Materials Research Bulletin 64 (2015) 327–332

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Facile preparation of nitrogen-doped porous carbon from waste tobacco by a simple pre-treatment process and their application in electrochemical capacitor and CO_2 capture

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ARTICLE INFO

Article history:
Received 14 May 2014
Received in revised form 10 December 2014
Accepted 4 January 2015
Available online 6 January 2015

Keywords:
Carbon materials
Biomass
Carbonization
Electrochemical capacitor
CO_2 capture

ABSTRACT

Preparing nitrogen-doped porous carbons directly from waste biomass has received considerable interest for the purpose of realizing the atomic economy. In this study, N-doped porous carbons have been successfully prepared from waste tobaccos (WT) by a simple pre-treatment process. The sample calcinated at 700 °C (WT-700) shows a micro/meso-porous structures with a BET surface area of $1104\,m^2\,g^{-1}$ and a nitrogen content of ca. 19.08 wt.% (EDS). Performance studies demonstrate that WT-700 displays $170\,F\,g^{-1}$ electrocapacitivity at a current density of $0.5\,A\,g^{-1}$ (in 6 M KOH), and a CO_2 capacity of $3.6\,mmol\,g^{-1}$ at 0 °C and 1 bar, and a selectivity of ca. 32 for CO_2 over N_2 at 25 °C. Our studies indicate that it is feasible to prepare N-enriched porous carbons from waste natural crops by a pre-treatment process for potential industrial application.

1. Introduction

Porous carbons have received considerable interest because of their high surface area, excellent chemical stability and electro conductivity [1–8]. Depending on the carbon sources and synthetic methods, various porous carbons have been prepared during the past decades, which have shown controllable structures and tunable pore sizes [9–12]. Although these features greatly promote their performance [13–16], the intrinsic chemical inertness limits their wide application such as in oxygen reduction reaction, pseudo-Faradaic reactions, CO_2 adsorption and separation. In this regard, it is urgently desired to develop functionalized porous carbons. Nitrogen-doped porous carbons have gained an increasing interest, since the incorporation of nitrogen into aromatic/graphitic carbons indeed contributes to the enhancement of electrical conductivity [17,18], oxidation reduction [19–22] and surface properties (surface polarity and base sites) [23–27], as well as electro-donorability of the carbon matrix [28–30]. Consequently, it remarkably boosts their potential applications.

Previously reported N-doped carbon materials are commonly synthesized via bottom–up strategy, by either in-situ doping [12,18,27,31,32] or post-treatment [23,24,33–35]. Although samples with uniform pore structures and high nitrogen contents could be achieved in this way, the complex steps greatly limit their wide industrial preparation. Moreover, many other factors such as the preparation procedure, the precursor used, and kinds of surfactants could also affect the performances of N-doped porous carbons [12,18,34]. Therefore, preparation of carbon materials from naturally cheap occurring sources becomes a hot topic [36], in which preparing porous carbons from various waste biomasses has drawn considerable interest in recent years. For example, porous carbons with specific surface areas could be prepared from polysaccharides and saw dust, bamboo and so on [37–43]. However, the isolated products either show low surface areas or negative nitrogen content. Actually, in order to prepare N-doped carbon materials from waste biomass, it is necessary to have abounded of inherited nitrogen precursors. Tobacco is a kind of natural crops with high content of alkaloid. Nicotine is the principle alkaloid present in tobacco, serving as the nitrogen precursors. Even in waste tobacco (WT), there still contains high levels of nicotine [44]. When tobacco plant is harvested, its stems and some leaves are usually not used for the production of cigarette, and they are simply decayed in soil without treatment. It is toxic and highly soluble in water, which causes serious pollution in this field, making it the main limiting factor for the disposal.

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http://dx.doi.org/10.1016/j.materresbull.2015.01.015
0025-5408/

Therefore, investigating alternative ways to manage WT, during which a value can be recovered, becomes an important issue. Although numerous ways have been previously explored for preparing porous carbons from WT [45–48], it is still hampered by the low nitrogen content at high carbonization temperature.

We have successfully prepared functional carbon materials from various crude biomass [49,50]. In this paper, we report the preparation of N-doped porous carbons with specific surface area and nitrogen content using waste tobacco as raw materials by a simple pre-treatment process with melamine. Three kinds of samples calcinated at 500, 700, 900 °C were prepared respectively and characterized by FT-IR, TG, PXRD, SEM, TEM, XPS and N_2 sorption. The results demonstrate that the sample carbonized at 700 °C (WT-700) shows a BET surface area of 1104 $m^2\,g^{-1}$, and with a nitrogen content of ca. 19.08 wt.% (EDS). Performance studies demonstrate that WT-700 displays 170 $F\,g^{-1}$ electrocapacitivity at a current density of 0.5 $A\,g^{-1}$, which is much higher than that of WT-900 (116.7 $F\,g^{-1}$) and WT-500 (53.3 $F\,g^{-1}$). Furthermore, the WT-700 shows a CO_2 capacity of 3.6 $mmol\,g^{-1}$ at 0 °C and 1 bar, isosteric heat of 28.6 $kJ\,mol^{-1}$, and a selectivity of 32 for CO_2 over N_2 at 25 °C.

