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Heteroatom-doped porous carbon electrodes derived from a carbonyl-based aromatic porous polymer for supercapacitors

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ABSTRACT

Two different heteroatom-doped microporous carbon materials, c-CBAP-N (nitrogen-doped) and c-CBAP-NS (nitrogen/sulfur co-doped), were prepared using a carbonyl-based aromatic porous polymer (CBAP) after amine-functionalization or chemical impregnation, followed by carbonization at 800 °C. The surface areas of c-CBAP-N and c-CBAP-NS were 1060 $m^2\ g^{-1}$ and 1047 $m^2\ g^{-1}$, respectively, which are predominantly microporous with a uniform pore size distribution centered at 0.4 nm. Their electrochemical performances as supercapacitors were measured by a three-electrode system using a 6 M KOH solution as the electrolyte. The specific capacitances of the c-CBAP-N and c-CBAP-NS electrodes were 203.2 F g^{-1} and 157.7 F g^{-1}, respectively, as measured by galvanostatic discharge–charge analysis at a current density of 1 A g^{-1}. Notably, these values are significantly higher than that of commercial activated carbon (130 F g^{-1} at 1 A g^{-1}).

1. Introduction

Supercapacitors are promising energy storage devices owing to their high-power density, excellent rate capability, and long cycle-life stability [1–3]. Activated carbons have been primarily used as supercapacitor electrode materials due to their high surface area and pore volume, ease of processability, and chemical stability [4,5]. Despite these intrinsic properties, however, the low energy density of carbon-based supercapacitors has been a major limitation, because activated carbon electrodes often suffer from isolated and irregular pore tunnels, resulting in insufficient accessibility of the electrolyte ions into the pores [6,7]. Consequently, the specific capacitance of activated carbon supercapacitors has often been limited to below 120 F g^{-1} [8,9].

To solve this problem, the relationship between the geometry of a carbon material or its porous structure and the specific capacitance of supercapacitors has been rigorously investigated. Carbon structures with spherical morphologies provide a fixed geometry, controllable porosity, and particle size that are better than carbon powders and flakes [10,11]. Further, supports with stacked porosity provide good pathways for the electrolyte ions to enter the active sites of the electrodes, leading to enhanced electrochemical performance [12]. Moreover, the micropores (< 2 nm) in carbon materials have a significant effect on anomalous ion adsorption; when solvated electrolyte ions enter carbon pores with diameters less than 1 nm, distortion or desolvation of the solvated ion shell occurs, which contributes to double-layer charge storage and results in excellent capacitive behavior [13–16].

Heteroatom doping on the carbon surface is another method employed to achieve high specific capacitance in aqueous systems [17]. Generally, carbon materials have inert surfaces because of the high temperature carbonization process to which they are subjected. The resultant surfaces hinder the electrolyte from entering into the carbon interior to form an electrochemical double-layer [17,18]. Consequently, doping carbon materials with nitrogen has been regarded as a promising approach to improve their surface wettability, electric conductivity, and capacitance properties [19,20]. Doping with heteroatoms such as sulfur and boron has also been reported to influence the electronic properties of the material; specifically, changes to the spin densities and charge distribution of the heteroatoms among the adjoining carbon atoms were found to improve the formation of electro-catalytic active sites for higher capacitance [21,22]. Therefore, a microporous, heteroatom-doped structure with regular porosity is expected to lead to high-performance supercapacitors. Recently, several nitrogen-doped porous carbons for supercapacitor applications have been reported. Zhao and Han have produced nitrogen-doped porous carbon derived from porous organic frameworks (POFs) with high surface area in nitrogen-doped structures prepared via a Schiff base reaction; porous carbons for supercapacitors were obtained after pyrolysis and demonstrated good electrochemical performances [23,24].

In this contribution, two heteroatom-doped porous carbon materials

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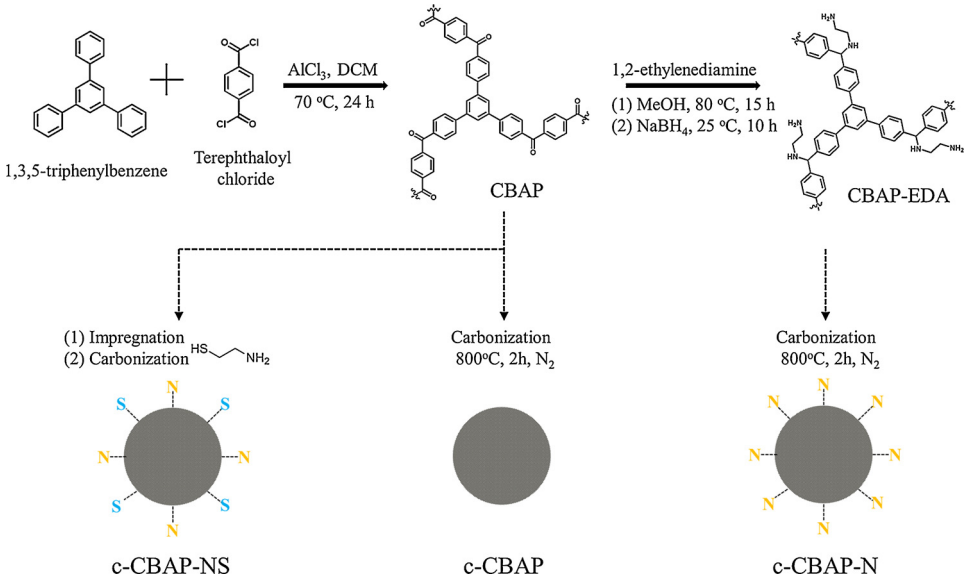

Scheme 1. Procedure for fabricating various porous carbon materials derived from carbonyl-based aromatic polymers.

