Nitrogen-doped carbon nanofibers derived from polypyrrole coated bacterial cellulose as high-performance electrode materials for supercapacitors and Li-ion batteries

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Abstract: Nitrogen-doped carbon nanofiber (NDCN) was synthesized via carbonization of polypyrrole (PPy) coated bacterial cellulose (BC) composites, where BC serves as templates as well as precursor, and PPy serves as the nitrogen source. The synthesized NDCN was employed as electrode for both supercapacitors and Li-ion batteries. The large surface area exposed to electrolyte **resulting** from the 3D carbon networks **leads** to sufficient electrode/electrolyte interface and creates shorter transport paths of electrolyte ions and Li⁺ ion. Besides, the three types of N dopants in NDCN improve the electronic conductivity, as well as superior electrochemical performance.

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Introduction

Fast growing energy demands have attracted much attention in the exploring of high performance materials for electrochemical energy storage. On the one hand, supercapacitors as one of the potential candidates for next-generation energy storage device, have been widely studied due to their higher power density, faster charge/discharge rate as well as cycling stability compared with conventional battery and electrolytic capacitor [1]. Carbon-based materials, such as activated carbons, carbon nanotubes, and graphene, have been widely studied as electrode materials for supercapacitors [2]. However, the relatively low specific capacitance of carbon materials is one of the obstacles limiting their further developments [3]. Great efforts have been devoted to functionalizing carbon materials with chemical moieties; for example, nitrogen, boron, and sulfur have been considered as an effective approach to introduce pseudo-capacitance into the system [4]. The heteroatom functional groups are capable of enhancing the specific capacitance of the electrode materials due to their pseudo-capacitive reactions. Up to now, several strategies, including in-situ doping and post-processing procedure have been proposed to introduce heteroatoms into carbon materials [5-6]. The in-situ doping method generally involves a direct carbonization of heteroatom containing carbonaceous species (e.g. polymers, biomass materials or ionic liquids) [7-9]. For post-processing procedure, the pristine carbon materials are subjected to specified chemical reagent(s) (e.g. H_2S , NH_3 or $\text{CO}(\text{NH}_2)_2$) at a high temperature and the functional groups could be covalently attached onto the carbon surfaces [10-12].

On the other hand, lithium ion batteries (LIBs) have also been extensively investigated and used in various portable electronics because of their high energy density. Among the

anode materials for LIBs, carbon-based material is widely and commercially used one [13]. However, it encounters some disadvantages, such as low theoretical specific capacity and limited rate capability. Therefore, great efforts have been devoted to exploring candidates for carbon-based materials with enhanced Li^+ storage capability. It is hypothesized that the robust nanostructure with abundant hierarchical (meso- and macro-) porosities and large specific surface areas will ineluctably lead to sufficient contact between electrolyte ions and electroactive sites for energy storage [14]. In particular, the building blocks with robust and high surface-to-bulk ratio provide a shorter diffusion path and are the key factors, which are benign for the kinetics and high capacities. Besides, another approach to improve the capacity performance for the carbon-based anode for LIBs is to introduce surface functional groups with heteroatoms, such as N and B, etc [15-16]. It has been proved that N doping can induce active sites to absorb Li^+ and thus enhance the electrochemical performance.

Exploring highly active and cost-effective materials for both supercapacitors and LIBs is of paramount significance due to their indispensable role in energy storage system. Bacterial cellulose (BC), a special bio-product, produced in large quantities from fermentation of bacteria in static or agitated culture [17], has attracted increasing interests owing to its ultrafine three-dimensional (3D) network, high porosity, abundant hydroxyl groups, excellent biodegradability, and biocompatibility [18]. Since BC has a high initial level of inter-fiber bonding through extensive hydrogen bonding of the continuous nano-ribbons, N-H groups in pyrrole could form multitopic hydrogen bonds with the hydroxyl group of BC [19], thus, introducing nitrogen source into the carbon nanofibers. Herein, we present a facile strategy to prepare nitrogen-doped carbon nanofiber (NDCN) by using BC as both templates and precursors with polypyrrole (PPy) coating, followed by calcining the robust 3D network of

BC/PPy composites. The obtained NDCN exhibits enhanced capacity behaviors as electrode materials for both supercapacitors and LIBs.

