Nitrogen and oxygen co-doped broccoli-like porous carbon nanosheets derived from sericin for high-performance supercapacitors

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Abstract. Broccoli-like porous carbon nanosheets with high levels of heteroatoms doping was successfully synthesized from the wasted sericin via an environmental friendliness and cost-effective strategy. The hierarchical porous carbon nanosheets was formed from chemical expansion and activation by Mg₂(OH)₂CO₃ · xH₂O simultaneously. Benefiting from the elaborate structure of NPCN-4, the prepared material shows the satisfactory energy storage ability in electrical double-layer capacitors (EDLCs) area with an outstanding specific capacitance of 214.5 F g⁻¹ at 0.5 A g⁻¹ in an alkaline solution and high capacitance retention of 87% at 10 A g⁻¹ after 10000 cycles.

1. Introduction
All human activities are inseparable from energy supply. Especially since the first industrial revolution, human society relied more on fossil fuels than ever before. Lessening the recline on exhaustible resources and searching for green and renewable energy sources have always been a hot topic for scientists [1-3]. The EDLCs are advanced supercapacitors, which store energy by using the reversible adsorption/desorption of ions during the charge/discharge process and show the advantages of ultra-high power density, and ultra-long cycle life [4]. Converting biomass into activated carbon for EDLCs is promising strategy. However, conventional chemical and physical activation methods always involve time-consuming synthesis steps or corrosive chemical agents (like KOH and H₃PO₄), which result in corrosion of equipment and environmental pollution [5-8]. Therefore, we seek to carve a new path to active carbon derived from biomass resource.

In this work, we carried out an environmentally friendly pyrolysis strategy using sericin to prepare broccoli-like N, O co-doped porous carbon nanosheets (NPCN) and applied for potential supercapacitors electrode material. Unlike the conventional active methods involving time-consuming multistep processes, corrosive or hazardous activation agents, the facile one-step pyrolysis strategy was environmental friendliness and cost-effective.

2. Experimental section
The sericin was purchased from the market without further purification. The schematic diagram of the synthesis for broccoli-like carbon nanosheets is given in Figure 1. Firstly, 2 grams of sericin powder
was dissolved in 50 ml deionized water to form protein solution. Then, 4 grams of Mg$_2$(OH)$_2$CO$_3$·xH$_2$O (≥99%, Shanghai Baiyan Bio-Technology Co., Ltd) was added into the protein solution and continuously evaporated in a water-bath at 80 °C to gain biomass-template precursor. Secondly the solid-state precursor was carbonized at 700 °C for 2 hours under the inert gas (Ar) flow. At last, 2 mol L$^{-1}$ hydrochloric acid has been used to remove the template agent. Eventually the black power was collected and named as NPCN-4. For comparison, the sericin precursor was directly carbonized at 700 °C and named as non-active carbon (NC).

![Figure 1. One-step synthesis strategy for preparing NPCN-4.](image)

A foam nickel with a diameter of about 8 mm was washed by acetone, hydrochloric acid and ethanol and used as current collector. Then, the foamed nickel was uniformly coated with a mixed slurry composed of conductive agent (acetylene black), binder (PVDF) and active material, corresponding to the mass ratio of 8:1:1. Next, the electrode was completely dried in the vacuum oven overnight and compressed under 10 MPa for seconds. Eventually, the mass of active material per square centimeter on the obtained electrode sheet was about 2.0±0.5 mg. In a standard three-electrode system, 6.0 mol L$^{-1}$ KOH solution, platinum (Pt) electrode and saturated calomel (SCE) electrode were used as electrolyte, counter electrode and reference electrode, respectively. The electrochemical measurements, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were tested on electrochemical workstation. The long-term cycling test was performed on LAND battery system.

