

Non-activated, N, S-co-doped Biochar Derived from Banana with Superior Capacitive Properties

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Abstract In this study, the non-activated N, S-co-doped biochar carbon for supercapacitors were successfully prepared from banana without any activation. In addition, our electrochemical test demonstrated that the as-prepared carbon materials exhibited a high specific capacitance and excellent cycling performance due to the co-existence of N and S.

Keywords: biochar, electrochemical properties, supercapacitor, carbon

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1. Introduction

The development of energy-sustainable and energy-efficient economy depends on the ability to produce novel renewable materials for electrical energy storage devices. To this regard, supercapacitors with long cycling lifetime, high power density and low maintenance cost are being extensively researched to bridge between conventional dielectric capacitors with high power density and lithium-ion battery with high energy density [1-10]. Generally, supercapacitors can be divided into electrical double-layer capacitors (EDLCs) and pseudocapacitors based on their charge/discharge mechanisms. Although pseudocapacitors provide dozens of times more capacitance than EDLCs due to the high energy transfer during the faradaic reaction, their high cost (usually using some expensive metal oxides as electrode, such as RuO₂) and poor cycling performance greatly restrict their further application in industry. Thus the current commercial supercapacitors mainly focus on EDLCs with carbon materials as electrodes. Energy storage in EDLCs rely on the accumulation of charge at electrodes purely by electrostatic forces, since no chemical reactions are involved, high rates of energy delivery, and stable and reversible cycling can be achieved [11-21]. Until now, the most common electrode material used in commercial EDLCs is activated carbon (AC), therefore a key challenge is to develop low cost carbons with high energy and power densities.

Petroleum coke, pitch and coal used to be the most common precursors for commercial AC productions, but the decreasing availability of fossil fuels and increasing

awareness of environmental impacts by fossil fuel combustion led to AC productions from natural materials, which are sustainable and renewable resources, usually denoted as biochar, such as agricultural, forest and animal residues [22-30]. Considering the supercapacitor industry, the employment of renewable biochar to prepare carbon electrode would be an economical and environmentally friendly route. In addition, element doping can improved capacity [31,32]. Banana is a kind of fruit with a lot of elements, such as C, N, S and O. In this study, we extend this strategy to use banana to prepare carbon materials without activation, and systematically investigate their electrochemical performances in supercapacitors. Our experimental results demonstrate that the as-prepared carbon materials exhibit a high specific capacitance of 100.5F/g and excellent reversibility with cycling efficiency of about 85% after 6000 cycles in 2M KOH. It is highly expected this sample and environmentally friendly strategy may open up a new route for the preparation of carbon electrodes in supercapacitor industry.

2. Materials and Methods

2.1. Material Preparation

The biochars were prepared by the carbonization of the hydrothermal product of bananas (purchased from common supermarket). In a typical procedure, 5g of banana and 40mL deionized water were placed in a commercial Teflon-lined autoclave with a capacity of 45mL. The autoclave was sealed and heated at 180°C for 12h, and then allowed to cool to room temperature. The resulting carbonaceous solid, denoted as biochar, was recovered by filtration, washed with ethanol and deionized

water for several times, and dried in an oven at 60°C. Subsequently, the biochar material was heated at 550°C or 750°C for 2h under argon flow. After that, the activated samples were thoroughly washed by ethanol and deionized water. Finally, the carbons were dried in an oven at for 100°C 12h.

2.2. Characterization

XRD analysis was performed using a Bruker AXS D8 Discover diffractometer with a Cu KR radiation source. SEM was conducted with a Hitachi S-4800 scanning electron microscope. XPS was performed using an Axis Ultra spectrometer. Nitrogen adsorption-desorption analysis was performed using Micromeritics ASAP 2020 gas adsorption apparatus (USA) at -196°C.

