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Supplementary Materials

Sustainable Synthesis of N/S-Doped Porous Carbon from Waste-Biomass as Electroactive Material for Energy Harvesting

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Abstract: It is absolutely essential to convert biomass waste into usable energy in a rational manner. This investigation proposes the economical synthesis of heteroatom (N and S)-doped carbon (ATC) from *Aesculus turbinata* seed as a natural precursor by carbonization at 800 °C. The final product obtained was characterized using field emission scanning electron microscopy with energy-dispersive X-ray spectroscopy, high-resolution transmittance electron microscopy, X-ray diffraction, Raman spectroscopy, nitrogen adsorption-desorption isotherms, attenuated total reflectance Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy in order to investigate its structural property and chemical composition. The porous carbon achieved by this method contained oxygen, nitrogen, and sulfur from *Aesculus turbinata* seed and had pores rich in micropores and mesopores. Crystalline ATC obtained with a high surface area (560 m^2 g^{-1}) and pore size (3.8 nm) were exploited as electrode material for the supercapacitor. The electrochemical studies revealed a specific capacitance of 142 F g^{-1} at a current density of 0.5 A g^{-1} using 1 M H_2SO_4 as an electrolyte. ATC had exceptional cycling stability, and the capacitance retention was 95% even after 10,000 charge-discharge cycles. The findings show that ATC derived from biomass proved to be a potential energy storage material by converting waste biomass into a high-value-added item, a supercapacitor.

Keywords: *Aesculus turbinata*; waste-biomass; porous carbon; supercapacitor; energy harvesting

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Materials

Seeds of *Aesculus turbinata* were obtained from the Yeungnam University Campus, Republic of Korea. Sigma-Aldrich, Republic of Korea, supplied N-Methyl-2-pyrrolidone (NMP), polyvinylidene fluoride (PVDF), and sulfuric acid (H_2SO_4). Duksan, Republic of Korea, supplied the nitrogen gas. FuelCellStore in the United States supplied the carbon cloth (CC) electrode. All of the chemicals were used exactly as they were purchased, and distilled water was used across the experiment.

Instrumentation Methods

The *Aesculus turbinata* seed-derived carbon (ATC) was characterized by various physicochemical techniques such as field emission scanning electron microscopy (FESEM)

with energy-dispersive X-ray spectroscopy (EDS), high-resolution transmittance electron microscopy (HRTEM), X-ray diffraction (XRD), Raman spectroscopy, nitrogen adsorption-desorption isotherms, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). FESEM with EDS analysis was carried out on a Hitachi S-4800 equipped with EDX at an accelerating voltage of 10 kV. TEM/HRTEM images were performed with an FEI-Tecnai TF-20 transmission electron microscope with an operating accelerating voltage of 120 kV. XRD measurements were made with a PANalytical X'Pert3 MRD diffractometer using monochromatized Cu Kα radiation (λ = 1.54 Å) at 40 kV and 30 mA in the range of 10 to 80° (2 θ). At Yeungnam University's key research support centre for natural products and medical materials, the Raman spectrum was measured on an XploRA Micro-Raman spectrophotometer (Horiba) with a range of 50 to 4000 cm^{-1}. Micromeritics ASAP 2000 was used to measure nitrogen physisorption isotherms at −197 °C. Prior to the analysis, the samples were dried at 120 °C and evacuated for 8 hours at 140 °C in streaming argon at a flow rate of 60 standard cubic centimeters per minute. The Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) equations were used to calculate surface area, pore size, and pore volumes from isotherms. ATR-FTIR spectra in the wavenumber range of 400 to 4000 cm^{-1} were obtained in transmittance mode on a Perkin Elmer Spectrum Two by the addition of 8 scans at a resolution of 8 cm^{-1}. Thermo Scientific's K-Alpha was used to get XPS spectra. The high-resolution XPS spectra were deconvolved using CasaXPS software.

Fabrication of Working Electrode and Electrochemical Measurements

The working electrodes were made from the ATC that had been created. ATC and polyvinylidene fluoride (PVDF) with wt. % of 95 and 5 were crushed well in an adequate amount of N-methyl-2-pyrrolidone (NMP) to create a homogenous paste, respectively, to fabricate the working electrode. The resulting homogeneous paste was applied to a 1 cm^2 area on the CC, and the electrodes were then dried in a hot air oven at 100°C for 24 hours. The supercapacitor activity of the upgraded working electrodes was tested after fabrication. All electrochemical experiments, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), were done on the CorrTest-CS350 electrochemical workstation using 1 M H_2SO_4 solution as electrolyte.

The reference electrode was a commercial Hg/Hg_2SO_4 (Sat. K_2SO_4) electrode, the counter electrode was a platinum plate (1 cm^2), and the working electrode was ATC loaded CC (ATC-CC), respectively. The CV measurements were performed in a potential window ranging from -0.3 to 0.5 V (vs. Hg/Hg_2SO_4) and at various scan rates ranging from 5 to 100 mV s^{-1}. GCD tests were performed out with a potential window ranging from -0.3 to 0.5 V (vs. Hg/Hg_2SO_4) and current densities ranging from 0.5 to 3 A g^{-1}. EIS measurements were made with an alternating current amplitude of 5 mV in the frequency range of 0.01 kHz–10 kHz. At room temperature, all electrochemical tests were carried out for specific capacitances (C_s) of the capacitors.

The specific capacitances (C_s) of the electroactive materials were calculated using the following equation and their GCD curves (S1).

$$C_s = \frac{I\Delta t}{m\Delta V} \qquad \text{(S1)}$$

whereas C_s is the specific capacitances, I is the current in the charge-discharge process (A), Δt represents the discharge time (s), ΔV stands for the potential window during the charge-discharge measurement (V), and m donates the mass of the electroactive materials (g).