Supporting information for

2D Nitrogen-Rich π-Conjugated Microporous Polymer for Lithium-Ion Batteries

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Materials preparation

NGA-CMP was obtained as black graphene-like powers by low temperature solution approach. Briefly, HATP (100 mg, 0.186 mmol) and HKH (58 mg, 0.186 mmol) were charged in a 25 mL round bottom flask under nitrogen atmosphere. NMP (12 mL) was injected to disperse them in ice bath. Then, 400 μ L H₂SO₄ was added slowly to avoid the oxidation of reagents. The reaction flask was allowed to warm up to room temperature for 2 h. The mixture was heated to 175 °C with oil bath for 24 h. The flask was cooled to room temperature and water was added. The result dark brown precipitated product was collected by centrifugation, followed by a 6 days Soxhlet extracted with methanol and water, respectively, and freeze-dried at -78 °C under reduced pressure (0.001 mbar) for 48 h.

Characterization

All reagents were purchased commercially and used without further purification. Powder X-ray diffraction (PXRD) data were obtained using a Rigaku D/Max 2550 automated diffractometer (Cu-K α , 1.5418 Å). IR spectra were measured with KBr pellets on a Bruker IFS-66 V/S FT-IR spectrometer. Thermogravimetric measurement was performed on pre-weighed samples in a nitrogen stream using a Netzsch STA 449C apparatus with a heating rate of 10 °C min⁻¹. Low-pressure N₂ gas sorption experiments at 77 K were carried out on a Micrometrics ASAP 2020 volumetric gas sorption instrument. Before gas adsorption measurements, the samples were heated to 150 °C to completely remove the solvent molecules. Morphology of NGA-CMP and NGA-CMP400 was examined through scaning electron microscopy (SEM JSM-6700F) and transmission electron microscopy (TEM, FEI Tecnai G2S-Twin with a field emission gun operating at 200 kV). AFM of NGA-CMP was performed in Bruker Dimension iCON using tipping mode with 256 lines. The as-synthesized NGA-CMP is dispersed in DMSO with a high concentration (0.5 mg mL⁻¹), ultrasonicated for 20 min, and then centrifuged at 15,000 rad min⁻¹ to remove the dissolved polymer up-layer (repeated for 5 times). Then centrifugation at 8000 rad min⁻¹ was applied to get rid of large particles and aggregations. UV-vis absorption of the pellet was recorded on Shimadzu U-4100. X-ray photoelectron spectroscopy (XPS) was recorded on ESCALAB 250 with Mg-K α as X-ray source.

Simulation

The single layer NGA-CMP was constructed in Materials Studio 2017 software and

then fully optimized by Compass II force field in Forcite module. GGA/PBE method

was employed to do the further geometrical optimization in CASTEP module. The energy cutoff is 570 eV, the K-points $4 \times 4 \times 1$ and the SCF tolerance 5.0×10^{-6} .

Electrochemical measurements

Electrochemical characterization was conducted on CR2032-type coin cells using a piece of metallic Li foil as the reference electrode. The anode was composed of 60 wt%

active material, 30 wt % active carbon and 10 wt% carboxymethyl cellulose binder (CMC), which was pasted on a Cu current collector and then cut into square shape with an area of 0.64 cm² and dried in vacuum oven at 120 °C for 12 h. Loading mass of the active material was 1 ± 0.3 mg cm⁻². The cathode and anode were separated by a glass fiber filter (Whatman GF/C). The electrolyte was prepared through mixing 1 M LiPF₆ in a solution consisting of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, by volume ratio) and 5 wt% fluoroethylene carbonate (FEC). CV curves of NGA-CMP anode were measured at a scanning rate of 0.2 mV s⁻¹ in the voltage range of 3–0 V vs. Li⁺/Li. Galvanostatic charge–discharge was performed on a LAND-2010 automatic battery tester within a voltage window of 0.01–3.0 V. Electrochemical impedance spectroscopy (EIS) and CV was performed on a Bio-Logic VSP multichannel potentiostatic–galvanostatic system. Impedance data were recorded at 5 mV (ac voltage) over a frequency range from 1 MHz to 1 mHz.



Fig. S1. FTIR spectrum of NGA-CMP.



Fig. S2. PXRD patern of NGA-CMP and simulated one.



Fig. S3. AA-stacking mode of NGA-CMP along Z and Y axis.



Fig. S4. Results of optical band-gap measurements and a plot of the absorbance squared vs. photon energy (hv) extrapolated to zero absorption. Insert: the UV-vis absorption curve



S5. (a) XPS survey spectrum of the as-prepared **NGA-CMP**. (b) High-resolution N1s, (c) C 1s and (d) O 1s (d) XPS spectra acquired from the **NGA-CMP**



Fig. S6. TGA plot of NGA-CMP and NGA-CMP400



Figure. S7. (a) SEM image of NGA-CMP400; (b) TEM image of NGA-CMP400



Figure. S8. TEM image of NGA-CMP with FFT pattern in the left inset.