



Nitrogen-doped herringbone carbon nanofibers with large lattice spacings and abundant edges: Catalytic growth and their applications in lithium ion batteries and oxygen reduction reactions



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ABSTRACT

N-doped herringbone carbon nanofibers (N-HBCNFs) were efficiently fabricated by chemical vapor deposition on Ni nanoparticles derived from layered double hydroxide precursors. The as-obtained CNFs were with an average diameter of ~ 60 nm, a high purity of $\sim 91.6\%$, and a large specific surface area of $108.1 \text{ m}^2 \text{ g}^{-1}$. When employed as anode materials, the N-HBCNFs yielded a reversible capacity of 500.0 mAh g^{-1} at a current density of 0.10 C ($1.0 \text{ C} = 372 \text{ mA g}^{-1}$) and rapid lithium storage properties with a high capacity of 141.6 mAh g^{-1} at 5.0 C . When the N-HBCNFs were used as catalyst for oxygen reduction reaction, an onset potential of 0.85 V , an electron transfer number of 3.1 , and a current retention of 69.1% after $16,000 \text{ s}$ test were detected, indicating the good reactivity of N-HBCNF catalyst for electrocatalysis application. The superior performance of N-HBCNFs was attributed to their enlarged graphitic lattice spacings and abundant edges on the surface, which afforded more active sites for both Li ion storage and oxygen reduction reaction. Thus, the N-HBCNFs are promising nanocarbon materials for various applications in lithium ion batteries, lithium-sulfur batteries, lithium-air batteries, fuel cells, and so on.

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1. Introduction

Energy storage systems represented by rechargeable batteries and fuel cells are receiving increasing attention, as their applications are successively expanding from small-scale mobile electronics to large-scale transportations and utility grids [1–5]. The nanostructured carbon is one of the core materials for high performance energy storage devices [1,3,5]. The intensive investigations of nanocarbons, especially the highly conductive sp^2 carbon, shed a light on the improvement of the conductive nature and thus efficient utilization of the electrodes [5,6] and boosting the researches of next-generation energy storage systems.

Well arrangement of sp^2 carbon layers renders one-dimensional (1D) carbon nanotubes (CNTs) or carbon nanofibers (CNFs), two-dimensional (2D) graphene nanosheets, and three-dimensional (3D) nanostructured carbon with unexpected properties for vast applications in heterogeneous catalysis [7–10] and energy storage

[1,5,11,12]. The key issue for the successful applications of nanocarbon lies in the ability to pack the sp^2 carbon layers into the desired 3D structures. Among these materials, the herringbone CNFs (HBCNFs) are one kind of promising nanocarbons [13] for rechargeable batteries due to their cavities, open tips, and graphite platelets, which may provide more active sites and enhance the utilization rate of active materials in the composite electrodes.

Another approach to improve the electrochemical performance for the carbon-based electrode is to modify its surface functional groups by non-carbon element doping [14–16]. The presence of heteroatoms on the carbon surface enhance the reactivity and electric conductivity [10,14,15,17], and hence the energy storage capacity [14]. Consequently, the chemical properties of HBCNFs can be tailored by heteroatom functionalization on nanocarbon sheets or molecular carbon geometries at the edges, defects, or strained regions. A particularly exciting example is the nitrogen (N)-doped carbon nanosheet that bears five valence electrons. A shift in the Fermi level to the conducting band is presented when N is doped in carbon lattice as electron donors. With the incorporation of N into the carbon framework, the activity of HBCNFs for oxygen reduction [18,19] or lithium ion storage [20] is expected to be significantly

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improved. The promising behaviour of N-doped HBCNFs is due to the introduction of additional n-type carriers in carbon systems and the hybridization between the nitrogen lone pair electrons and the carbon π -electron system [21]. Thus, exploring N-doped nanocarbons with controllable doping manner and tailored microstructures is scientifically necessary to demonstrate the material chemistry and potential applications of N-doped HBCNFs (N-HBCNFs), as well as to allow mechanistic insight into the roles that heteroatoms played on their textures and activities. Furthermore, N-HBCNFs are expected to be a promising material in electrochemical energy storage and metal-free catalysis (e.g. oxygen reduction reaction (ORR) in fuel cells and lithium-oxygen (Li-O₂) batteries) [18,19].

In this contribution, N-HBCNFs were efficiently fabricated by catalytic chemical vapor deposition (CVD) of C₂H₄ and NH₃ on Ni nanoparticles derived from layered double hydroxide (LDH) precursors at 600 °C. Electrochemical measurements demonstrated that N-HBCNFs presented a higher specific capacity and excellent rate performance, as well as cycling stability when compared with HBCNFs and CNTs. N-HBCNFs also exhibited great potential to serve as an anode material in lithium ion batteries and nanocarbon based catalysts for ORR.

2. Experimental

2.1. Catalyst preparation

The Ni based LDH catalysts were synthesized through the coprecipitation reaction by adding urea into aqueous solution of nickel nitrate and aluminum nitrate similar to our previous reports [22,23]. In detail, both Ni(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were dissolved in 250 mL deionized water with [Ni²⁺] + [Al³⁺] = 0.15 mol L⁻¹ (n(Ni): n(Al) = 3: 1). The urea was then dissolved in the solution with [urea] = 3.0 mol L⁻¹. The as-obtained solution was kept at 100 °C under continuous magnetic stirring (equipped with a reflux condenser in ambient atmosphere) for 9.0 h in a 500.0 mL flask, and then at 94 °C for another 12.0 h with the stirring off. After several steps of filtering, washing, and freeze-drying, the final products of Ni/Al LDH catalyst precursors were available for N-HBCNF growth.

