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Oxygen- and nitrogen-co-doped activated carbon from waste particleboard for potential application in high-performance capacitance

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ABSTRACT

Oxygen- and nitrogen-co-doped activated carbons were obtained from phosphoric acid treated nitrogen-doped activated carbons which were prepared from waste particleboard bonded with urea-formaldehyde resin adhesives. The activated carbon samples obtained were tested as supercapacitors in two-electrode cell and extensive wetting 7 M KOH electrolytes. Their structural properties and surface chemistry, before the electrical testing, were investigated using elemental analysis, X-ray photoelectron spectroscopy, scanning electron microscopy, X-ray diffraction, Raman spectra, and adsorption of nitrogen. Activated carbon treated by 4 M phosphoric acid of the highest capacitance (235 F/g) was measured in spite of a relatively lower surface (1360 m^2/g) than that of the activated carbon treated by 2 M phosphoric acid (1433 m^2/g). The surface chemistry, and especially oxygen- and nitrogen-containing functional groups, was found of paramount importance for the capacitive behavior and for the effective pore space utilization by the electrolyte ions.

1. Introduction

Activated carbons (ACs) are solids constituted principally by carbon, having a well-developed porous texture (surface area, pore volume, etc.) and deserving a number of applications in different fields such as gas and liquid purification, mixture separation, catalysis, etc. [1–3]. Besides the classic uses, these materials are potentially useful for emerging applications of great interest such as storage of combustible gases (hydrogen, methane) or electrical energy storage (anodes in Li-ion batteries or electrodes in supercapacitors) [4,5]. Supercapacitors are one kind of electrochemical energy storage devices with a high specific power density, which are promising in many energy-related applications, and currently can fill the gap between batteries and traditional capacitors. Generally, two types of electrochemical capacitors have been studied: (i) an electrochemical double-layer capacitor, in which capacitance arises from the charge separation at the electrode/electrolyte interface; and (ii) the pseudocapacitor, in which capacitance arises from a faradic reaction occurring at the electrode surface in contact with the electrolyte.

In the development of electric double-layer supercapacitor, a proper control over the specific surface area and the pore size of activated carbons are crucial to ensure a good performance of the supercapacitor. However, the electric double-layer capacitance cannot be enhanced illimitably because the excessive increase of surface area causes a huge decrease of mesoporosity, thus reducing the mass transfer capacity. A simple way in developing high-capacitance supercapacitors is combining the electric double-layer capacitance and pseudocapacitance [6]. Usually, pseudocapacitive properties are attributed to electrode materials undergoing redox process during polarization like transition metal oxides [7], electrically conducting polymers [8], transition metal nitrides [9] or carbon materials enriched by heteroatoms such as oxygen or nitrogen [10,11] where the pseudocapacitance originates from faradaic reactions of functional groups present on carbon surface accessible for protic electrolyte [12]. In general, the heteroatom-doped structures of activated carbons are believed to provide pseudocapacitance contributed from the redox faradic reactions of these electrochemically active functional groups. Usually, heteroatoms in the supercapacitors are oxygen and nitrogen, such as hydroxyls, anhydride et al. acidic surface oxygen groups. Acidic surface oxygen groups (SOGs) have been characterized as chemical precursors behind the beneficial electrochemical [13] and adsorption [14] applications of surfactants on carbon substrates. SOGs

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form only on the edges of pores, known as the zigzag and armchair sites of the carbon substrate [15–18]. These sites of chemical attachment are considered to be active surface area on which the most chemical surface reactivity transpires. Functionality known to be associated with surface acidification (carboxylic acids, anhydride, lactones, lactols, and hydroxyls with phenolic character) is reported to form from chemical attachment of oxygen functionality to carbon surface [15,18–21]. A variety of methods for adding oxygen to the carbon surfaces have been investigated, such as chemical treatment, chemical vapor deposition, plasma, oxidation and oxyfluorination methods [22]. Among these methods, physicochemical base tuning using phosphoric acid has the advantage of permitting the facile introduction of oxygen functional groups onto the carbon surface. Thus, phosphoric acid treatment of activated carbon (AC) should enhance the specific capacitance of an AC electrode-based supercapacitor. Although phosphoric acid has been used as an activation agent in several previous studies, our study investigates new effects of phosphoric acid as a surface treatment agent [23]. In most cases, nitrogen-doped carbon materials were achieved by introducing nitrogen into carbon frameworks through the post treatment, for example, being treated with ammonia gas/air, which results in a lower content of nitrogen [24,25]. The drawback can be overcome by employing N-containing materials as precursors [26]. By this method, nitrogen in the carbon materials can be preserved at a relatively large content. Biomaterials (such as ginkgo shells [27], gelatin biomolecule [28], silk proteins [29], collagen [26]) and polymers (such as phenolic resin [30], polyacrylonitrile [31], poly (vinylpyrrolidone) [32], polyacrylamide [32]) have been reported as suitable precursors for synthesizing N- and O-doped carbonaceous materials due to their inherent high heteroatom content. Our study investigates a new methodology directed to prepared nitrogen containing ACs by waste particleboards, which are bonded with formaldehyde-based adhesives, especially urea-formaldehyde (UF) adhesive.

