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Solution-processed nitrogen-rich graphene-like holey conjugated polymer for efficient lithium ion storage

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ABSTRACT

Preparing well-defined single-layer two-dimensional (2D) holey conjugated polymers (HCP) is very challenging. Here, we report a bottom-up method to produce free-standing single-layer nitrogen-rich graphene-like holey conjugated polymers (NG-HCP) nanosheets through solution-process. The as-prepared 2D NG-HCP sheet possesses a thickness of 1.0 ± 0.2 nm and consists of graphene-like subunits as well as homogeneous hexagonal micropores (ca. 11.65 Å). The synergistic effect of high porosity, heteroatomic doping and good dispersity of NG-HCP nanosheets make them suitable as excellent anode materials for Li-ion batteries (LIBs), leading to an extremely high reversible capacity of 1320 mAh g^{-1} (at 20 mA g^{-1}), a good rate performance, and an excellent cycle life with an approximate 100% Coulombic efficiency for more than 600 cycles. Our findings would open new opportunities to develop state-of-the-art free-standing 2D-HCP materials for low-cost and high performance energy storage as well as optoelectronic devices.

1. Introduction

Microporous materials with various building blocks can generally afford outstanding performance in the areas of catalysis, gas separation, energy conversion, energy storage, and optoelectronics attributing to their ordered micro-channels, high surface areas and large pore volumes [1–8]. Among all porous materials, hierarchically porous graphene provides a versatile platform for rechargeable lithium-based energy storage system as its specific edge effects, large ion-accessible surface area and rapid ionic transport [9–11]. Especially, heteroatoms (e.g. N, P, e.g. N, P, S, or B, or B) doping would introduce an abundance identified of electrochemical active sites for high density lithium-ion storage [12,13]. Inspired by porous graphenes, scientists believe that the exotic nanoscaled π-conjugated systems should take advantage of high chemical activity rising from the massive edge of aromatic ring. The most exciting factor is that a recent research based on organic/polymer electrodes has been demonstrated to confirm the possibility of a Li6/C6 mechanism, where each carbon in an aromatic ring can accept one Li ion [14–18]. All these interesting reports suggest that

heteroatom-rich microporous graphene or nanosheets of graphene-like holey conjugated polymers (**HCPs**) can represent the most promising electrochemical electrodes beyond pristine graphene [19–24].

Heteroatoms-doped meso-/macro-porous (2–50 nm or sub-μm to several μm) graphene have been successfully fabricated by selective chemical-etching [9–12,25]. However, it is still very challenging to develop microporous graphene sheets with both precise composition and homogeneous porosity through a "top-down" method. An alternative approach is to employ predesigned graphene nano-units as building unites and repeatedly link them together to construct well-defined microporous frameworks [26,27]. Unfortunately, such processing is impractical for large-scale fabrication due to its tedious multistep synthetic pathway. In addition, it is also very difficult to tune their electrical/optical properties through modification. Such gap strongly encourages us to investigate **2D-HCPs** with graphene-like subunits towards desirable optoelectronic properties and cost-effective fabrications. **2D-HCPs** have porous skeletons, where predesigned organic units are precisely integrated into holey nanostructures. Recently, great efforts have been devoted to the design and fabrication of 2D covalent

organic frameworks (COF) films through surface-mediated polymerization of polyfunctional monomers [28–30]. Nevertheless, the conversion of high crystalline 2D-COFs into free-standing atomic nanosheets is extremely difficult, owing to the strong supramolecular interaction among layers [31], although one strategy to realize such single-atomic-layer carbon nitrides has been demonstrated under high temperature [32–34]. Unfortunately, most polymers are not stable at high temperature, which makes the preparation impractical. On the other hand, most 2D-COFs contain a lot of non-conjugated bonds, which have limited their applications in energy-related filed. Very recently, only two examples about 2D nitrogen-containing **HCP** sheets have been reported [35], however, high temperature processing is required to prepare these sheets.

Herein, we report a free-standing nitrogen-rich graphene-like HCP (**NG-HCP**) nanosheet with well-defined microporous graphene-like subunits through a low-temperature solution-processed polycondensation. The morphology, porosity and packing motifs of **NG-HCP** nanosheets are systemically investigated by a series of characterization tools. With **NG-HCP** nanosheets as anodes, high-capacity lithium-ion storage with excellent cycle performance has been observed.

2. Material and methods

2.1. Synthesis of NG-HCP powder

All the reagents (1 mmol HKH, 312 mg; 1.5 mmol TAB, 426 mg) are mixed in a 50 mL degassed flask. 30 mL degassed N-methyl-2-pyrrolidone (NMP) solvent was injected to dissolve them at 100 °C in oil bath. After cooling to the room temperature, ice bath was replaced, and ca. 500 μL H_2SO_4 was added slowly to avoid the oxidation of reagents. After string for 1 h, the mixture was heated to 180 °C in oil bath for 8 h. When cooling down, the reaction was quenched with 200 mL methanol, where dark brown precipitate was observed. The crude product was rinsed with methanol, $NaHCO_3$ aqueous solution and DI water for 3 times (to nearly neutrality) through a centrifugation with 10,000 rad min^{-1}, respectively, followed by a 7 days' Soxhlet extraction in methanol. The black powder was dried at 60 °C in vacuum oven for 3 days, and 246 mg product was finally obtained.

