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Promising biomass-based activated carbons derived from willow catkins for high performance supercapacitors

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ABSTRACT

Unusual sheets-like primary activated carbon particles interconnected into three-dimensional micrometer-level large pores were prepared from a novel biomass named willow catkins (WCs) by KOH chemical activation process and used as electrode materials for supercapacitors. The pore structures, surface area and chemical properties could be facilely adjusted by changing the activation temperature. When the activation temperature increased from 600 to 800 °C, the specific surface area of the porous carbon product increased remarkably while the contents of nitrogen and oxygen co-doped decreased, which significantly affected the electrochemical properties of the porous carbon-based supercapacitors. The activated carbons from 600 °C activation possesses despite moderate specific surface area (645 $m^2 g^{-1}$), concentrated pore size distribution of 0.77 nm, but high nitrogen (2.51 wt.%) and oxygen (13.28 wt.%) contents, high graphitization degree as well as good electrical conductivity. The supercapacitors with the carbon electrode reached maximal specific capacitances of 340 $F g^{-1}$ and high specific surface capacitance of 52.7 $\mu F cm^{-2}$ at the current density of 0.1 $A g^{-1}$, good rate capability (231 $F g^{-1}$ at 10 $A g^{-1}$) and good cycling stability (92% capacitance retention over 3000 cycles). The favorable capacitive performances make the waste biomass WCs act as a new resource of carbonaceous materials for high performance supercapacitors.

1. Introduction

Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have attracted more and more attention due to the advantages of high power density, long cycle life (>100 000 cycles), rapid charging–discharging rate, simple principles and fast dynamics of charge propagation [1–3]. As a result, supercapacitors are widely used in consumer electronics, electric vehicles, pulsing techniques as well as industrial power and energy management [4,5]. A more recent application for supercapacitors in emergency doors on the Airbus A380 highlights their security and reliability. Generally, on the basis of the energy storage mechanism, supercapacitors can be classified into two categories: electrical double layer capacitor (EDLC) and pseudo-capacitor [6–8]. The capacitance for EDLC comes from the pure electrostatic charge accumulation at the electrode/electrolyte interface, which is greatly dependent on the surface area of the electrode materials that is accessible to electrolyte ions. The pseudo-capacitor is related with the fast and reversible faradic process of the electroactive species within the electrode materials. For pseudo-capacitive materials, mainly metal oxides and electrical conductive polymers, have been widely used as high specific capacitance electrode. However, low conductivity, poor cycle stability as well as high cost that greatly limited its practical application as electrode materials.

Porous carbonaceous materials with tunable porosities, including activated carbons (ACs) [7,9], ordered mesoporous carbons [10], carbon aerogels [11,12] and graphene-based materials [13], have been extensively used as electrode materials in the commerical supercapacitors. Among these carbon materials, ACs is considered as one of the most attractive candidates for supercapacitors due to its high specific surface area, well-developed porous structure, high electrical conductivity and electrochemical stability. Traditionally, the preparation of ACs mainly involves the coal, petroleum and their derivatives that are expensive and non-renewable. Considering the potentially scalable and sustainable of supercapacitor applications, the development of low-cost carbon materials from renewable raw materials is very worthwhile. Biomass materials, benefiting from the renewable, low-cost and eco-friendly properties as compared

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to the non-renewable and diminishing fossil resources [14,15], are rich sources of carbon but may also contain other elements such as oxygen, nitrogen and so on. Usually direct burning of the biomass materials will lead to environmental pollution because of the emission of the CO_2 and/or nitrogen oxides (NO_x) into the atmospheres. Therefore, how to make use of these plentiful waste biomasses efficiently has greatly attracted researchers' attention. Up to now, a wide variety of waste biomass materials, including celtuce leaves [16], tea leaves [17], dead neem leaves [18], corn grains [19], sunflower seed shell [20], pistachio and firwood [21,22], coconut shell [23,24], rice husk [25], bamboo [26], entermorpha prolifera [27], seaweed [2], fermented rice [28], waste newspaper [29], bacteria [6], fungi [30], animal's bones [31,32] and animal's feather [33], etc., have been utilized as carbon precursors to prepare porous carbonaceous materials that have shown great potential as electrode materials for supercapacitors.

Willow, which belongs to genus Salix of deciduous trees, has widely distributed in cold and temperate regions of the Northern Hemisphere. Catkins are willow flowers appearing on the branches, produced in the early spring before the leaves or as the new leaves open. Every spring innumerable white floccule floating in air, brings a lot of trouble for people, for examples, respiratory ailments or skin anaphylaxis. A reasonable and effective approach for overcoming this air pollution problem is very limited. In this regard, a practical and feasible technique to solve this problem is to transform these waste biomasses to high value-added products rather than just burn them. Recently, Ma and co-workers used willow catkins (WCs) as precursors to prepare carbon microtubes by simple carbonization and the carbonaceous materials exhibit good activity in the oxygen reduction reaction [34].The specific hollow tubular-liked structure or morphology and rich heteroatoms compositions of WCs would lead to the generation of carbonaceous materials with specific pore structure or morphology and chemical properties. Herein, the aim of our research work is to exploit a new way for biomass waste application, which could not only solve the problems of biomass pollution but also enrich the choice of precursors for electrode materials.