2.3. Electrochemical Measurement

The carbon materials derived from biochar were used as electrode material for supercapacitors. The working electrodes were fabricated The working electrodes were fabricated by mixing the active material, acetylene black and binder (PVDF) in a weight ratio of 80:10:10. The formed paste was pressed at 20MPa to a piece of nickel foam (1.0cm×1.0cm), and dried under vacuum at 80°C for 10h. Electrochemical measurements were conducted in a three-electrode configuration in 2M KOH electrolyte with Pt wire as counter electrode, Hg/HgCl₂ as reference electrode, respectively. The electrochemical performance of the electrodes was tested by cyclic voltammetry (CV) measurements and galvanostatic charge-discharge on an electrochemical workstation (RST 5000, Ruisite, Suzhou). CV was tested in a potential range from -1V to 0V at a scan rate of 10mV/s, 30mV/s, 50mV/s, 80mV/s, and 100mV/s. The galvanostatic charge-discharge tests were also performed using various current densities between 1 and 10A/g. The gravimetric specific capacitance of the electrodes was calculated by the following equation (1):

$$C = \frac{I \times \Delta t}{m \times \Delta U} \quad (1)$$

I is the discharge current (A), Δt is the discharge time (s), ΔU is the potential difference of the electrodes during discharge (V), m is the total mass of activated carbon in electrodes (g), and C is the specific capacitance of the electrodes (F/g).

3. Results and Discussion

3.1. Structural and Morphological Characterization

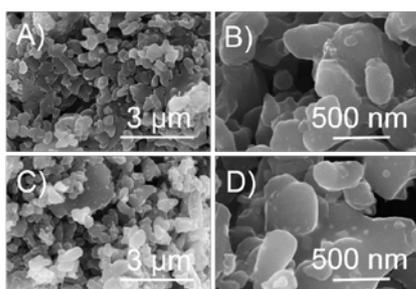


Figure 1. SEM images of the as-prepared carbon materials at different activation temperature: (A and B) CM-550, 550°C; (C and D) CM-750, 750°C

As reported, the hydrothermal process can cause biochar, which usually resembled a macroscopic yarn, to break up into smaller pieces with micro- or nanometers. Figure 1 presents the images of banana after hydrothermal carbonization and subsequent thermo-treatment. Although the shape and size of the obtained carbon materials with different temperatures (denoted by CM-X, where X refers to the thermo-treatment temperature) are similar, the specific surface areas are significantly different. CM-550 exhibits a larger surface area (138m²/g) than CM-750 (6 m²/g), indicating that the thermo-treatment temperature plays critical role for the preparation of carbon materials with large specific surface area, and also hinting their different electrochemical performance in supercapacitors. Both XRD patterns of CM-550 and CM-750 show two broad peaks (Figure 2) at 2θ of about 23° and 43° corresponding to the (002) and (110) plane reflection, and reveal the amorphous nature of as-prepared carbon materials.