2. Experimental

2.1. Sample preparation

The waste tobacco (WT) used in this study was directly obtained from Shanghai Cigarette Factory, which includes tobacco stems and leaves collected from tobacco field. Other chemicals were purchased from commercial sources. In a typical preparation procedure: (1) the waste tobacco were soaked into distilled water at room temperature under ultrasound condition for 30 min for making the surface clean. Then the precursors were collected by filtration and dried in vacuum condition at 60 °C for 2 h; (2) pre-treatment: 5 g of milled precursors (in millimeter scales, manually grinded in a mortar with grinding time of 20–30 min, before grinding raw materials were cut into pieces.) was added into solution of methanol (200 mL) containing melamine (1 g), then the mixture was stirred at room temperature until methanol was full evaporated; (3) pyrolysis: the precursors were loaded on a ceramics boat, in which a stainless steel tubular reactor was placed inside. Then, it was heated up to a carbonization temperature (500, 700, 900 °C) with a heating rate of 1 $K\,min^{-1}$ and was held at this temperature for 1 h under N_2 gas (99.9%) flow, followed by cooling down to room temperature under N_2 flow. The carbonized samples were washed with 3×50 mL HCl (2 M), 3×50 mL HNO_3 (1 M), and then 3×50 mL distilled water in sequence, finally the products were obtained by filtrated and dried at 80 °C, which denoted as WT-500, WT-700 and WT-900, respectively. About 8 wt.% weight loss was observed before and after sample acid washing, which could mainly be ascribed to the weight loss caused by filtration, sample transferring and leaching of metal ions.

2.2. Sample characterization and measurements

IR spectra were measured on a Nicolet 470 FT-IR spectrometer in the range of 4000–400 cm^{-1} with KBr pellets. Thermogravimetric analyses (TGA) were carried out using a METTLER TOLEPO TGA/SDTA851 analyzer under air flow with a heating rate of 10 °C min^{-1}. Elemental analysis was measured on Vario EL III (Elementar, Germany). X-ray diffraction (XRD) patterns were recorded on a Bruker D8 X-ray diffractometer (Germany) with Cu Kα radiation (40 kV, 40 mA). XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (PerkinElmer) with Mg Kα radiation ($h\nu = 1253.6$ eV). Binding energies were calibrated by using the containment carbon (C1s = 284.6 eV). Field-emission scanning electron microscopy (FE-SEM) images were collected on the Hitachi Model S-4800 field emission scanning electron microscope (Japan) and the samples without further gold-spraying treatment were used for the observations. EDS (QUANTAX 400, Bruker) is adopted to analyze the content of elements. Mapping images were also taken by SEM to analyze the distribution of nitrogen atom. Transmission electron microscopy (TEM) experiments were performed on a JEOL Model 2011 microscope (Japan) operated at 200 kV.

Gas adsorption property was measured on ASAP 2020 gas adsorption analyzer. Before the measurements, all samples were degassed at 200 °C for 8 h. The surface areas (S_{BET}) were calculated based on the Brunauer–Emmett–Teller (BET) method with the sorption data of N_2 obtained at −196 °C. The sorption data of CO_2 at 0 and 25 °C, and N_2 at 25 °C were used to assess their gas sorption and separation property.

The electrode was prepared by mixing active materials (85 wt.%), carbon black (10 wt.%), and poly(tetrafluoroethylene) (PTFE) binder (5 wt.%) in isopropanol solution. The above slurries were pasted onto a nickel foam (1×1 cm^2) and then dried at 120 °C for 12 h to remove the isopropanol and water. The typical mass load was about 5 $mg\,cm^{-2}$. Cyclic voltammetry (CV), electrochemical impedance spectroscopy and charge–discharge tests were carried out at room temperature using a three-electrode glass cell, in which platinum and $Hg/HgCl_2$ electrodes were used as the counter and reference electrodes, 6 M KOH solution was used as the electrolyte, respectively. The experiments were performed using an electrochemical analyzer, CHI 606B under ambient conditions.

3. Results and discussion

3.1. Characterization and Structure

FT-IR measurements clearly show the sorption bands around 3145, 2933, and 1612 cm^{-1} for raw material [44], which could be ascribed to the asymmetric stretching vibration of O—H (H_2O), C—H (alkyl groups), O—C=O (carboxylate group), respectively. After carbonization, these sorption bands disappeared, and only the weak band located between 1500 and 1600 cm^{-1} was remained, which could be attributed to the C=C stretching vibrations, confirming the disappearance of organic species after thermal treatments (Fig. S1). TGA data of WT shows a continuous weight loss in the whole temperature range (Fig. S2) [44,45]. In contrast, WT-500, WT-700 and WT-900 show a weight loss in the temperature range of 30–150 °C respectively, which could be ascribed to the release of physical adsorbed guests, after that it follows a plateau from ~150 to ~400 °C, respectively. Then a huge weight loss is observed, indicating the structural collapse in air condition. It could be concluded that WT-700 and WT-900 show better thermal stability compared with that of WT-500 from the TGA data. The amorphous phase of these three samples were confirmed by PXRD patterns (Fig. S3). Two typical broad peaks at 2θ values of approximately 25° and 43° respectively for WT-500, WT-700, and WT-900, which could be ascribed to the (0 0 2) and (1 0) planes of turbo stratic carbon, respectively. Generally, the reflection (0 0 2) attributes to the interlayer reflections among irregularly oriented polycyclic aromatic C sheets of amorphous carbon, and the reflection (1 0) is attributed to the in-plane two-dimensional diffraction of graphene sheets.

Irregular bulk solids with the size ranged from a few to dozens microns are observed from the SEM images (Fig. 1 and Fig. S4a). The glossy surface can be observed for WT-500, whereas the degree of surface roughness gradually increases for WT-700 and WT-900. The roughness could be ascribed to the increase of the carbonization temperature. TEM images further identify the differences