In this study, willow catkins were used as the precursor to synthesize unusual porous activated carbons by simple KOH activation process for the first time. The activated carbon products have three-dimensional large pores at micrometer size and narrow micropores of 0.77–1.2 nm and are significantly doped by nitrogen/oxygen. The AC products can be milled and sonicated to make a colloidal dispersion that is convenient to make a uniform film. We found that the specific surface area of ACs increased but surface heteroatoms contents decreased when the activation temperature increased from 600 °C to 800 °C. The relationship between the structure characteristics, surface chemical properties of the porous carbon and its electrochemical performance are investigated intensively. Interestingly, electrochemical performances of the ACs based supercapacitors depends more on heteroatoms contents than the specific surface area of the ACs. The sample obtained at 600 °C despite have moderate specific surface area, controllable pore size distribution and rich suface nitrogen- and oxygen-containing functional groups, high graphitization degree as well as good electrical conductivity that resulting in higher specific capacitance than those obtained at 700 °C and 800 °C. The results further demonstrated that the as-prepared ACs is a promising electrode material in energy storage application.

2. Experiments

2.1. Preparation of WCs derived ACs

WCs were collected in large quantity from Taiyuan city, Shanxi province between March and April. As a facile and scalable synthesis method, the porous ACs from WCs were prepared as follows. First, a certain amount of WCs was washed with deionized water for several times to remove adherent soil and impurities. Then, it was dried at 120 °C for 12 h. The dried WCs were fully stirred in aqueous KOH solution (the mass ratio of KOH to WCs equals to 1(g/g)) for 1 h at room temperature and followed by evaporating water at 80 °C under vacuum and dried at 120 °C overnight. The dried sample was pyrolyzed in a nickel crucible at 600–800 °C for 1 h with a heating rate of 5 °C min^{-1} under a nitrogen flow (30 ml min^{-1}). Then, the resulting solid was repeatedly washed with 1 M HCl and deionized water until the pH value of filtrate reached to about 7. The residue was dried at 90 °C for 5 h. The resultant porous ACs were denoted as AC-*T*, where *T* was corresponding to the heat treatment temperature.

2.2. Characterization of Samples

The thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses were carried out on a NETZSCH STA 409 PC/PG thermal analysis instrument at a heating rate of 10 °C min^{-1} in N_2 atmosphere. Field emission scanning electron microscopy (FESEM) images were performed on a JEOL JSM-7001F microscope at an accelerating voltage of 10 kV. The TEM images were taken on FEI Tecnai G2 F20 S-twin transmission electron microscope with an acceleration voltage of 100 kV. Powder X-ray diffraction (XRD) patterns were examined on a D8 ADVANCE diffractometer with CuKα radiation (λ = 1.5418 Å) operating at 40 kV, 15 mA. The Raman spectra were recorded on a Horiba (XploRA) spectrometer. The source of radiation was a laser operating at a wavelength of 514 nm and power of 25 mW. X-ray photoelectron spectra (XPS) were measured on a Kratos AXIS Ultra DLD spectrometer with Al target, Kα radiation, from a double anode X-ray source. Nitrogen sorption isotherms and physical properties were examined by ASAP 2020 physisorption apparatus at 77 K. The samples were degassed at 250 °C for 5 h prior to the measurement. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method based on the nitrogen adsorption data in the P/P_o range corresponding to the linear region. The total pore volume was estimated with the amount of nitrogen adsorbed at a relative pressure of $P/P_o = 0.99$. The pore size distribution (PSD) was obtained by the non-local density functional theory (NLDFT) method with an assumption of slit pore model. The Fourier transformation infrared (FT-IR) spectra in the region from 400 to 4000 cm^{-1} were recorded on a Bruker VERTEX 70 spectrometer by using KBr pellet technique. The element contents in the feed and carbonaceous materials were measured by Vario EL Cube elemental analyzer.

2.3. Electrochemical Measurements

Three-electrode configuration was adopted to evaluate the capacitive performance of the as-prepared activated materials on a CHI 660C electrochemical workstation (Shanghai ChenHua Instruments Co., China). The test was performed in 6 M KOH aqueous electrolyte solution under ambient conditions. A platinum foil and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The working electrodes were prepared by mixing the activated materials, acetylene black, conducting graphite, and polytetrafluoroethylene (PTFE) binder at a weight ratio of 75:10:10:5. A small amount of ethanol was added and the mixture was pestled by mortar to form an evenly slurry. The slurry was coated onto a nickel foam current collector and dried at 60 °C overnight in a vacuum. The capacitive performance of samples were studied by using cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance spectroscopy (EIS) techniques. The working voltage windows were between −0.9 and 0 V. EIS was performed in a