Experimental section

Pre-treatment of BC:

BC pellicle was treated with diluted NaOH solution at 50 °C for 2 h to remove bacteria and residues and then thoroughly washed with distilled water until neutral pH. The obtained gel-like pre-treated BC pellicle was frozen in liquid nitrogen and then placed in a freezer drier at a sublimating temperature of -50 °C and a pressure of 0.015 mbar for 48 h to remove water. The dried BC was treated under high-speed homogenate machine to form uniform dispersion slurry, the concentration of BC was controlled at 0.25 g L⁻¹ by adding distilled water.

Preparation of NDCN:

Concentrated HCl solution was added into the 400 mL as-prepared BC suspension to adjust the pH. 0.02 mol of pre-treated pyrrole monomer was then added into the above solution and stirred for 2 h under nitrogen atmosphere. Subsequently, 20 mL of 1.0 M ferric trichloride aqueous was added dropwise into the pyrrole containing solution. The reaction system was placed in an ice-bath to control the temperature below 5 °C for 24 h. The resulting black precipitate was then suction-filtered in air and washed with copious amounts of distilled water and ethanol. After drying in an oven at 60 °C for 12 h, the carbon sources were calcined at 700 °C for 2 h in a tube furnace under argon atmosphere and then heat-treated at 300 °C for 1 h in air. The obtained black product was dissolved in 0.1 M HCl and sonicated for 15 min, and then washed with distilled water until the pH value is close to 7. After drying in an oven at 60 °C for 12 h, the final product was collected and subsequently dried in air over night.

Material Characterization

Scanning transmission electron microscopy (S-TEM) and TEM images were obtained on JEOL 2100F. Elemental mapping were conducted using electron energy loss spectroscopy (EELS) attached on JEOL 2100F. Powder X-ray diffraction (XRD) was performed by using an X'Pert PRO diffractometer, and diffraction patterns were collected at a scan rate of $4^{\circ} \text{ min}^{-1}$. X-ray photoelectron spectroscopic (XPS) was collected on an AXIS-ULTRA DLD-600W Instrument. FTIR measurements were conducted on a Bruker Vector-22 FTIR spectrometer at $4000\text{-}400 \text{ cm}^{-1}$. Raman spectra were taken by a LabRam HR800 spectrometer with a 532 nm laser excitation.

Electrochemical Measurements

Electrochemical measurements for supercapacitors were carried out in a three-electrode system on a CHI 760E electrochemical workstation at room temperature. Electrodes were prepared by mixing electroactive materials with acetylene black and polytetrafluoroethylene (PTFE) emulsion to make homogeneous slurry in the presence of absolute ethyl alcohol. The slurry was pressed onto a nickel foam with an apparent area of 1 cm^2 under the pressure of 5.0 MPa. The mass loading of active materials on every electrode is approximate 8 mg. Platinum sheet was used as counter electrode, as prepared electrode as working electrode referred to Ag/AgCl reference electrode, and 6.0 M KOH solution was used as electrolyte. For two-electrode testing system, electrochemical measurements were conducted in a 2032 type cell with two nearly identical (by weight and size) electrodes using glass fiber (GF/D, Whatman) as separator.

Electrochemical measurements for Li-ion battery were carried out in CR 2032 coin cells with lithium metal as the anode. The working electrodes are assembled of active material, carbon black (super-p) and polymer binder (polyvinylidene fluoride; PVDF) in a weight ratio

of 85:5:10, and Li metal as the counter and reference electrodes. The two electrodes were separated by Celgard 2320 and electrolyte was 1.0 M LiPF₆ in a 1:1 ratio of EC (Ethylene carbonate): DEC (Diethylene carbonate).

Results and discussion

The synthetic procedure for nitrogen-doped carbon nanofibers is illustrated in Scheme 1. BC was dispersed into [deionized](#) water to form uniform dispersion slurry and then combined with pyrrole monomer through hydrogen bond. By adding ferric chloride as an initiator, pyrrole monomer was polymerized and uniformly coated onto the surface of BC, forming a robust 3D network of BC/PPy. The BC/PPy composites were then carbonized by [calcination](#) under an argon atmosphere to form NDCN. [The following heat-treated procedure at 300 °C for 1h in air was to make sure the removal of impurities from the incomplete carbonization process and may produce the pores to provide new electronic transmission channels \[5\].](#)

SEM image in Figure 1a shows that BC exhibits an interconnected nanofiber [network](#) with a diameter ranging from 30 to 100 nm (See supporting information, Figure S1a) and a length up to several micrometers. The unique 3D network structure contains numerous -OH groups which [act](#) as bridging ligands for assembling nanoscaled building units to control the desired morphology. Moreover, the 3D network-like structure could significantly increase the effective reaction surface, facilitating the combination of pyrrole monomer. As shown in Figure 1b, the SEM image clearly shows that PPy particles coated evenly on the surface of 3D framework of BC after polymerization, forming a BC/PPy core-shell structure. By scattering the BC into dispersion, the original smooth surface of BC was uniformly coated with granular particles during the polymerization, presenting comparatively rough surfaces, and the diameter of the composite was increased to 100-300 nm (See supporting information, Figure

