



Hybrid symmetric supercapacitor assembled by renewable corn silks based porous carbon and redox-active electrolytes

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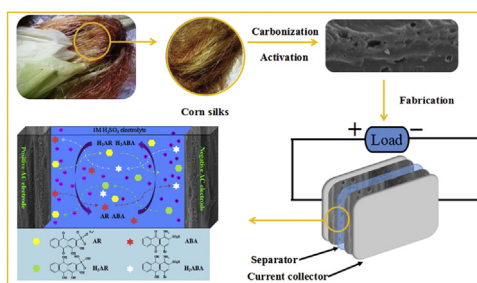
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HIGHLIGHTS

- Nitrogen-doped porous carbon derived from a renewable corn silks.
- The CSC-1 displays high specific surface area and large specific capacitance.
- The alizarin red (AR) and bromoamine acid (ABA) are employed as redox-active species.
- The hybrid symmetric supercapacitor exhibit high energy density and cyclic stability.

GRAPHICAL ABSTRACT



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ABSTRACT

We have prepared nitrogen doped biomass activated carbon (CSC-1) using the agricultural wastes corn silks as raw materials and ZnCl_2 as activating agent (the same weight of corn silks and ZnCl_2) carbonized at 800°C . The activated carbon has high specific surface areas of $1764.8\text{ m}^2\text{ g}^{-1}$, large specific capacitance of 358.0 F g^{-1} at 0.5 A g^{-1} , 67% of the capacitance retention at 20 A g^{-1} , and 99.2% of initiatory specific capacitance after 5000 consecutive cycles. To improve the energy density of the symmetric supercapacitor based on CSC-1 electrodes, we employed the $1\text{ M H}_2\text{SO}_4$ aqueous solution with alizarin red (AR) and bromoamine acid (ABA) as an advanced electrolyte to fabricate a novel hybrid symmetric cell. Surprisingly, the above device obtains a high specific capacitance of 260.8 F g^{-1} and a high energy density of 17.8 Wh kg^{-1} , which are markedly higher than those in the conventional electrolyte. The improved energy storage is attributed to Faradaic pseudocapacitance related to the redox-active species of AR and ABA in the H_2SO_4 electrolyte. Based on the excellent characteristics, the device is expected as a promising candidate to fabricate high performance supercapacitors.

1. Introduction

With the growing energy demand and the consumption of fossil fuels in recent years, there has been requirements to exploit cost-effective, environmentally-friendly and high performance electrochemical energy storage devices for sustainable mobile power source

[1,2]. Supercapacitors (SCs) have attracted much attention because of the maintenance-free operation, high power density and significantly long cycling life than lithium ion battery. In addition, supercapacitors can be directly utilized or coupled with other batteries for energy output toward certain electrical facilities, such as electric braking assistance, starter and generators [3].

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Based on the charge storage mechanisms, supercapacitors can be divided into electrical double layer capacitor (EDLC) and pseudocapacitor [4]. The energy storage in EDLCs results from the electrostatic attraction of the opposite charges and the charge accumulation occurred on double-layers at the electrode/electrolyte interface, whereas the capacity of pseudocapacitor depends on the Faradaic reactions of electroactive species on the surface of the electrode [5]. Specially, the electrode active material of SCs are three groups: metal oxide, electronically conducting polymer and carbon materials [6]. Among them, carbon materials especially derived from biomass precursors for EDLC application have been the most developed because of the relatively low cost, easy accessibility, extraordinary cycling stability, high rate performance and high power density. On the other hand, the carbon materials derived from agricultural wastes might be inherently rich in hetero-atom species (such as nitrogen, oxygen, boron and sulfur) [7], which can improve the surface wettability of the carbon materials, significantly facilitate rapid electrolyte ion transport within the micropores and mesopores and induce pseudocapacitive behavior of carbon materials [8]. Except to hetero-atom species, high specific surface area and appropriate pore size have also been considered important factors to improve the specific capacitance of carbon materials [9]. And it is believed to achieve larger specific surface area and more developed pores of carbon materials commonly through chemical activation methods. Compared to the KOH and NaOH, the $ZnCl_2$ activating agent shows practical advantages such as minor erosion and low cost [10]. Making use of the agricultural wastes can not only reduce the environmental pollution but also create the economic value. The carbons prepared by the biomass precursors would have a profound and lasting impact on the investigation of SCs. However, the large-scale industrialization of the carbon materials is limited by their relatively low energy density [11].

