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The porous carbon derived from water hyacinth with well-designed hierarchical structure for supercapacitors

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HIGHLIGHTS

- This is the first investigation on supercapacitors derived from water hyacinth.
- Water hyacinth has a well-designed three-level hierarchical structure.
- The supercapacitors possess a specific capacitance of 344.9 F/g at 0.5 A/g.
- The supercapacitors possess 95% of the capacitance retention after 10000 cycles.
- This work supports sustainable development and the control of biological invasion.

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ABSTRACT

A hierarchical porous water hyacinth-derived carbon (WHC) is fabricated by pre-carbonization and KOH activation for supercapacitors. The physicochemical properties of WHC are researched by scanning electron microscopy (SEM), N_2 adsorption-desorption measurements, X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The results indicate that WHC exhibits hierarchical porous structure and high specific surface area of 2276 m^2/g. And the electrochemical properties of WHC are studied by cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) tests. In a three-electrode test system, WHC shows considerable specific capacitance of 344.9 F/g at a current density of 0.5 A/g, good rate performance with 225.8 F/g even at a current density of 30 A/g, and good cycle stability with 95% of the capacitance retention after 10000 cycles of charge-discharge at a current density of 5 A/g. Moreover, WHC cell delivers an energy density of 23.8 Wh/kg at 0.5 A/g and a power density of 15.7 kW/kg at 10 A/g. Thus, using water hyacinth as carbon source to fabricate supercapacitors electrodes is a promising approach for developing inexpensive, sustainable and high-performance carbon materials. Additionally, this study supports the sustainable development and the control of biological invasion.

1. Introduction

The impact of growing petroleum crisis and environment pollution has seriously restricted the world's sustainable development. Thus, the researches on sustainable, low-cost, high-powered and clean energy storage and energy conversion components are of great important on both science and technology [1–5]. Currently, supercapacitors, which have considerable power density and energy density, long cycle life, and wide applications such as mobile phones and electric cars, have drawn worldwide attention as one of the most promising energy storage and energy conversion devices [6,7]. There are two kinds of energy storage ways in supercapacitors, one is charge accumulation at the interface between electrode and electrolyte (electric double-layer capacitors, EDLC), such as carbon materials; the other one is redox reactions on the surface of the electrode (pseudocapacitors), such as metal oxides

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[8–10]. Nowadays, about 80% of the electrode materials of commercially available supercapacitors are made by carbon materials (include carbon nanotubes, graphene, fullerence, activated carbon and so on), because of its high specific surface area, hierarchical porous structure, and easy to dope heteroatoms (include N, P, O, etc) [11–13]. Generally speaking, macropores offer ion-buffering tanks to short the distances between interior surfaces and interfaces; mesoporous provide fast pathways for the electrolyte ions; and micropores further increase the electric double-layer capacitance [14–17]. Therefore, macropores and mesopores improve ion transport, ensuring fine rate performance and considerable power density; and mesopores and micropores offer a large ion-accessible specific surface area, leading to a good specific capacitance and excellent energy density [18,19]. Additionally, heteroatoms doping can increase the capacitance of carbon materials as well, by offering pseudocapacitance and improving electrical conductivity [20].

In recent years, comparing to traditional feedstock (coal and petroleum), the supercapacitors prepared from biomass (such as watermelon [21], pomelo peels [22], sugarcane [23], winter melon [24], mollusc shell [25], cellulose [26], banana peels [27], tobacco rods [28], oil palm kernel shell [29], and butterfly wing [30]) have drawn more attention because of their low-cost, high-output, renewable and easy to obtain. Moreover, some of the biomass has hierarchical structure and abundant heteroatom. Most of these biomass-derived supercapacitors exhibit good performance, some of them even better than commercial supercapacitors. However, most of biomass-derived supercapacitors are prepared from agricultural products, such as watermelon, sugarcane, winter melon, and tobacco rods, which will definitely affect the provisionment and thus strongly limit their large-scale applications. Therefore, fabricating high-performance supercapacitors from waste or even harmful natural resources is an urgent study in order to extend biomass-derived supercapacitors' applications.