2.2. Catalytic growth of N-HBCNFs

The N-HBCNFs were synthesized over Ni/Al LDH derived catalysts with C₂H₄ and NH₃ as carbon and nitrogen sources, respectively. A fixed-bed reactor was used for nanocarbon deposition. During the catalytic deposition, the reactor was heated to 900 °C at a heating rate of 20 °C min⁻¹ in Ar (100 mL min⁻¹). Then, the LDHs were reduced by H₂ (100 mL min⁻¹) for catalyst nucleation into large active Ni particles with well defined crystal surfaces for N-HBCNF deposition. After that, H₂ was stopped and the reduced catalysts were cooled down to 600 °C to synthesize CNFs in C₂H₄/NH₃/Ar (100/100/100 mL min⁻¹). Finally, the reactor was cooled down under Ar atmosphere. The HBCNFs were obtained with the same route except the feedstocks were solely C₂H₄ instead of C₂H₄/NH₃ mixture.

The as-grown products were treated by NaOH (12.0 mol L⁻¹) aqueous solution at 150 °C for 6.0 h and subsequent HCl (5.0 mol L⁻¹) aqueous solution at 80 °C for 3.0 h to remove the residual catalysts. The N-HBCNFs with high carbon purity were fabricated after filtering, washing, and freeze-drying.

2.3. Characterization

The CNF products were characterized by a JSM 7401F scanning electron microscope (SEM) and a JEM 2010 high-resolution transmission electron microscope (TEM). The level of CNF graphitization was determined by X-ray diffraction (XRD) on a Bruker D8

Advance diffractometer at 40.0 kV and 120 mA with Cu K α radiation. Raman spectra were collected on a Horiba Jobin Yvon LabRAM HR800 Raman spectrophotometer. TG analysis was operated by Mettler Toledo TGA/DSC-1 to calculate the purities of CNFs. The N₂ adsorption-desorption isotherms were obtained using an N₂ adsorption analyzer (Autosorb-IQ₂-MP-C system). The specific surface area of all samples was calculated by BET method. The pore size distribution plots were obtained by the non-linear density functional theory method.

2.4. Li-ion storage performance of N-HBCNFs

The Li-ion storage performance of N-HBCNFs was evaluated in a routine two-electrode cell configuration using standard 2025 coin-type cells. A homogeneously slurry was prepared by mixing N-HBCNFs and polyvinylidene difluoride (PVDF) binder in N-methylpyrrolidinone with a mass ratio of N-HBCNFs: PVDF = 9: 1, followed by magnetic stirring for ca. 24.0 h. The areal loading amount of N-HBCNFs was ca. 1.8 mg cm⁻². The slurry was then coated onto a Cu foil and dried in a vacuum drying oven at 60 °C for 6.0 h. The as-obtained foil was punched into 13 mm disks as the working electrodes. 1.0 mm-thick Li metal foil was employed as the counter electrode. An electrolyte of LiPF₆ (1.0 M) in a mixed solution of ethylene carbonate-dimethyl carbonate-ethylene methyl carbonate with a mass ratio of 1:1:1 was used. A microporous Celgard 2400 membrane was used as the separator. The assembling of cells was conducted in an Ar-filled glove box with oxygen and water content below 1 ppm. The coin cells were tested in the galvanostatic mode within a voltage range of 0.01–1.5 V using Neware multichannel battery cycler. The cyclic voltammogram (CV) measurements were performed on a Solartron 1470E electrochemical workstation at a scan rate of 0.10 mV s⁻¹. The CNT and HBCNF electrodes were obtained with the same methods. In addition, to maximize the electrochemical performance of N-HBCNFs, CNTs were added as the conductive agents in the long cycling test.

2.5. ORR performance of N-HBCNFs

The as-purified N-HBCNF samples were firstly dispersed in ethanol (5.0 mg mL⁻¹) by sonication. 10 μ L N-HBCNF suspension was pipetted onto the glass carbon disk electrode surface, which was polished mechanically with 0.05 μ m alumina slurry and then washed with deionized water and acetone to obtain a mirror-like clean surface prior to use. After solvent evaporation for 10 min in air, a thin layer of Nafion solution (1.0 wt%) was coated onto the electrode surface and then dried in an oven at 60 °C for 30 min before measurement.

The electrochemical measurements were conducted on a rotating ring-disk electrodes (RRDE) configuration (Pine Research Instrument, USA) in a three-electrode electrochemical cell using a computer-controlled potential station (CHI 760D, CH Instrument, USA). A rotating ring disk electrode with a disk diameter of 5.0 mm served as the substrate for the working electrode. A saturated calomel electrode (SCE) and Pt foil electrode were used as the reference and counter electrode, respectively. The oxygen reduction tests were carried out in O₂-saturated 0.10 mol L⁻¹ KOH solution at room temperature. The disk electrode was scanned cathodically at a rate of 5.0 mV s⁻¹ in the potential range of 0.2 to -0.8 V vs. SCE and the ring potential was set constant at +0.5 V vs. SCE to monitor the formation of peroxide intermediate. The electron transfer number *n* and HO₂⁻ intermediate production percentage (%HO₂⁻) were calculated based on the disk and ring current as followed:

$$n = \frac{4I_d}{I_d + I_r/N} \quad (1)$$

$$\%HO_2^- = 100(2/n) - 50 \quad (2)$$

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