Since the energy density (E) of SCs is proportional to the capacitance (C) and the square of the voltage (V), according to the equation: $E = 1/2CV^2$, increasing the capacitance or the cell voltage can effectively increase the energy density. In order to improve the capacitance of supercapacitors, there are two strategies can be used, one way is to prepare transition metal oxides/hydroxides, metal chalcogenides and conducting polymers composite carbon materials as electrode materials. Unfortunately, they still suffer from low power density and short cycle life because of their poor electrical conductivity and instability [12]. Another way is to introduce redox additives in electrolytes. Many inorganic cationic redox couples such as VO_2^+/VO^{2+} [13], I_2/I^- [14], and organic redox mediators such as p-benzenedial [15], p-phenylenediamine [16], methylene blue [17] and indigo carmine [18] are as redox additives have increased the total specific capacitance and energy density of the EDLCs through reversible redox reactions. Frackowiak et al. [19] applied KI and $VOSO_4$ aqueous solutions as electrolytes on the sides of the positive and negative electrodes of supercapacitor based on activated carbon electrodes, and used an expensive Nafion Membrane to separate them into two compartments. Except for two different electrolytes with the positive and negative electrodes with a membrane, it is a challenge to find different redox-active electrolytes coexisting in the solution without expensive Nafion Membrane which can produce two or more redox reactions as well. Generally, there are some necessary properties of the redox additives into the liquid electrolytes immensely: involve in redox reaction, better solubility, electrochemically stable, easy preparation and nontoxic [20]. Therefore, to build high-performance supercapacitors, the electrode materials and advanced electrolyte should be elaborately designed.

In this work, we have prepared novel SCs using AC derived from corn silk as the efficient electrode materials and 1 M H_2SO_4 aqueous solution with two redox additives of alizarin red and bromoamine acid as electrolyte. Benefiting from the high specific surface area and effective hetero-atom doping, the activated carbon exhibits high specific capacity, excellent rate capability and long cycling life. More importantly, the energy densities of symmetric supercapacitors by

assembling activated carbon electrode and redox-active H_2SO_4 electrolytes are obviously higher than that of the symmetric supercapacitors based on activated carbon electrode and pristine H_2SO_4 electrolyte, because the reversible redox reactions of redox-active species effectively enhance the potential window and supply the extra pseudocapacitance.

2. Experimental section

2.1. Materials

Corn silks are derived from the local environment (Lanzhou Gansu province, China), zinc chloride ($ZnCl_2$, Yantai Shuang shuang Chemical Co., Ltd, China), Nafion solution (DuPont, USA), alizarin red (AR) (Shanghai Zhongqin Chemical Co., Ltd, China), bromoamine acid (ABA) (Tokyo Chemical Industry Co., Ltd, Japan) and N-methyl-2-pyrrolidone (Shanghai Zhongqin Chemical Co., Ltd, China) were in analytical grade and used as produced without any further treatment.

2.2. Synthesis of nitrogen-doped porous carbon based on corn silk

The physical mixing as the contacting method in most cases can lead to better porosity development than impregnation. In a typical preparation of the activated carbon CSC-1: 1.0 g of dried corn silk was thoroughly mixed with the same quality powder of $ZnCl_2$ in the crucible, and carbonized at 800 °C for 2 h with the heating rate of 5 °C min^{-1} in a tubular furnace in nitrogen atmosphere. For comparison purpose, the raw material was carried out under the same conditions without mixing activating agent, and the resulting sample was named as CSC. The two samples were washed in 2 M HCl at room temperature for 6 h to remove the impurities, and then washed with distilled water until the pH reached neutral. In final, CSC and CSC-1 are dried at 60 °C overnight.

2.3. Materials characterization

The morphology of the carbons were performed using the field emission scanning electron microscopy (FE-SEM, Ultra Plus, Carl Zeiss) at an accelerating voltage of 5.0 kV. X-ray diffraction (XRD) of samples was examined on a Rigaku D/Max-2400 diffractometer (Tokyo, Japan.) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 100 mA. Raman spectra was recorded through an Via Raman spectrometer (Renishaw) with an Argon ion laser ($\lambda = 514.5 \text{ nm}$) at ambient temperature. The Brunauer-Emmett-Teller surface area (S_{BET}) and pore structure of the carbon samples were analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (U.S.A.), and all samples were degassed at 200 °C prior to nitrogen adsorption measurements. The structure of CSC-1 was further carried out by a transmission electron microscopy (TEM, JEM-2010 Japan). X-ray photoelectron spectroscopy (XPS) measurement was performed on an Escalab 210 system (Germany).

2.4. Electrochemical measurements

2.4.1. Three-electrode systems

The electrochemical performance of the CSC and CSC-1 were investigated and compared using three-electrode systems. A high purity carbon rod and saturated calomel electrode (SCE) in 1 M H_2SO_4 solution were used as the counter electrode and reference electrode, respectively. Typically, 4 mg of CSC or CSC-1 were dispersed in 0.4 mL of 0.25 wt% Nafion ethanol solutions with assistance by ultrasonic vibration. Then, 8 μ L of above suspension were dropped onto the glassy carbon electrode as working electrode and dried for 10 min at room temperature.

2.4.2. Two-electrode systems

Electrochemical measurements were further taken using two-

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