Sandwich-like nitrogen-enriched porous carbon/graphene composites as electrodes for aqueous symmetric supercapacitors with high energy density

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ABSTRACT

Sandwich-like nitrogen-enriched porous carbon/graphene composites were prepared by carbonization of polyacrylonitrile (PAN) nanofiber paper with bulk-doped and/or surface-coated graphene oxide (GO), and followed by activation with KOH at high temperatures. The composites exhibit high specific surface areas in a range of $1957.2–2631.8 \, m^2 \, g^{-1}$, as well as superior energy storage capability as electrodes for supercapacitors. A very high specific capacitance of $381.6 \, F \, g^{-1}$ at a current density of $0.1 \, A \, g^{-1}$ was achieved in 6 M KOH aqueous electrolyte for N-ACGrF@Gr1 that contains two types of graphene. According to the investigation results, the surface-coated graphene plays a more positive effect on improved supercapacitance than the bulk-doped graphene in the composites. Additionally, the assembled aqueous symmetric supercapacitors deliver a high energy density of $13.2 \, W \, h \, kg^{-1}$ at a power density of $25.0 \, W \, kg^{-1}$, and $8.3 \, W \, h \, kg^{-1}$ at $4.7 \, kW \, kg^{-1}$ with a retention rate of 62.9%.

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1. Introduction

Activated carbons (AC) have advantages of high surface area, controllable pore-size distribution, low-cost, and excellent electrochemical stability and environmental compatibility, therefore they are widely applied as promising electrodes for supercapacitors [1,2]. However, AC-based double layer supercapacitors generally suffer from a disadvantage of low energy density (E), the E values are generally lower than $10 \, W \, h \, kg^{-1}$ in aqueous electrolytes as reported [3–6], this is why most commercial supercapacitors utilize high-voltage organic electrolytes that, however, are generally flammable and toxic. It is more competitive to develop advanced aqueous supercapacitors, hence, more and more researchers are focusing on the development of advanced electrode materials with significantly enhanced supercapacitance [7,8].

To substantially promote the supercapacitive performance of activated carbons, one strategic way is to dope nitrogen, phosphor, sulfur or boron species into carbon structure, or to functionalize carbon surface with oxygen-containing groups. In this respect, an extra pseudo-capacitance will be achieved, which is originated from the faradaic interactions between heteroatom-enriched carbon surface and electrolyte ions [9–16]. Moreover, nitrogen-doped carbons exhibit improved electronic conductivity and wettability to electrolytes [10,11,15]. Experimentally, oxygen groups functionalized carbon can be achieved by an oxidizing treatment with O_2 or nitric acid [13,17], while the heteroatom-enriched carbons can be prepared by carbonizing N, P, S or B-containing precursors, or by a reaction carried out in an ammonia atmosphere [10–12,15,18]. Further performance enhancement can be achieved by introducing carbon nanotubes (CNTs) or graphene nanosheets (GNs) into carbons. The superior electrical conductivity, high mechanical properties, as well as large specific surface area of nanostructured CNTs and GNs can dramatically boost the supercapacitance of the carbon composites [19–22]. Zeng synthesized the CNTs/graphene composite with a high capacitance of $244 \, F \, g^{-1}$ at a scan rate of $50 \, mV \, s^{-1}$ in $1 \, M \, H_2SO_4$, the super-short CNTs in the composite effectively increases the utilization of the closed pore volume of multi-walled CNTs and inhibits the restacking of GNs accounting for the enhanced electrochemical performance [20].

Polyacrylonitrile (PAN) is a good precursor of N-enriched carbons. For enhanced supercapacitive performance, PAN carbons

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were generally fabricated into a form of nanofibers using a precursor prepared by electrospinning, because the carbon nanofibers (CNFs) have a few advantages such as extremely high length-to-diameter ratio, high surface area and excellent electrical conductivity [23,24]. F. Béguin prepared the N-enriched porous CNFs by one-step carbonization/activation of PAN nanofiber paper at temperatures from 700 to 1000 °C in CO_2 atmosphere [25]. The 900 °C treated material exhibited high capacitances of 200 F g^{-1} in 1 M H_2SO_4 and 240 F g^{-1} in 6 M KOH at 2 mV s^{-1}, it is much better than commercial activated carbons with higher specific surface area and micropore volume. Moreover, doping CNTs or GNs into the PAN-based carbons can enhance supercapacitive performance as well. Zhou prepared a film of porous GNs/CNFs by electrospinning a solution of PAN (10 wt.%)/graphene oxide (GO, 1 wt.%) in N,N-dimethylformamide (DMF), followed by carbonization at 800 °C. The GNs/CNFs composite demonstrated a high specific capacitance of 263.7 F g^{-1} in 6 M KOH at a current density of 0.1 A g^{-1} [26].