3. Discussion

The morphological features are shown in Figure 2a and Figure 2b, after dehydrogenation and deoxygenation, the carbon atoms in the protein skeleton transformed into the sp$^2$-hybrid aromatic structure and the formed carbon sheets tended to be stacked tightly to reduce the surface free energy and resulted in smooth surface of NC. While the NPCNs-4 exhibited a unique broccoli-like clusters with a fluffy and three-dimensional architecture (Figure 2c), and the formed broccoli-like clusters were about 10 microns in diameter. In addition, the high-magnification scanning electron microscope (SEM) image (Figure 2d) showed that the broccoli-like clusters consisted of massive porous carbon nanosheets. At the same time, a typical lamellar pattern with mutually permeable network structure composed of carbon nanosheets was clearly observed in the transmission electron microscope (TEM) image (Figure 2e). Additionally, the high-magnification transmission image (Figure 2f) showed a partly regular lattice fringes, which suggests the high degree of graphitization. At the same time, the irregular lines were also observed, which was caused by the amorphous regions in the carbon material.
Figure 2. (a) SEM image of NC; (b) High-magnification image of NC; (c) SEM image of NPCN-4; (d) High-magnification image of NPCN-4; (e) TEM images of NPCN-4; (f) High-magnification TEM images of NPCN-4.

The high molecular weight and high crosslinking of sericin enhanced the formation of aromatic carbon, and combined with the activation of Mg$_2$(OH)$_2$CO$_3$·xH$_2$O at high temperature, eventually resulted in the unique broccoli-like morphology of NPCN-4. The function of the Mg$_2$(OH)$_2$CO$_3$·xH$_2$O, compared to the traditional KOH method, not only presented less chemical corrosion and more environmentally friendly, but also greatly promoted the porosity of the final carbon materials. From the thermogravimetric analysis (TG) curve (Figure 3a), two significant mass attenuation appeared at 450 °C and 230 °C. The CO$_2$ emitted at 450 °C leads to expansion effect and forcefully expand the carbon skeleton and do great help to the formation of sheet-like morphology; the MgO nanoparticles decomposed from 230 °C and embedded in biomass-template precursor also act as hard templates to increase the micro porosity of the final carbon materials.

X-ray diffraction (XRD) experiments were used to investigate the effect of the activation process on the crystalline form of carbon materials. Figure 3b visually shows that the diffraction peak of NC has a narrower diffraction peak width, indicating that the higher degree of graphitization. The NPCN-4 displayed a lower peak response intensity and a larger diffraction peak width, which suggests that the porosity expansion effect caused the long-range ordered structure inside the material to decrease, and the amorphous phase region and the degree of defects increased [9]. In the Raman spectrum (Figure. 3c), the peak at 1580 cm$^{-1}$ is considered to be in-plane vibration caused by graphitized carbon atoms (G-band), while the peak at 1326 cm$^{-1}$ is believed to be caused by various defects in the carbon material (D-band) [10]. The intensity ratio of D-band to G-band suggests the disorder degree of the carbon materials [11]. NC exhibited a relatively lower ratio (I_D/I_G) of 0.95, while the NPCN-4 presented a higher ratio of 1.17, which suggested the deterioration of the long-range order in NPCN-4 due to the presence of heteroatom and porosity, which also corroborates the above analysis about the evolution of the material's crystal form. The X-ray photoelectron spectroscopy (XPS) pattern shows a strong N1s peak signal around 400.0 eV in Figure 3d, indicating that it is highly feasible to use high nitrogen content biomass as a self-doped precursor. The NPCNs-4 had a high nitrogen content of 12.55% and a high oxygen content of 8.36%. The high-resolution N1s spectrum has three peaks at 398.24 eV, 400.06 eV and 401.04 eV corresponding to Pyridinic N, Pyrrolic N and Quaternary N, respectively [12]. By embedding higher electronegative nitrogen atoms into the carbon matrix, on the one hand, it helps to improve the conductivity of the material and reduce the energy loss during the power transmission. On the other hand, it is also expected to contribute additional pseudocapacitance effect to EDLCs system. The O1s peak appears around 532 eV in Figure 3e and the doping of oxygen contributes to expose the effective
surface area needed for charge storage [13]. Specific surface area (SSA) is one of the key factors that determine the energy storage capacity of the active carbon. At the same time, the pore size distribution also has an impact on the dynamics of ions transport. The NPCN-4 contains the high SSA of 700.5 m² g⁻¹, which provides a sufficiently large wettable surface for charge storage. From the Figure 3f, we have observed the hysteresis loop caused by the mesoporous structure at the higher relative pressure range and the almost overlapping adsorption-desorption curve caused by microporous structure around the lower relative pressure area. The prepared NPCN-4 has a high level of mesoporous and microporous structure, which not only ensures that the material contains a high specific capacity, but also make electrolyte ions rapidly wetted and transferred inside the material, which will help the electrode achieve better rate performance at the high current density[14].