S1b). The structures of BC, PPy and BC/PPy were characterized with FTIR spectra and XRD patterns (Supporting information, Figure S3a and b). Pure BC exhibits typical FTIR spectra as reported in literature [20, 21], with a O-H stretching vibration at a broad peak at 3400 cm^{-1} , the aliphatic C-H stretching vibration located at 2850 cm^{-1} , and the strong band at 1047 cm^{-1} attributed to C-O-C stretching vibration. Obviously, BC/PPy exhibited the identical features of PPy, resulting from the complete wrapping of PPy around BC fibers. For the XRD patterns, the typical diffraction peaks of BC disappeared [22], while a broad asymmetric peak located at around 25° for PPy was clearly observed in BC/PPy nanocomposites. Based on above analysis, it is reasonable to draw a conclusion that the crystalline structure of the BC fibers was hindered by the coating of amorphous PPy [20].

The typical interconnected nanofiber structure of NDCN was observed with a diameter of 100-300 nm (Figure 2a). BF-TEM image and the SAED pattern of one NDCN were shown in Figure S2, suggesting a typical polycrystalline structure of carbon. The EELS elemental mappings in Figure 2c-e reveal that N and O have been successfully doped into NDCN with a homogeneous distribution. This unique 3D interconnected network structure provides enhanced surface area, facilitating electron and ion diffusion.

XPS measurement was performed to evaluate the chemical identities of the heteroatoms in the NDCN (For comparison, XPS spectrum of CBC was shown in Figure S4). The survey XPS spectrum in Figure 3a clearly shows that C1s, N1s and O1s peaks appeared in NDCN. The surface atomic percentages of N and O were calculated to be 8.34 at% and 12.01 at%, respectively. The high-resolution C1s spectrum of NDCN (Figure 3b) can be deconvoluted into four individual component peaks, which were attributed to C-C (284.5 eV), C-N (285.3 eV), C-O (286.5 eV) and C=O (288.5 eV) [23]. The presence of C-N peak further confirms

the successful doping of N into 3D carbon nanofiber network. The N1s spectrum (Figure 3c) was fitted into three peaks located at 398.2, 399.9 and 400.8 eV, corresponding to pyridinic N, pyrrolic N and quaternary N, respectively, which was typically observed in nitrogen doped carbon materials [24]. The XPS fine spectrum of O1s was deconvoluted into two peaks, i.e., 530.1 eV for -C=O and 532.0 eV for -OH or -O-. The presence of G and 2D band in the Raman spectroscopy (Figure S5) located at $1575\pm 20\text{ cm}^{-1}$ and $2800\pm 20\text{ cm}^{-1}$, respectively, which have been reported to be signatures of graphitic carbon materials [25]. The G band of NDCN slightly shifts toward to lower frequency compared to that of pristine CBC, indicating the successfully doping of N in the NDCN structure. The slightly higher intensity ratio of the D to G bands (I_D/I_G) on NDCN is ascribed to more defect sites or heteroatoms incorporation in the carbon network.

To evaluate the electrochemical performance of the NDCN as supercapacitor electrode materials, CV measurements with different scan rates were performed. As shown in Figure 4a, the CVs between -1.0 and 0 V exhibited typical quasi-rectangular and symmetric shapes, and the instant response upon the reversal of voltage at scan rates range from 5 mV s^{-1} to 50 mV s^{-1} , indicating an excellent electrochemical reversibility and capacitive behavior. There was no pronounced reversible redox peaks appeared in the CV curves in this work, which agreed with the previous reports [26]. The area under the CV curve of NDCN was much larger than that of pristine carbonized BC (CBC), demonstrating an enhanced specific capacitance on NDCN electrode (Figure 4b). The superior capacitance performance of NDCN could be ascribed to the pseudocapacitive contribution from the N functional groups, which improved the wet ability and hence maximize the electroactive surface area [27]. The 3D network structure provides a high electrochemical active surface area, facilitating faster charge transfer and