Water hyacinth, one kind of floating plants, was a native in Amazon river, but now can be seen everywhere around worldwide water systems. This invasive species has no natural enemy outside its origin, therefore overrun. Additionally, water hyacinth insulates sunlight and oxygen, blocks river, lake and stream, and finally damages water quality and ecological system because of its floaty ability, which seriously affects the normal production and living of human and other species. However, this floaty ability of water hyacinth strongly causes our attention as we want to turn this disadvantage into advantage. We strip away the epidermis of modified stem of water hyacinth and find many millimeter-level and hollow cells inside it. Moreover, we also find micrometer-level structure on the millimeter-level structure of water hyacinth. Furthermore, there is nanometer-level structure on the micrometer-level structure of water hyacinth as well. This well-designed three-level structure greatly reduces the density of water hyacinth and therefore helping it to float on the water. Recently, many researches indicate that a well-designed hierarchical porous three-dimensional (3D) structure with high specific surface area can be very suitable for being the template of supercapacitors [31–34]. In the past decades, people try to find the way to make use of water hyacinth, such as for pig feed and paper feedstock, but the effect is limited. In this case, we want to prepare supercapacitors from water hyacinth in order to make fully use of this useless and even harmful natural resources and its annoying floaty ability.

In this work, novel high-performance supercapacitors were prepared from water hyacinth through pre-carbonization and KOH activation. Interestingly, water hyacinth has well-designed hierarchical structure (three levels: millimeter-level, micrometer-level and nanometer-level), which leading to the high specific surface area, good electrical conductivity and considerable electrochemical properties of WHC. Specifically speaking, WHC displays excellent specific capacitance of 344.9 F/g at a current density of 0.5 A/g, good rate performance with 225.8 F/g even at a current density of 30 A/g, and long cycle life with 95% of the capacitance retention after 10000 cycles of charge-discharge at a current density of 5 A/g. Moreover, WHC cell can deliver an energy density of 23.8 Wh/kg at 0.5 A/g and a power density of 15.7 kW/kg at 10 A/g. Thus, using water hyacinth as carbon source to fabricate supercapacitors is a promising approach for developing inexpensive, sustainable and high-performance energy materials and providing a potential application of the waste or even harmful natural resources. This method is also help for solving biological invasion, which is a great problem of world.

2. Experimental section

2.1. Materials

Water hyacinth was purchased from Beijing flower market. Potassium hydroxide and hydrochloric acid were purchased from Beijing Chemical Reagent Co. in China, and were used without further purification.

2.2. Preparation of WHC

WHC was prepared by pre-carbonization and KOH activation. And the specific methods are according to our previous work after improvement [35]. Firstly, the fresh tissue of water hyacinth was turned into aerogel by freeze-drying (−60 °C, 36 h). Then, the aerogel was pre-carbonized at 400 °C for 2 h with a heating rate of 5 °C/min under a nitrogen atmosphere. Subsequently, the pre-carbonized product was mixed evenly with 0.2 mol/L KOH aqueous solution (the weight ratio of KOH and carbon is 1: 1, 1.5: 1 and 2: 1, and the obtained WHC was named as WHC-1, WHC-1.5 and WHC-2, respectively). After that, the mixed solution was dried at 120 °C for 12 h (with stirring) to remove water and further make sure that the pre-carbonized product was mixed thoroughly with KOH. Afterwards, the mixed powder was placed in a crucible with a heating rate of 5 °C/min under a nitrogen atmosphere by the following process: at the beginning, the mixed powder was heated to 400 °C and hold for 1 h; next, the temperature was raised to 600 °C and kept for another 1 h; finally, the temperature was increased to 800 °C and hold for 1.5 h. Lastly, the resulting black powder was washed by 1 mol/L HCl aqueous solution to remove residual inorganic impurities, and then dialyzed by distilled water until pH reached 7.

2.3. Characterizations

Scanning electron microscopy (SEM) images of water hyacinth, pre-carbonization WHC, and KOH activation WHC were observed under a scanning electron microscope (S-4800, Hitachi Co., Japan). And the fresh tissues of water hyacinth were freeze-dried in order to remove water before observation.

N_2 adsorption-desorption isotherms of WHC-1, WHC-1.5 and WHC-2 were carried out at 77 K on a N_2 adsorption-desorption analyzer (BK200C, JWGB SCI. & TECH. Co., China) after the samples were degassed at 300 °C for 5 h. The specific surface area of WHC samples was calculated by the Brunauer-Emmett-Teller (BET) method. The pore size distribution of WHC samples was calculated by the Horvath-Kawazoe (HK) method (<2 nm) and the Barrett-Joyner-Halenda (BJH) method (>2 nm) by using nitrogen adsorption data.

Wide-angle X-ray diffraction (WAXD) patterns of WHC-1, WHC-1.5, and WHC-2 were measured on a wide-angle X-ray