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Spent coffee grounds derived P, N co-doped C as electrocatalyst for supercapacitor applications

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ABSTRACT

Spent coffee grounds, an abundant daily waste, were utilized to produce P, N co-doped C (PNDC) by a novel microwave-assisted method employing ammonium polyphosphate as the only other reactant. Different PNDCs (namely PNDC-1, PNDC-2 and PNDC-3) were synthesized by varying the ratio of spent coffee grounds to ammonium polyphosphate. The synthesized materials were found to contain spherically shaped particles as evidenced from scanning electron microscopy. X-ray photoelectron spectroscopy revealed PNDCs to contain P and N in addition to C and O. PNDC-3 was discovered to possess a surface area of 999.64 $m^2 g^{-1}$ with the presence of micropores, mesopores and macropores. PNDCs exhibited high specific capacitance values in acid and alkaline conditions with PNDC-3 exhibiting the highest specific capacitance value of 286 $F g^{-1}$ in 1 M H_2SO_4. Also, PNDC-2 was observed to be highly stable under acidic and alkaline conditions with continuous cycling.

1. Introduction

Along with a growing global population, the demand for energy has continued to grow rapidly. Currently, energy largely comes from non-renewable fossil fuel sources and the limited reserves of fossil fuels are being depleted at an alarming rate, which creates a demand for alternate energy sources in order to sustain our ever-growing energy demands. This has warranted the necessity of using renewable, natural resources for energy generation and storage and therefore, the development of low cost, sustainable energy conversion and storage technologies has become a primary motive for researchers today.

Supercapacitors have been established as a superior means of economically storing energy [1,2]. They have high power density than batteries and high energy density than traditional dielectric capacitors [3]. Supercapacitors also have high lifetime cycling, which enables them to be used over a very long period of time [4,5]. These characteristics are a consequence of the high surface area, excellent electrical conductivity, good thermal conductivity and porosity of the electrode material [6]. There are two known mechanisms by which a supercapacitor can store electrical energy. The primary mechanism in supercapacitor energy storage is the electrical double-layer capacitance (EDLC). In general, EDLC is due to the electrostatic separation of charges across the electrode-electrolyte interface. This is essentially a molecular dielectric. In a supercapacitor, this facilitates the need for high porosity and a high surface area. This charge separation occurs within the carbon material, and is present at both electrodes. The second mechanism for storage is the phenomenon of pseudocapacitance. This method of storing charge is accomplished by a reversible faradic redox process, due to an electron transfer reaction between the electrode and the electrolyte [7].

Recent research has shown that many different carbon-based materials have high capacitance capabilities. Such materials include carbon nanorods, single/muti-walled carbon nanotubes, conducting polymers, nanosheets, and melamine based carbon [8–13]. However, it has been discovered that highly porous carbon based materials produce the most promising supercapacitor materials [14,15]. Graphene is a carbon material that has shown favorable results for capacitance due to its high porosity and conductivity [16,17]. However, its electrical performance is limited due to the absence of a band gap [18]. This limitation can be eliminated by the presence of metals or nonmetals doped into the carbon lattice.[19] Many common non-metal dopants used are N, [20–25] O,[23] P,[26,27] B,[18,28] S,[29] and Si [30–32]. Doped carbons exhibit better electrocatalytic activity compared to their un-doped counterparts due to their altogether different properties like electrical conductivity, band gap, porosity and others [21]. Double doping can especially enhance the electrochemical performance of the supercapacitor by breaking the electro neutrality of the carbons and making them catalytically active [17,33,34].

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There are many processes that have been established to develop doped carbon materials, for example, chemical vapor deposition, arc discharge, nitrogen plasma, and template guided synthesis [35,36]. However, the most common method for the development of these materials remains pyrolysis of precursor materials at high temperatures for an extended period of time (6–8 h) in the presence of reducing gases [37]. Such processes are not ideal, for they are expensive, time consuming, low yielding and require specialized equipment [38]. However, we report a microwave assisted process which is rapid, easy, economical, environmentally friendly, and can produce doped carbon in only 30 min [39–41].

As one of the most highly consumed beverages around the world, coffee amounts to the production of a considerable amount of waste. In the year 2000 alone, the global consumption of coffee beans amounted to over 6 million tons [42]. Considering the amount of waste that is being produced, efforts have been made to reuse spent coffee grounds for energy production [43,44]. The main constituent of coffee grounds is carbon, 51.31%, but it also has a significant nitrogen content, 2.14% (with C to N ratio of 24:1) [45]. In this project, ammonium polyphosphate was used as a microwave absorber, dehydrating agent and a source of phosphorus and nitrogen dopants. Herein, we report the synthesis of a novel Phosphorus, Nitrogen co-doped carbon (PNDC) using spent coffee grounds, as an electrode material for supercapacitor applications.