Particleboard wastes are zero-cost materials which have already been tested as attractive precursors for producing ACs from a two steps thermo-chemical process [33]. Currently China is a big country in wood-based panel production and consumption, and there is a great quantity of wood-based panel (especially particleboards) produced every year. Unfortunately the resource is not used very effectively, open burning and land filling are common practices to eliminate waste particleboards which cause environmental pollution and put adverse impact on the ecosystem. Consequently, ensuring the rational use of these wastes has vital significance. Indeed, in such materials, wood is the precursor of the AC, while nitrogen is provided by the aminoplastic adhesive: urea-fomaldehyde and melamin-formaldehyde resins, dispersed all through the board, and impregnating each particle of wood. The research by Girods et al. [33] showed that the nitrogen content of AC prepared by waste particleboard and activated with steam at 800 °C still reach 2%.

In this paper, we develop a straightforward methodology directed to prepare nitrogen-containing AC by waste particleboards which can not only recycle waste particleboards but also take full advantage of UF resin. In addition, the nitrogen-containing AC was treated by phosphoric acid, meanwhile the oxygen- and nitrogen-co-doped AC was investigated the physical properties and electrochemical characteristic.

2. Experimental

The waste particleboards was kindly provided by Beijing Jiahekailai Furniture and Design Company, which was obtained in the furniture manufacturing process containing 10% urea-formaldehyde resin adhesive of the mass. Other chemicals were analytical grades and were purchased from Beijing Lanyi Chemical reagent.

2.1. Preparation of activated carbon materials

First of all, the waste particleboards as raw materials were carbonized in a high-purity nitrogen atmosphere at the temperature increase rate of 10 °C/min to the final temperature of 500 °C (maintained for 60 min). Secondly, the products after carbonization were activated that mixed with KOH at the mass ratio 2.5:1 at the temperature 750 °C for 60 min in oven. The obtained ACs were boiled first with distilled water, then with 1 M HCl solution until the pH of solution reach to about 6-7, and dried at 105 °C in an oven for 8 h, as well as marked with RAC. Finally, RAC was modified by phosphoric acid solutions [34]. 3 gram RAC and 120 mL phosphoric acid solution (2, 4, and 8 M) were mixed with vigorous stirring for 24 h at room temperature and filtered to separate the AC. The separated AC was treated in an oven for 48 h at 100 °C, washed with distilled water until the filtrate was neutralized, and then dried for 8 h at 105 °C. The treated AC samples are referred to as OAC-2, OAC-4, and OAC-8, depending on the phosphoric acid concentrations, which were 2, 4, and 8 M, respectively.

2.2. Characterization of precursors and AC samples

Chemical surface composition and state of the samples were determined by elemental analysis and X-ray photoelectron spectroscopy (XPS). Analyses of C, H, N, and O content in all samples were done using CHNOS Elemental Analyzer Vario EL III (Elementar Analysensysteme GmbH, Germany). XPS was performed on an Axis Ultra (Kratos Analytical Ltd. UK) using a monochromatic Al Kα radiation (1486.7 eV). The acceleration tension and power of X-ray source were 15 kV and 225 W, respectively. The sample charging was corrected by using the C1s peak (284.6 eV) as an internal standard. The surface atomic ratios were calculated from the ratio of the corresponding peak areas after correction with Vision (PR2.1.3) and CasaXPS (2.3.12Dev7).

Scanning electron microscopy (SEM) investigations were carried out on S-3400 N (Hitachi). The X-ray diffraction (XRD) patterns were acquired on a XRD-6000 (SHIMADZU) diffractometer operating at 40 kV and 20 mA using Cu Kα radiation ($\lambda = 1.5406$ Å). Raman spectra were recorded with LABRAM HR EVOLUTION (HORIBA) at 473 nm with a charge-coupled device detector.

The BET surface area, pore volume, and pore diameter of ACs were determined from the corresponding N_2 adsorption-desorption isotherms obtained at -196 °C with an automatic instrument (ASAP 2010, Micromeritics). Prior to the adsorption measurements, all samples were outgassed in vacuum at 300 °C for 11 h. The specific surface area (S_{BET}) was determined by the Brunauer-Emmett-Teller (BET) method. The total pore volume was calculated from the N_2 adsorption isotherm at a relative pressure of 0.995. The micropore volume and mesoporous surface area were measured by the V-t method and Barrett-Joyner-Halenda (BJH) method, respectively. The pore size distribution was calculated by means of the Density Functional Theory (DFT).

2.3. Fabrication of the supercapacitors and electrochemical testing

Electrodes used for fabrication of supercapacitors were prepared by mixing AC, acetylene black, and polytetrafluoroethylene (PTFE) in a mass ratio of 87:10:3. Next, the resulting mixture was coated onto a nickel foam (square, about 1 cm^2) substrate and dried in an oven at 105 °C for over 4 h. To investigate the electrochemical behavior of the as-prepared samples,