The electrochemical performance of prepared carbon materials was studied in 6 mol L⁻¹ KOH. Compared to NC, the CV curves of NPCN-4 presented higher response current at the same scan rate (Figure 4a), which suggested the higher specific capacitance of NPCN-4. Figure 4b showed the CV curves of NPCNs-4 from 10 mV s⁻¹ to 100 mV s⁻¹, which exhibited typical EDLCs behavior with the similar rectangular shapes. Furthermore, the slightly bent shape of CV curves in high potential region indicated the presence of pseudocapacitance, which should be ascribed to the oxygen-containing functional groups and the doping of heteroatoms. Figure 4c displayed the GCD curves of NPCNs-4, the symmetrical approximately linear charge-discharge curve indicated that the electrode had a high degree of reversibility during the charge/discharge process. As shown in Figure 4d, the specific capacitance of NPCN-4 was 214.5 F g⁻¹ at 0.5A g⁻¹ and 150.5 F g⁻¹ at 10.0 A g⁻¹. Obviously, the NPCNs-4 exhibits a much better specific capacitance at the same test conditions, which was 114% and 49.8% higher than NC at 0.5 A g⁻¹ and 10 A g⁻¹, respectively. The Nyquist plot of NPCN-4 was performed on Figure 4e. The mass of ions is much larger than that of electrons. When the direction of the applied electric field changes, the movement direction of ions often has a hysteresis. Therefore, in the high frequency region, the Nyquist curve exhibits the characteristic that the semicircle intersects the real axis, and its intersection point reflects the equivalent series resistance (Rs). As the frequency decreases, the diameter of the semicircle in the mid-frequency region corresponds to the charge-transfer resistance (Rct) [15]. The charge-transfer resistance of NPCN-4 was 0.58 Ω and the equivalent series resistance was 0.47 Ω.
In addition, the almost vertical plot around lower frequency area of NPCN-4 suggested the low diffusion resistance and excellent wettability. Figure 4f reflected the cycling durability of NPCNs-4 at 10 A g\(^{-1}\), which retains 87% of the initial capacitance and almost 100% coulombic efficiency after 10000 cycles, suggesting the high durability in aqueous electrolyte. As shown in Figure 5, we have compared similar low-dimensional carbon materials derived from other biomass with NPCN-4. Obviously, NPCN-4 has better energy storage capacity. [16–20].

**Figure 4.** (a) CV curves of NC and NPCN-4 at 100 mV s\(^{-1}\); (b) CV curves of NPCN-4; (c) GCD curves of NPCN-4; (d) Specific capacitance of NPCN-4; (e) Nyquist plots of NPCN-4; (f) The cycling performance of NPCN-4 at 10 A g\(^{-1}\).

**Figure 5.** Ragone plot of NPCN-4 and other biomass-derived carbon materials.

4. Conclusion

Biomass resources are abundant in nature and exist in various forms. Converting biomass to functional carbon materials usually yields unexpected results. In this work, we have introduced a simple strategy to synthesis the carbon nanosheets from the wasted biomass resource. The prepared NPCN-4 displays a special broccoli-like morphology consisting of multiple carbon nanosheets with developed porosity and high levels of heteroatoms doping. The excellent electrochemical performance provides a possible strategy to manufacture high-capacity electrochemical energy storage.
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