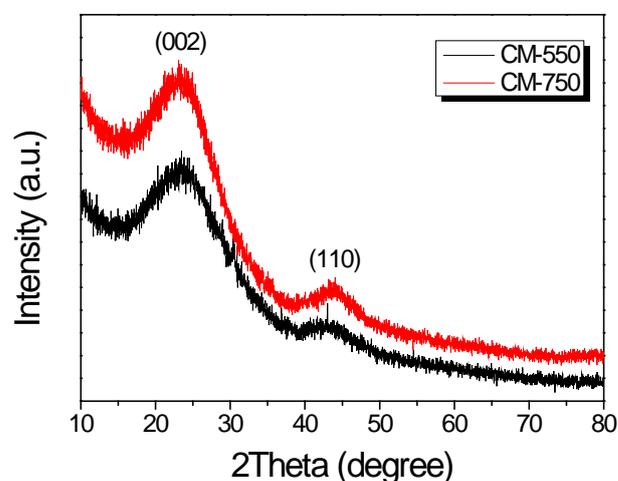


Figure 2. XRD patterns of CM-550 and CM-750

3.2. Electrochemical Properties

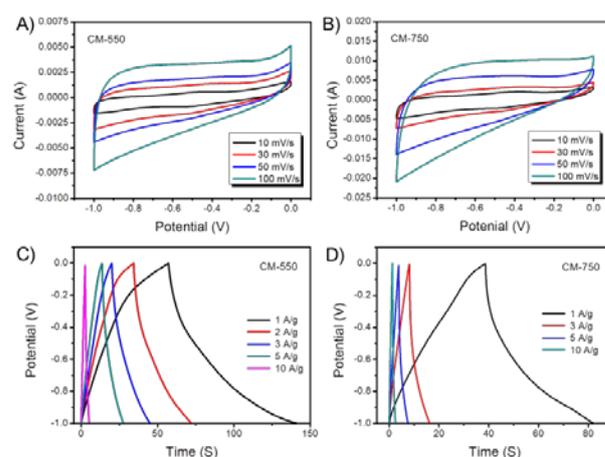


Figure 3. (A, B) CV curves of CM-550 and CM-750 at various scan rates, respectively; (C, D) Galvanostatic charge and discharge curves of CM-550 and CM-750 at different current densities, respectively

Electrochemical performance of the as-prepared carbon materials was tested for supercapacitors in 2 M KOH solution. Figure 3A and B show the typical cyclic voltammetry (CV) curves of CM-550 and CM-750 electrodes at scan rates of 10mV/s, 30mV/s, 50mV/s and

100mV/s. All the patterns at different scanning rates display the quite rectangular shape of CV curves, inferring the capacitance is stored by an accumulation of electrolyte ions between the electrode/electrolyte interfaces which is known as electric double layer capacitance. With the increasing of scan rate, the rectangular shape of the curves still keep well, indicating excellent ion transport behavior for CM-550 and CM-750. Compared CM-750, the leveled current separation of CM-550 is much larger, suggesting well electrochemical performance of CM-550. The galvanostatic charge-discharge curves of CM-550 and CM-750 measured at different current densities are shown in Figure 3C and Figure 3D. The charge-discharge curves are nearly linear and almost symmetrical at current densities from 1 A/g to 10 A/g, demonstrating the excellent reversibility and capacitive property for electrode materials. The specific capacitance can be calculated from the discharge curves according to the previous equation (1). For CM-550, the specific capacitance is 100.5F/g, 76.2F/g, 66.3F/g, 58.1F/g, 26.4F/g for the current densities 1A/g, 2A/g, 3A/g, 5A/g, 10A/g, respectively, which is higher than CM-750. The high specific capacitance of CM-550 may be attributed to its higher surface area, which can offer more active sites for electrode materials and electrolyte thus maximize the utilization of the electrode materials. Compared with the reported values of activated carbons [33,34] the capacity of the as-synthesized CM-550 is much larger, although it has low surface area. This may be attributed to the existence of N, S element except O supported by XPS (Figure S1 and Table S1), which facilitate the improvement of capacity [31,32].

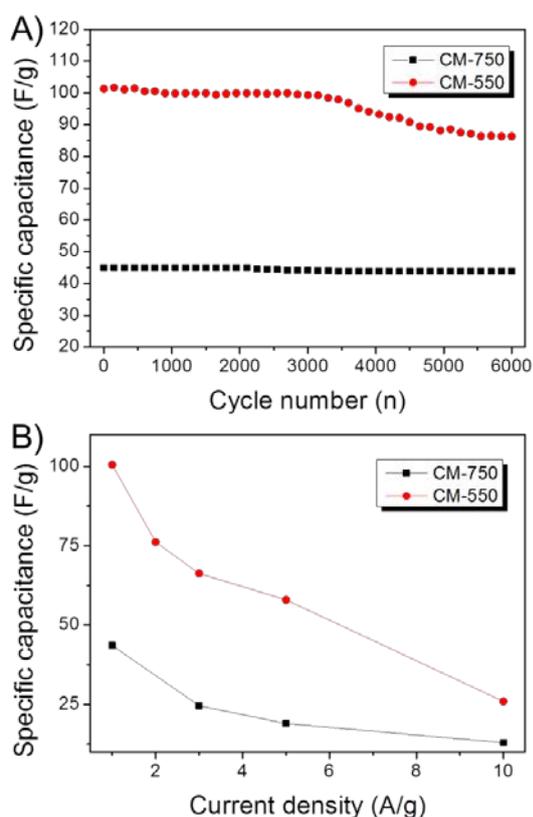


Figure 4. (A) the cycling performances of CM-550 and CM-750 at the current density of 1 A g⁻¹, (b) the rate performances of CM-550 and CM-750 at various current densities