2. Experimental

2.1. Materials

Spent coffee grounds were obtained from a local coffee shop, dried and powdered after received. Ammonium polyphosphate was obtained from JLS Chemicals, China. All the chemicals obtained were of analytical grade and were utilized without further purification.

2.2. Method of synthesis

All PNDCs were synthesized by a novel microwave-assisted method. A 1.0 g sample of powdered spent coffee grounds was mixed with pre-determined amounts of ammonium polyphosphate in a mortar and pestle. The contents were then transferred to a crucible (boron nitride crucible) and microwaved with a similar cap and Al_2O_3 cover in an Al_2O_3 muffle with lid for 30 min in a commercial table top microwave oven operating at 2.45 GHz and 1.25 KW power. During the microwave treatment process temperatures greater than 1000 °C were believed to be achieved resulting in the breakdown of biomass (spent coffee grounds), thereby generating reducing gases which assist in the carbonization process. After the microwave duration, the product was allowed to cool in the oven for about 2 h, after which the product was recovered, weighed and powdered in a mortar and pestle. The amounts of precursor materials utilized in developing PNDCs and the products recovered are summarized in Table 1. Each PNDC has been synthesized three times and the results obtained (seen in Table 7) exhibit high degree of conformity.

Table 1
Summary of amount of precursor materials used in synthesizing PNDCs and the corresponding yields obtained.

Sample	Spent coffee grounds (g)	Ammonium polyphosphate (g)	Product (g)
PNDC-1	1.0	0.2	0.22 ± 0.01
PNDC-2	1.0	0.4	0.16 ± 0.01
PNDC-3	1.0	0.8	0.15 ± 0.01

2.3. Characterization of PNDCs

The synthesized PNDC materials were extensively studied by different characterization techniques. Morphology (size and shape) of the materials were studied by JEOL 7000F Scanning Electron Microscope. To understand the different vibrational modes of carbon in PNDC materials, Raman spectra were recorded using Horiba Jobin Yvon LabRam 800 equipped with 633 nm He–Ne laser. Surface elemental composition and bonding environments of elements in PNDCs were studied using Thermo K-alpha X-ray Photoelectron Spectrometer (Source - Al Kα radiation, 1486 eV, 12 kV, spot size - 200 μm, and carbon internal standard at 284.8 eV). Surface area and porosity analysis of PNDCs were performed using Micromeritics Surface Area Analyzer ASAP-2020 by nitrogen (N_2) sorption on powdered samples using Brunauer–Emmett–Teller (BET) method at a bath temperature of 77.3 K.

2.4. Electrochemical methods

A three electrode system was utilized to perform cyclic voltammetric studies using AFCBP1 bipotentiostat from Pine Instrument Company in both aqueous 1 M H_2SO_4 and aqueous 6 M KOH. A glassy carbon electrode (5 mm diameter and 0.196 cm^2 geometric area) enclosed in a polytetrafluoroethylene holder was chosen as the working electrode and a Pt wire as the counter electrode. In 1 M H_2SO_4 electrolyte solution, a Ag/AgCl reference electrode was used and in 6 M KOH, a Hg/HgO reference electrode was used. To minimize the interference due to O_2, N_2 gas was purged through the electrolytic solution for atleast 1 h before the studies were performed and a continuous N_2 flow above the electrolyte was maintained during the studies. The glassy carbon electrode was cleansed several times using distilled water followed by polishing the surface using 0.05 μ alumina. A 1 mL ethanol suspension of active material, carbon black and polytetrafluoroethylene (PTFE) in a mass ratio of 90:5:5 was made by sonication using an ultrasound for 2 h. A 10 μL sample of the prepared catalyst suspension was drop-casted onto glassy carbon electrode, air dried, followed by an additional 10 μL, air dried and finally dried in a vacuum oven. Cyclic voltammograms were recorded at scan rates ranging from 5 mV s^{-1} to 100 mV s^{-1} in a potential range of 0 to 800 mV in 1 M H_2SO_4 and −800 to 0 mV in 6 M KOH.

Specific capacitance (C_s) and interfacial capacitance (C_i) values were calculated from cyclic voltammograms recorded in both acid and alkaline conditions based on the following equations:

$$C_s = \int i(dV)/V.m.\ \nu = Q/\Delta V.m = \int idt/\Delta V.m = i\Delta t/\Delta V.m$$

$$C_{s,total} = (C_{anode} + C_{cathode})/2 \quad (1)$$

$$\text{and } C_i = (C_{s,total} / S_{BET}) \quad (2)$$

where i is the current density, V is the potential applied, Q is the charge generated, m is the mass of the active material, ν is the potential scan rate and S_{BET} is the surface area of the active material determined by BET method.

3. Results and discussion

3.1. Scanning Electron Microscopy (SEM)

SEM images of PNDC-1, PNDC-2 and PNDC-3 can be seen in Fig. 1 with enlarged view shown in inset. All the PNDCs exhibit more or less ordered morphology with some spherical shaped