2.2. Simulation

The single layer NG-HCP was constructed in Materials Studio 8.0 software and then fully optimized by CompassIIforce field in Forcite module. GGA/PBE method was employed to do the further geometrical optimization in CASTEP module, where the pseudopotentials is Norm conserving, the energy cutoff 400 eV, the K-points $4 \times 4 \times 1$ and the SCF tolerance 5.0×10^{-7}. The same conditions were used to calculate band structure of NG-HCP.

2.2.1. Nanostructured NG-HCP nanosheets

40 mg as-prepared NG-HCP was dissolved into 200 mL methanesulfonic acid (MSA) and ultrasonicated for 2 h. The black solution was stirred overnight and then added dropwise into 500 mL DI water with vigorous string. The mixture was stabilized for 12 h. The precipitations were centrifuged and then washed with ethanol and DI water, respectively for several times to ensure that MSA is completely removed. The finally obtained product was vacuum dried at 60 °C.

2.3. Atomic force microscope (AFM) sample preparation

To obtain the single layer from the as-synthesized NG-HCP, the dispersion solvent was change from methanol to DMSO with a high concentration ($\sim$ 0.5 mg mL^{-1}), ultrasonicated for 20 min, and then centrifuged at 15,000 rad min^{-1} to remove the dissolved polymer uplayer (repeated for 5 times). Then 8000 rad min^{-1} was applied to get rid of large particles and aggregations. The final NG-HCP nanosheet

suspensions can stabilize for at least 3 weeks. AFM of NG-HCP nanosheets was performed in Bruker Dimension iCON using tipping mode with 256 lines. The NG-HCP nanosheets after nanostructuring were spin-coated from methanol suspension onto a silicon wafer with the speed of 5000 rad min^{-1}.

2.4. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer Frontier infrared spectrometer. XPS analysis was performed on a ULVAC-PHI 5000 Versa Probe photoelectron spectrometer with a monochromatic Al K$_\alpha$ X-ray source and calibration with the C-C peak at 284.8 eV. Cyclic voltammetry of NG-HCP was tested in DMSO suspension at a scan rate of 50 mV s^{-1} using a Ag/AgCl reference electrode (using tetrabutylammonium hexafluorophosphate as supporting electrolyte). For scanning electron microscopic (SEM) studies, a drop of 20 μL as-prepared NG-HCP dispersed in methanol or DMSO (ca. 0.05 mg mL^{-1}) was placed onto the silicon substrates after ultrasonic mixture for 20 min, and the solvent was left to evaporate at 60 °C on a hotplate. The concentration of NG-HCP suspension in DMSO was $\sim$ 0.5 mg mL^{-1}. The samples were then examined with a field emission SEM (JEOL JSM-6340F) at an accelerating voltage of 5 kV. TEM/HRTEM/STEM/EDX and elemental mapping characterizations were performed on a JEM 2010F JEOL, operated at an accelerating voltage of 200 kV. A drop of 10 μL NG-HCP in DMSO (ca. 0.05 mg mL^{-1}) dispersion was deposited on a carbon-coated copper micro-grid without further purification. The TEM sample of single layer NG-HCP was prepared on copper grid coated with ultra-thin carbon film. X-ray diffraction (XRD) patterns were collected from a NG-HCP compressed pellet in a Bruker AXS D8 Advance diffractometer using nickel-filtered Cu K$_\alpha$ radiation (λ = 1.5406 Å). UV–vis–NIR absorption of the pellet was recorded on a Lambda950. Thermogravimetric analysis (TGA) was recorded by TA Instruments TGA Q500 under a nitrogen flow (40 mL min^{-1}) by heating to 830 °C at a rate of 10 °C min^{-1}. The differential scanning calorimetry (DSC) was performed on a TA DSC Q10 from TA Instruments from 40 to 300 °C with the rate of 5 °C min^{-1}. Nitrogen sorption isotherm was measured at 77 K with an ASAP 2020 analyzer. Before measurement, the samples were degassed in vacuum at 150 °C for more than 10 h. Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. The BET surface area was calculated at p/p$_0$ = 0.05–0.11 using the adsorption branch. By using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve. Raman spectra were obtained by using WITec CRM200 confocal Raman microscopy system (WITec, Germany) with a laser wavelength of 532 nm.

2.5. Battery fabrication and electrochemical measurements

Electrochemical tests were carried out through the fabrication of 2032 coin-type cells assembled inside an argon-filled glove box with both moisture and oxygen contents below 1 ppm. The working electrodes for the samples of NG-HCP before and after nano-engineering were prepared by pasting of the viscous slurry containing 70% active material, 20% CNTs, and 10% poly(vinylidene fluoride) (PVDF) onto a copper foil current collector. The working electrodes for the samples of NG-HCP without the addition of CNTs were prepared by pasting of the slurry containing 90% active material, and 10% PVDF onto a copper foil current collector. The electrode for testing of the CNT contribution was prepared by mixing of 90% CNTs and 10% PVDF. All the electrodes were dried in a vacuum oven at 60 °C overnight to remove the NMP solvent away. Pure lithium foils were used as the counter electrodes. 1 M LiPF$_6$ solution in a 1/1 (w/w) mixture of the ethylene carbonate (EC) and dimethyl carbonate (DMC) was served as the electrolyte. CV curves of NG-HCP nanosheets/CNT anode was measured at a scanning rate of 0.2 mV s^{-1} in the voltage range of 3–0 V vs. Li$^+$/Li. The galvanostatic charge–discharge tests were performed using a NEWARE