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Letter to the Editor

Preparation of porous carbon nanofibers derived from graphene oxide/polyacrylonitrile composites as electrochemical electrode materials

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ABSTRACT

Porous carbon nanofibers (CNFs) derived from graphene oxide (GO) were prepared from the carbonization of electrospun polyacrylonitrile nanofibers with up to 15 wt.% GO at 1200 °C, followed by a low-temperature activation. The activated CNFs with reduced GOs (r-GO) revealed a specific surface area and adsorption capacity of 631 m^2/g and 191.2 F/g, respectively, which are significantly higher than those of pure CNFs (16 m^2/g and 3.1 F/g). It is believed that rough interfaces between r-GO and CNFs introduce oxygen pathways during activation, help to produce large amounts of all types of pores compared to pure activated CNFs.

Polyacrylonitrile (PAN) has been previously used as a precursor for the production of commercial carbon fibers (CFs) [1], carbon nanofibers (CNFs) [2] and highly conductive carbon nanosheets [3]. PAN fibers require stabilization and carbonization treatments for obtaining CFs. The stabilization of PAN results in a ladder structure that prevents the fusion of its original fiber or film shape during subsequent heat and carbonization treatments that remove non-carbon elements at temperatures greater than 1200 °C [2,3]. The electrospinning of PAN has been shown to be a simple method for preparing nanofibers, which can then be converted into CNFs by a similar heat treatment to CF stabilization and carbonization [1,2]. Another processing method that takes place in an oxygen containing atmosphere at ~600 °C renders pores in CNFs, leading to an increase in surface area and improvement in electrochemical properties [2]. Furthermore, activated CNFs have been used as electrode materials in supercapacitors and Li-ion batteries [4,5].

Recently, PAN-based CNFs containing graphenes manufactured by electrospinning and thermal treatment have been reported to improve the capacitance of CNFs [5,6]. Zhou and Wu electrospun PAN containing 10 wt.% graphenes purchased from XG Science, USA, with a sheet size and thickness ranging between 1–5 μm and 6–8 nm, respectively. They also demonstrated that further treatments such as stabilization, carbonization, and activation produced porous graphene-beaded CNFs, which jointed to CNFs with diameters between 300 and 400 nm. These materials exhibited twice specific

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capacitance of pure CNF (114.6 F/g) due to the bridge-like connections between graphene platelets and CNFs [5]. Kim et al. incorporated 5 wt.% graphenes into PAN/tetraethoxysilane nanofibers using electrospinning, and the resulting activated CNFs exhibited a significant specific capacitance increase up to 144.8 F/g, over pure activated CNFs (60.0 F/g); however, they did not observe graphenes between CNFs [6].

Electrospun PAN nanofibers containing graphene oxide (GO) (from 5 to 15 wt.%) were synthesized (see experimental in Supplementary data). The GO with bi- or triple-layers exhibited various sheet sizes, ranging from the sub-microns to 3 micrometers (Fig. S1). Stabilization and carbonization resulted in CNFs with reduced GO (r-GO), and samples were designated as CNF-G0, CNF-G5, CNF-G10 and CNF-G15 for 0, 5, 10 and 15 wt.% GO, respectively. Further activation of all of the samples under air at 325 °C produced textured and porous structures, as characterized by scanning electron microscopy (SEM) and N_2 physisorption, respectively. The electro-chemical properties of the r-GO filled CNFs were also studied to determine their potential as electrode materials in supercapacitor applications.

Fig. 1a showed a morphological image of pure PAN nanofibers. Transmission electron microscopy (TEM) image of polymeric nanofibers containing 10 wt.% GO showed the graphitic structure of GO (Fig. 1b and c), which is placed inside nanofibers (Fig. S2), and a protrusion of GO was observed with nanofibers containing 15 wt.% GO (Fig. 1d and e). Electrospun nanofibers were stabilized under an air atmosphere at 250 °C for 5 h. Stabilized nanofibers were carbonized under nitrogen at 1200 °C, resulting in the conversion of stabilized fibers and GOs into CNFs and r-GOs [7]. The thermogravimetric analysis of GO was performed under conditions mimicking that of the nanofiber carbonization process, and the thermogram indicated a significant weight loss for GO below 250 °C (Fig. S3). It is well known that GO composites can be reduced by detaching surface functional groups with heat treatments [7]. Samples containing GO from 0 to 10 wt.% exhibited a narrow diameter (140–165 nm), whereas, CNF-G15 (235 nm), as shown in Fig. 2a–c and Fig. S4, did not. Interestingly, the surface morphology of CNF-G15 is rough, while other CNFs with r-GOs have relatively smooth surfaces and a similar diameter to pure CNFs, although they were filled with GOs by electrospinning. In addition, an excess GO leads to a larger diameter and rougher surface due to the entanglement and protrusion of GO, as seen in the CNF-G15 sample.

