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Nitrogen-doped bi-modal porous carbon nanostructure derived from glycine for supercapacitors

In-Ae Choi[1], Da-Hee Kwak[1], Sang-Beom Han, Kyung-Won Park*

Department of Chemical Engineering, Soongsil University, Seoul 156743, Republic of Korea

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ABSTRACT

We prepared a nitrogen-doped bi-modal porous carbon nanostructure (G-500/20) using a template method with 500 and 20 nm SiO_2 beads and glycine. The G500/20 has a surface area of 403 $m^2 g^{-1}$ with meso/macroporous structure and N-doping content of 5.9 at%. In the supercapacitor performance, G-500/20 exhibits superior specific capacitances of 19.5 and 5.3 $F g^{-1}$ at 200 mV s^{-1} and 20 A g^{-1} in 6 M NaOH, compared to a commercial activated carbon. In particular, the superior capacitances of G500/20 at high scan rates and current densities were achieved due to the bi-modal porous structure and nitrogen doping effect.

Introduction

Supercapacitors, used as energy storage devices, have attracted attention due to their high power density, excellent reversibility, and long cycle life [1–4]. In general, according to the charge storage mechanism, supercapacitors are classified into either electrochemical double layer capacitors (EDLCs) or pseudo-capacitors [2]. In the case of EDLCs, the electrical energies can be stored by the electrostatic charge at an interfacial region between the aqueous or non-aqueous electrolytes and the electrode [2,3]. The electrode materials require a highly effective surface area and pore structure that can accumulate mobile ions in the electrolytes. In particular, carbon materials have been used for supercapacitors due to their electrochemical stability, excellent conductivity, and well-defined porosity [5,6]. Porous carbon nanostructured materials, such as activated carbons, carbon nanotubes, and, carbon nanofibers, have usually been utilized as electrode materials in high-performance EDLCs [2,7–9]. In the porous structure, the micropores (<2 nm) provide a highly effective surface area for increased double layer capacitance and the mesopores (2–50 nm) or macropores (>50 nm) can act as ion-buffering reservoirs and ion transport pathways, resulting in a decreased diffusion distance [8,10,11].

Recently, mesoporous carbon electrode materials for supercapacitors with high capacitance and good rate capability have been intensively studied. In particular, carbon nanostructures doped with heteroatoms (N, B, P, and S) exhibited enhanced supercapacitor performance comparable to undoped carbons [12–14]. The heteroatom doping containing electron-donating or electron-withdrawing properties can provide carbon materials with improved electrochemical properties in acid/base electrolytes. Moreover, the doped carbon electrodes can improve the capacitance because of the pseudocapacitive effect due to the Faradaic interaction between the ions of electrolyte and surface functional groups. Among the doped electrodes, nitrogen doping can simply control the local electronic properties and thus enhance the electrochemical performance [15]. Nitrogen-doped carbons can increase the electrical conductivity and improve the wettability of the electrode materials with an aqueous electrolyte in supercapacitors [16]. The nitrogen-doped carbons have been prepared using post heat treatment of porous carbons under a nitrogen atmosphere and in situ doping using nitrogen-containing precursors [17–19]. Herein, we prepared a nitrogen doped bi-modal porous carbon material (G-500/20) using a template method with 500 and 20 nm SiO_2 beads and glycine as a dopant and carbon source. The G-500/20 has a surface area of 403 $m^2 g^{-1}$ with a meso/macroporous structure and N-doping content of 5.9 at %. In terms of the supercapacitor performance, G-500/20 exhibits superior specific capacitances of 19.5 and 5.3 $F g^{-1}$ at 200 mV s^{-1} and 20 A g^{-1} in 6 M NaOH electrolyte, compared to a commercial activated carbon.

* Corresponding author.
E-mail address: kwpark@ssu.ac.kr (K.-W. Park).
[1] These authors equally contributed to this work.

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Experimental section

Synthesis of nitrogen-doped porous carbon nanostructures

To synthesize doped porous carbon nanostructures, glycine (0.4 g, Aldrich) as both the carbon and nitrogen sources and SiO_2 beads were mixed in 50 mL de-ionized (DI) water for 5 h with continuous stirring and sonicating 500 nm (0.4 g, Alfa Aesar) and 20 nm (0.13 g, 40% in water, Alfa Aesar) SiO_2 beads were used as porous templates. The weight ratio of the 500 nm–20 nm SiO_2 beads were 3:1. The samples prepared with 500 nm beads were denoted as G-500 and both the 500 and 20 nm beads were denoted as G-500/20. The completely dispersed mixture solutions were transferred to a glass petri dish and thoroughly dried in an oven at 50 °C for 12 h. The dried sample was loaded on a glass boat and then heated at 900 °C in a tube furnace under an N_2 atmosphere for 3 h. Followed by the pyrolysis, the sample was washed with HF solution (10 vol.%, J.T Baker) for 2 h and then with DI water several times to remove SiO_2 template and impurities. The resulting black powder was obtained by drying in a 50 °C oven for 12 h [17–19].