lower resistance. The charge-discharge curves of NDCN in Figure 4c and Figure S6b show a nearly triangular shape without obvious IR -drop at different current densities, and the charge/discharge curves deviate slightly from the linear characteristics during charging by varying current densities, suggesting that NDCN electrode exhibited high reversibility of an ideal capacitor. The specific capacitances are calculated from the slope of the charge/discharge curves, on the basis of equation $C_s = I \Delta t / (m \Delta V)$, where C_s is the specific capacitance, I is the applied current, m is the mass of active material within the electrode, and $\Delta t / \Delta V$ was calculated from the discharge curve. Based on the discharge curve in Figure 4c, the calculated specific capacitance of NDCN was 120.0 F g^{-1} at current density of 1.0 A g^{-1} , which was almost two times as high as that of CBC (63.7 F g^{-1} , Figure S6a). The enlarged capacitance on NDCN electrode attributed to the nitrogen incorporation into the 3D carbon matrix, enhancing both the electrical conductivity and wet ability between the electrolyte and electrode materials. The capacitance decreased with increasing current density (Figure 4d) were probably due to the polarization, indicating that all the electrode material is not fully charged or discharged due to limited ionic diffusion in the electrode material. When tested at high scan rates typically causes the electrolyte ions to only reach the outer surface and consequently a decrease in the capacitance is expected [28].

The long-term cycling stability of NDCN electrode as supercapacitor electrode material was investigated using galvanostatic charge/discharge measurement at a current density of 3.0 A g^{-1} (Figure 4e). It was observed that the specific capacitance on NDCN electrode was slightly increased due to the electro-activation process during the first 1000 cycles [29]. The specific capacitance maintained at 98.4 F g^{-1} even after 5000 cycles, which is 98.2% of the initial capacitance, indicating excellent cycling stability. Meanwhile, according to the inset

figure in Figure 5a, no obvious change of CV curves was observed during cycling. On the other hand, the Coulombic efficiency of NDCN electrode exhibited to be closed to 100% during the stability testing.

NDCN was further evaluated by using electrochemical impedance spectroscopy (EIS) to investigate the capacitive behaviors before and after 5000 cycles. EIS measurements were performed at open-circuit potential in the frequency range from 100 kHz to 0.01 Hz with an ac perturbation of 5 mV. As shown in Figure 4f, the Nyquist plots show a semicircle in high-frequency region followed by a line at low-frequency region and it was observed the charge transfer impedances were approximately the same before and after 5000 cycles, indicating that the charge-transfer resistance for the electrode remained stable during the whole cycling process. Meanwhile, the solution resistances (R_s) for the material before and after 5000 cycles were both very low at 1.9 and 2.2 Ω , respectively. The slight change of R_s may be ascribed to the long term soaking in the electrolyte, which will lead to losing of adhesion of some active material and dissolving of oxygen in the electrolyte [30-31]. The linear region of Nyquist plots exhibited an angle between 45° and 90° relative to real axis, suggesting that the electrode process was desirable under diffusion control. The EIS results above further verified the good electrochemical cycling stability of as-prepared NDCN electrode.

For the two-electrode testing system, the CV of NDCN exhibited ideal rectangular and symmetric shapes (electrode polarization phenomenon was detected when the working potential window was selected from -1.0 to 1.0 V, Figure S7), and similarly, the area under the CV curve of NDCN was much larger than that of CBC (Figure 5a). Owing to excellent conductivity and porous structure of NDCN, the rectangular shape of the CVs at scanning

rates from 10 to 50 mV s^{-1} are generally retained (Figure 5c). The capacitance of a single electrode (C_s) is calculated from the charge-discharge curves according to the equation of $C_s = 4I\Delta t/m\Delta V$, where C_s is the specific capacitance of the electrode (F g^{-1}), I is the discharge current (mA), Δt is the discharge time, ΔV is the potential range (1.6V) and m is the mass of the electrode materials. Based on Figure 6b, the C_s values of NDCN and CBC were calculated at current density of 1.0 A g^{-1} to be 75.0 F g^{-1} and 46.5 F g^{-1} , respectively. The cycling stability tested in a coin cell was presented in Figure 6d. It can be seen that after 5000 charge-discharge cycles at a current density of 1.0 A g^{-1} , both of the C_s values of NDCN and CBC remain at approximately 100% of the initial cycle, suggesting excellent cycling stability.