All four samples were activated under oxygen at relatively low temperatures (~325 °C) [2]. There was no significant change in the fiber diameters or surface roughness when comparing activated CNFs (ACNF-GX) to CNFs as shown in Fig. 2d–f. This result indicates that the activation is mild enough to maintain nanofiber inherency. The specific surface

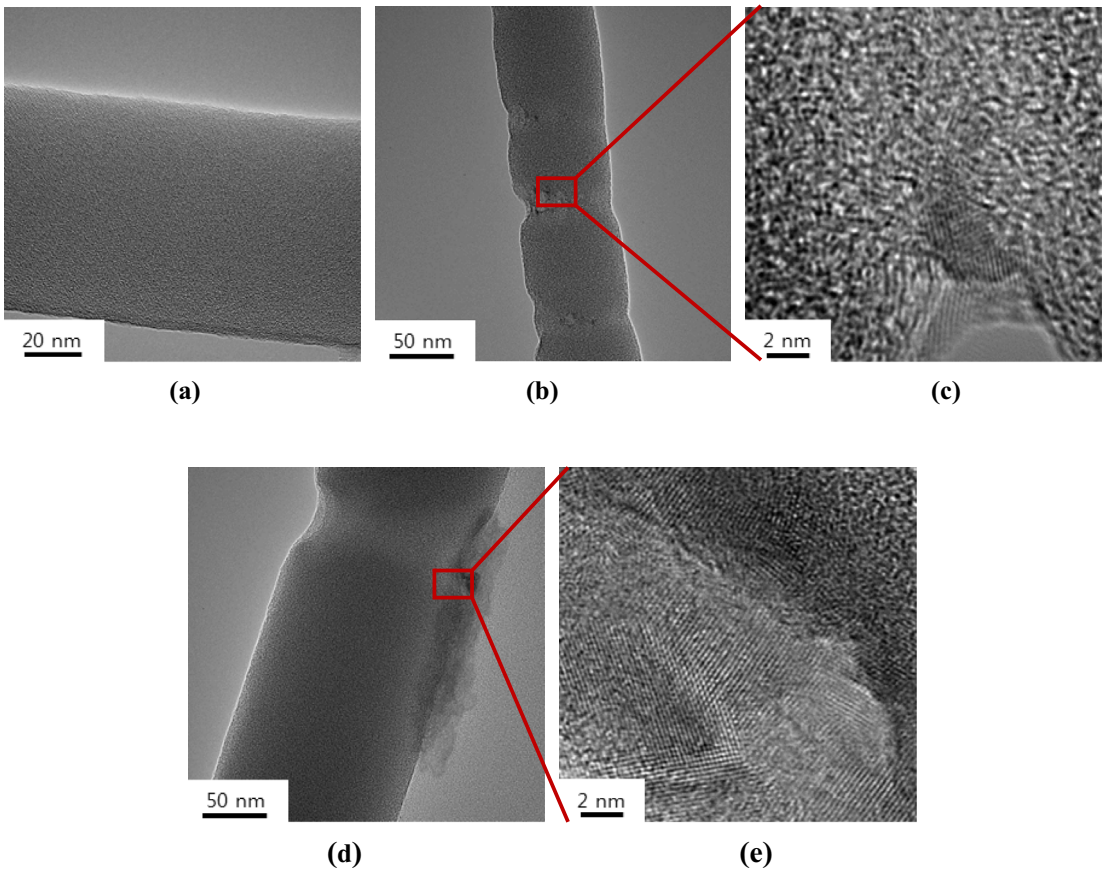

Fig. 1 – TEM micrographs of electrospun PAN nanofibers containing (a) 0 wt.%, (b, c) 10 wt.% and (d, e) 15 wt.% of GO. (A colour version of this figure can be viewed online.)