In despite of the great achievements reported in literatures, further enhancement is expected, and can be achieved by rationally tuned architecture, composition, morphology and particle size of the carbon composites. In this work, we reported a facile fabrication of N-doped porous carbon/graphene composites with a novel sandwich-like structure. The precursors are two types of PAN nanofiber paper prepared by electrospinning, including one doped with 0.5 wt.% GO, and the other without GO. The precursors were further coated with GO aqueous solution, then carbonized and activated using KOH at high temperatures. The as-prepared composites demonstrate remarkably enhanced supercapacitance and excellent rate capability. A very high specific capacitance of 381.6 F g^{-1} was achieved at a current density of 0.1 A g^{-1} in 6 M KOH aqueous electrolyte. The assembled aqueous symmetric supercapacitors with the composites as electrodes demonstrate good cycling stability, high energy density and high power density. The doped and coated graphene play an important role in the enhanced supercapacitance, their influence on microstructure, morphology, composition and electrochemical properties of the composites are discussed in detail.

2. Experimental section

All chemicals are analytical grade and used as purchased. Graphite oxide was prepared by a modified Hummers method [27], a detailed process is provided in the Supporting Info. A 0.1 wt.% aqueous solution of graphene oxide (GO) was prepared by ultrasonically dispersing 0.1 g graphite oxide in 100 mL of distilled water for 30 min, and centrifuged at a high-speed of 6000 rpm min^{-1} to remove unexfoliated graphite oxide.

2.1. Materials preparation

PAN nanofiber paper was prepared by electrospinning. Typically, a certain amount of PAN was dissolved in DMF under stirring to get a 10 wt.% solution. The solution was electrospun into nanofibers by applying a 20 kV bias between the syringe needle and a rotating collector. The total spinning time was 5 h. PAN/GO nanofiber paper was prepared using a similar process. Typically, 0.5 wt.% GO relative to PAN was first ultrasonically dispersed in DMF, then PAN was dissolved into the dispersion to get a viscous mixture for electrospinning. The as-prepared PAN and PAN/GO nanofiber paper were dried at 200 °C for 30 min before being peeled off from the collector.

The GO coated PAN (PAN@GO) and PAN/GO (PAN/GO@GO) nanofiber paper were prepared by a simple dip-coating method. In a typical process, the nanofiber paper was dipped into the GO aqueous solution, and sonicated for 30 min, then dried at 110 °C. This coating-drying procedure was repeated for several times until the accumulated coating amount of GO has reached 1 wt.%.

The PAN and PAN/GO nanofiber paper, as well as PAN@GO and PAN/GO@GO paper were heated up to 300 °C in air at a rate of 5 °C min^{-1}. After 1 h of stabilization, the nanofibers were then carbonized at 750 °C for 1 h in an inert N_2 atmosphere, and activated at 700 °C for 2 h with a C/KOH mass ratio of 1:4. The final products were designated as N-ACF, N-ACGrF, N-ACF@Gr1 and N-ACGrF@Gr1, respectively.
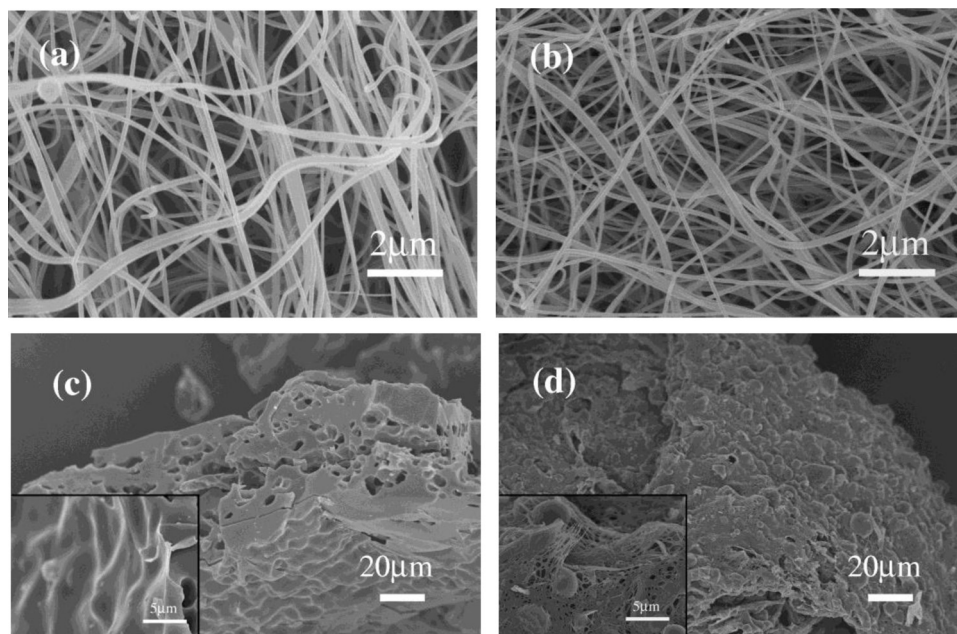
Fig. 1. SEM images of (a) PAN and (b) PAN/GO nanofibers, as well as the corresponding porous carbon including (c) N-ACF, (d) N-ACGrF.