The NDCN was also used as anode materials with excellent properties in LIBs as can be seen in Figure 6 (For comparison, the performance of CBC applied for LIBs is presented in Figure S8). In the first cycle, a discharge capacity of 737 mAh g^{-1} with a Coulombic efficiency of 45% (Figure 6a) was obtained at a current density of 500 mA g^{-1} . The large irreversible capacity loss is mainly attributed to irreversible formation of the solid electrolyte interface (SEI) layer, which is common for most anode materials [32]. However, in the second and third cycle, both the charge and discharge curves exhibited negligible changes, as shown in Figure 6a. It can also be seen that in Figure 6b, after the first 5 cycles at a low rate of 100 mA g^{-1} , the discharge capacity slightly reduced and reached at about 576 mAh g^{-1} . It then fluctuated at about 470, 400 and 330 mAh g^{-1} at current densities of 200, 500 and 1000 mA g^{-1} , respectively. Notably, the NDCN shows high capacity of 110 mAh g^{-1} even at very high rate at 10 A g^{-1} (about 27 C when calculated at theoretical capacity of 372 mAh g^{-1} for graphite). After experiencing various charge-discharge rates, the capacity of NDCN resumed to be about 500 mAh g^{-1} when the current density was back to 100 mA g^{-1} after 50 cycles. The cycling

stability of NDCN was evaluated during charge/discharge processes between 0.01 to 2.5 V at different current densities (Figure 6c). The NDCN shows stable cycle performance after 100 cycles, the capacities maintain at 445 mAh g⁻¹, 230 mAh g⁻¹ and 178 mAh g⁻¹ at current densities of 200 mA g⁻¹, 500 mA g⁻¹ and 1000 mA g⁻¹, and the corresponding capacitance retention are 64.4%, 53.5% and 50.3%, respectively.

The outstanding capacity and rate capability for NDCN could be ascribed to their 3D network and high-level of nitrogen doping (Figure 6d). The large surface area exposed to electrolyte result from the 3D carbon network leads to sufficient electrode/electrolyte interfaces to absorb Li⁺ ions and facilitate fast charge-transfer reaction (The BET surface area of NDCN was calculated as 364.8 m² g⁻¹ with a main micropore structure in the 1-10 nm region, Figure S9) [33]. The nano-scaled interconnected carbon fibers create shorter transport paths for Li⁺ ions. Besides, the three types of N doping in NDCN improved the electronic conductivity as well as endow peculiar [electrochemical activity](#), which contributes to the additional performance.

Conclusion

In conclusion, an effective and rational strategy has been developed for preparing nitrogen doped carbon network via a direct carbonization process of heteroatom containing carbonaceous species based on BC as template and precursor. For supercapacitor applications, the nitrogen-doped 3D carbon networks exhibit good capacitive performance when tested in both three-electrode system and two-electrode system in 6.0 M KOH. For LIBs applications, it presents a high reversible capacity of 737 mAh g⁻¹ at a current density of 100 mA g⁻¹, with good cycling stability and rate capability. Such a facile method of constructing high-level heteroatom (N: 8.34 at%, O: 12.01 at%) doped carbon materials will be of great significance

for the synthesis of nanostructured carbon materials in a low-cost, eco-friendly way for energy storage application.

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Graphical Abstract

The unique 3D network structure of NDCN provides a high electrochemical active surface area, facilitating faster charge transfer and lower resistance, resulting in an excellent cycling stability even after 5000 cycles.

Figure 2. (a) DF-STEM overview of NDCN; (b) DF-STEM image of one NDCN; EELS elemental mapping images of C (c), N (d) and O (e).

Figure 3. (a) Full XPS spectrum of NDCN; High-resolution XPS spectra of C1s (b), N1s (c) and O1s (d).

Figure 4. (a) CV curves of NDCN at different scan rates; (b) CV curves comparison between NDCN and BC; (c) Galvanostatic charge/discharge curves of as-prepared NDCN at different current densities; (d) Specific capacitance of NDCN at different current densities. (e) Cycling performance (black line) and Coulombic efficiency (red line) of NDCN at a current density of 3.0 A g⁻¹ (The inset is the corresponding CV curves during the cycling at a scan rate of 10 mV s⁻¹); (f) Nyquist plots of NDCN before and after 5000 cycles.

Figure 5. (a) CV curves of NDCN and CBC ; (b) Galvanostatic charge/discharge curves of NDCN and CBC; (c) CV curves of NDCN at different scan rates; (d) Cycling performance of NDCN and CBC.

Figure 6. (a) Charge/discharge curves of NDCN at the initial three cycles with a discharge current density of 500 mA g⁻¹; (b) Rate performance of NDCN; (c) Cycling stability of NDCN at different discharge current density; (d) Schematic representation of electron transmission and Li⁺ storage.