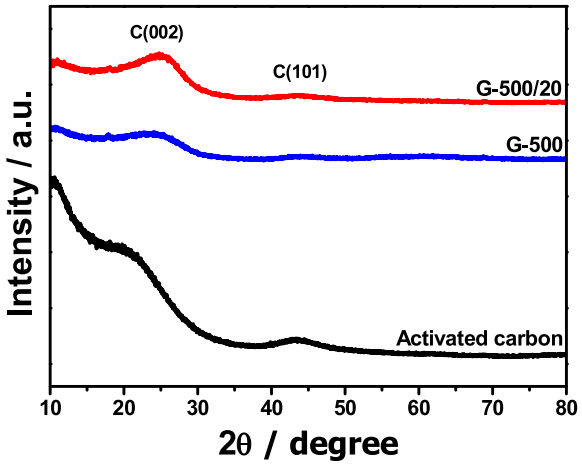

Fig. 1. XRD patterns of the as-prepared samples.

Structural characterization of nitrogen-doped porous carbon nanostructures

The morphology and structure of the as-prepared samples were characterized using field emission-scanning electron microscopy (FE-SEM, JSM-7800F, JEOL) with an accelerating voltage of 15 kV. The crystal structure of the samples was analyzed using an X-ray diffraction (XRD, D2 Phase System, BRUKER) system with a Cu K_α radiation source ($\lambda = 1.54056$ Å) and a Ni filter. The tube current and voltage were 10 mA and 30 kV, respectively. X-ray photoelectron spectroscopy (XPS, Thermo Scientific) with an Al K_α X-ray source of 1468.8 eV and power of 200 W was performed under a chamber pressure of 7.8×10^{-9} Torr in order to characterize the chemical composition of the samples. To characterize the specific surface area and pore structure of the samples, nitrogen

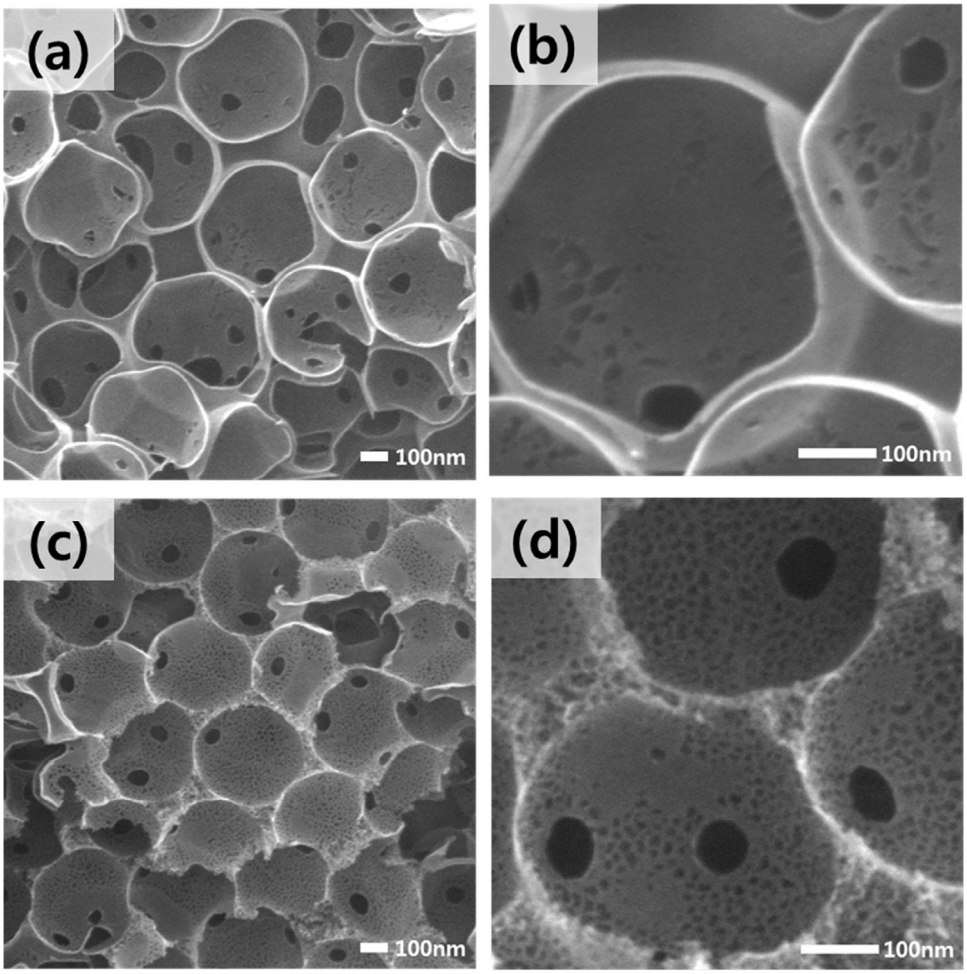

Fig. 2. SEM images of (a,b) G-500 and (c,d) G-500/20.

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