(nitrogen or nitrogen/sulfur co-doping) for use as supercapacitor electrodes were prepared. Firstly, a porous carbonyl-based aromatic polymer (CBAP) was synthesized via a simple $AlCl_3$-catalyzed Friedel–Crafts benzoylation reaction using cost-effective monomers (i.e., terephthaloyl chloride (TC) and 1,3,5-triphenylbenzene). Heteroatom-doped structures were then obtained by either amine-functionalization via a Schiff base reaction or impregnation using 2-aminoethanethiol, followed by carbonization at 800 °C in a nitrogen atmosphere. The resultant carbonized materials, featuring a high surface area (exceeding 1000 $m^2 g^{-1}$), narrow pore size distribution, and sufficient heteroatom incorporation, exhibited promising electrochemical performance.

2. Experimental

2.1. Materials

Terephthaloyl chloride (TC), 1,3,5-triphenylbenzene, anhydrous $AlCl_3$, 1,2-ethanedithiol, sodium borohydrate, polytetrafluoroethylene, dichloromethane (DCM), and methanol were purchased from Sigma Aldrich (USA). Biphenyl, 1,2-ethylenediamine, and 2-aminoethanethiol were acquired from TCI (Japan). Potassium hydroxide (KOH) was supplied from Ducksan Chemical (South Korea). Carbon black (Vulcan XC 72) was obtained from Cabot, USA. All solvents were used without further purification.

2.2. Synthesis of a carbonyl-based aromatic polymer

A carbonyl-based aromatic polymer (CBAP) network was synthesized by a Friedel–Crafts reaction between TC and 1,3,5-triphenylbenzene using anhydrous $AlCl_3$ as a catalyst, as described earlier [25]. A 250 mL round bottom flask was filled with 1,3,5-triphenylbenzene (10 mmol, 3.06 g), TC (15 mmol, 3.05 g), and DCM (180 mL) and purged with nitrogen gas for 15 min. Anhydrous $AlCl_3$ (30 mmol, 4.00 g) was added slowly while the mixture was refluxed at 70 °C for 24 h. When the reaction was completed, the precipitated materials were filtered and rinsed sequentially with DCM, methanol, and water. The collected products were further purified in a Soxhlet extractor for 24 h using water to thoroughly remove the catalyst. The dark brown solid (CBAP) was collected after drying under vacuum at 130 °C for 24 h.

2.3. Amine- functionalization of CBAP

Amine-functionalization of CBAP was carried out following the procedure where CBAP (1.00 g) was placed into a reactor containing a mixture of EDA (2 mL) dissolved in methanol (40 mL) followed by reflux at 80 °C for 15 h under vigorous stirring. After reflux, the mixture was cooled to 25 °C and the resulting Schiff base intermediate was reduced with excess $NaBH_4$ (ca. 2.00 g). After stirring at 25 °C for 10 h, the product was filtered and rinsed with methanol and water. The collected powders were dried under vacuum at 130 °C for 12 h and dark brown CBAP-EDA incorporated with 12.9 wt% nitrogen (Table S1) was acquired.

2.4. Impregnation and carbonization procedure

CBAP or CBAP-EDA (1.00 g) was loaded in an alumina boat and placed in a tubular furnace, where the temperature was increased to 800 °C at a rate of 5 min^{-1} in a nitrogen atmosphere (100 mL min^{-1}). Once 800 °C was reached, the temperature was maintained for 2 h and then cooled to 25 °C. The obtained carbon materials were designated as c-CBAP (porous carbon) and c-CBAP-N (nitrogen-doped porous carbon). For the nitrogen/sulfur co-doped carbon structure, CBAP (1.00 g) was added to an acetonitrile solution (20 mL, ACN) together with 2-aminoethanethiol (1.00 g), and the mixture was stirred at 25 °C for 6 h. The product was dried in a vacuum oven at 80 °C for 5 h. Carbonization was then conducted in a tubular furnace as before. The resultant carbon solid was designed as c-CBAP-NS (nitrogen/sulfur co-doped porous carbon).

2.5. Characterization of the prepared carbon materials

The morphology of the prepared porous carbon materials was examined by high-resolution scanning electron microscopy (HR-SEM, SU 8010, Hitachi, Japan). Before the SEM measurements, all samples were sputter-coated with platinum for 2 min. The specific surface area and pore size distribution were measured by nitrogen adsorption and desorption isotherms obtained from a BELSORP-MAX (BEL, Japan) instrument using Brunauer–Emmett–Teller (BET) theory and non-local density functional theory (NLDFT), respectively. The chemical composition of the polymer or the carbon surface and structure were detected by X-ray photoelectron spectroscopy (XPS, Thermo-scientific, ESCA 2000, USA) with monochromatic Al–Kα radiation (hυ = 1486.6 eV),