Both of cycling and rate performance are important factors for supercapacitors. The cycling performances over 6000 cycles of CM-550 and CM-750 were carried out with galvanostatic charge-discharge at the current density of 1 A/g, as shown in Figure 4a. The specific capacitances are 100.5F/g and 45.2F/g for the initial cycle, and retain at 86.3 F/g and 45.1F/g after 6000 cycles for CM-550 and CM-750, respectively, exhibiting high stable cycling performance. The rate performance is shown in Figure 4b. Obviously, CM-550 shows remarkable better electrochemical performance. Although there is a reduction of capacitance with the increased current density for CM-550, the capacitance at the current density of 1A/g is still high. The decrease of capacitance may be due to such as-synthesized carbon materials could not sustain the ion transitions completely.

4. Conclusion

Here we report the hydrothermal-based synthesis and thermo-treatment of carbon materials with superior electrochemical storage. We were able to achieve this by employing banana as biomass precursor. Our experimental results demonstrate that the activation temperatures play an important role for the preparation of high active carbon electrodes. CM-550 exhibits large specific surface area, thus resulting in a better electrochemical performance for supercapacitors. Specifically, it displays a high specific capacitance of 100.5F/g and excellent reversibility with cycling efficiency of about 85% after 6000 cycles in 2M KOH. It is highly expected this sample and environmentally friendly strategy may open up a new route for the preparation of carbon electrodes in supercapacitor industry.

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Supporting Information

Table S1. Element content of the as-prepared carbon materials

| Element | Atomic % | pp At. % |
|---------|----------|----------|
| C | 86.13 | 90.82 |
| N | 5.97 | 3.64 |
| O | 7.67 | 5.28 |
| S | 0.23 | 0.26 |

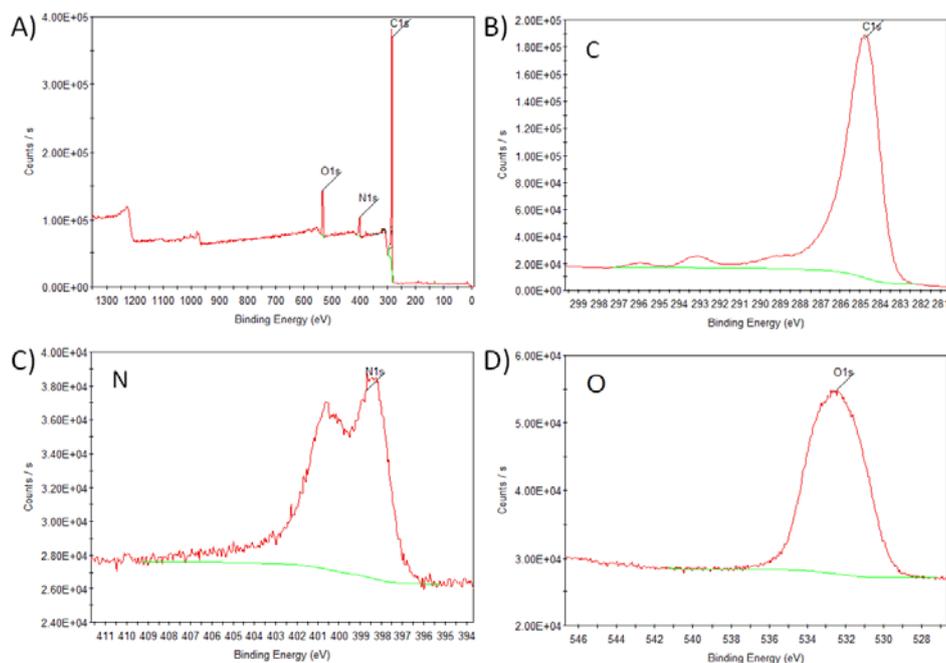


Figure S1. XPS spectra of CM-550: (A) the survey scan; (B) C 1s region, (C) N 1s region, and (D) O 1s region

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