1050 | 100 | 100 | 10 |

Table S1. The reversible capacities of carbon materials as anodes in LIBs.

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