Contents lists available at ScienceDirect

Materials Letters

Electrospun graphene nanoplatelets-reinforced carbon nanofibers as potential supercapacitor electrode

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ARTICLE INFO

ABSTRACT

The combination of graphene nanoplatelets and carbon nanofibers were successfully fabricated by utilizing a one-step solution based on the electrospinning technique. A distinctive morphology was observed in which the platelets were suspended between the fibrous structure that significantly improved the specific capacitance of the nanofiber to $86.11 \, \text{F g}^{-1}$, twice the increment from its original structure. Furthermore, all of the graphene nanoplatelets-reinforced samples recorded an optimal performance of over 90% capacitive retention after 1000 continuous charge/discharge cycles, regardless of the GnP concentration. These findings indirectly reflect the potential of CNF as the electrode material in the fabrication of high performance supercapacitor devices.

1. Introduction

The development of portable electronics such as flexible displays, bendable cellular phones and flexible television displays have attracted consumers in the commercial market in the past few years [1] which drive the progress of developing flexible, light weight energy storage devices. The recent development of fibrous carbon as an electrode material for energy storage devices has attracted the attention of researchers, which is attributed to its high surface area with accessible mesopores with the one-dimensional conductive nanostructures providing a shortened path in electron transportation [2]. It is mechanically flexible and easily prepared without the need of any binders [3].

However, the overall conductivity of carbon nanofibers remains low due to the amorphous nanofibers network [4]. Therefore, numerous efforts have been conducted to improve the overall conductivity of the network, including the introduction of metallic elements [4–6] and more recently, graphene-based nanostructures [7,8]. In this approach, electrospinning process was utilized to fabricate a continuous nanofibers reinforced with a minimal amount of graphene nanoplatelets. The combination of both graphene nanoplatelets and CNF gives rise to a continuous carbon framework with graphene nanoplatelets suspended within the carbon network, resulting in superior electrochemical properties, while maintaining the light weight and flexibility of the electrode material.

2. Experimental methods

2.1. Materials

Polyacrylonitrile (PAN, MW: 150,000) was purchased from Sigma Aldrich, Malaysia. N, N-dimethylformamide (DMF) and potassium hydroxide (KOH, 85%) was obtained from Systerm, Malaysia. Graphene nanoplatelets (GnP) were synthesized by the thermal exfoliation of expandable graphite (3772, Asbury, Inc.). The graphite was subjected to a thermal shock at 950 °C for 10 s, and sonicated for 1 h using a probe sonicator to obtain GnP powder. Whatman qualitative filter paper was purchased from Sigma Aldrich, Malaysia.

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2.2. Preparation of PAN nanofibers and PAN loaded with graphene nanoplatelets

A polymer solution of PAN (10 wt%) was prepared by dissolving PAN in a DMF solution and stirred for 24 h. The solution was electrospun using an electrospinner setup (Electroris, Nanolab Malaysia) with an applied voltage of 15.0 kV and collected after 2 h of spinning. Similarly, PAN reinforced with graphene nanoplatelets was prepared by adding the GnP powder into a DMF solution prior to the spinning procedure. The concentration of GnP varied from the total volume of the polymeric solution.

2.3. Carbonisation of polymer nanofibers

The carbonisation process was carried out using a quartz tube furnace (Thermolyne, Thermo Scientific). The nanofiber was first subjected to oxidative activation by heating to 280 °C for 1 h under atmospheric pressure, followed by 800 °C and maintained for 1 h under an inert atmosphere. Upon carbonisation, a conductive carbon nanofiber (CNF) was obtained.

2.4. Characterisation techniques

The surface morphologies and elemental mapping of nanofibers were analysed using a field emission scanning electron microscope (FEI Quanta SEM Model 400F) equipped with an energy dispersive X-ray (EDX) accessory.

2.5. Preparation of electrochemical cells and measurements

The electrochemical properties were evaluated using a two-electrode configuration with a potentiostat-galvanostat (Princeton VersaSTAT 3, Princeton Applied Research). The samples were prepared into approximate dimension of 1.0 cm^2. Nylon membrane filter (soaked in a liquid electrolyte overnight) was sandwiched between the prepared samples before being tightly fitted into an electrochemical cell. The specific capacitance was obtained from the slope of the galvanostatic discharge curve according to the following equation:

$$Cm = \frac{it}{\Delta v \cdot m} \quad [9,10] \tag{1}$$

where i = current, t = elapsed time during the discharge process, Δv = total working potential (minus the IR/voltage drop), and m = mass of the electrode materials.

3. Results and discussion

3.1. Morphology study of the electrospun carbon nanofibers

The stabilization heat treatment induced a series of oxidative complex reactions which eventually strengthened the physical properties of the nanofibers by forming a ladder structure [11,12]. Carbonisation treatment in inert atmosphere caused formation of bridging links between the fibers by means of oxidative functional groups such as ether and carbonyl groups [13], which eventually formed a continuous overlapping carbon framework, as shown in Fig. 1a and b (magnified) [14]. A distinctive feature was recorded when the FESEM image of CNF/GnP showed an obvious two-phase nanostructure, at which the GnP remained suspended and decorated within the nanofibers (Fig. 1c). The discontinuous morphology was further magnified, and the GnP particles were found to be suspended between the nanofiber strands (Fig. 1d).

3.2. Electrochemical performance of CNF and CNF/ GnP

CV profiles were successfully broadened as the function of GnP introduction and concentration increment (Fig. 2a), indicating an enhancement in conductivity and capacitance performance of the
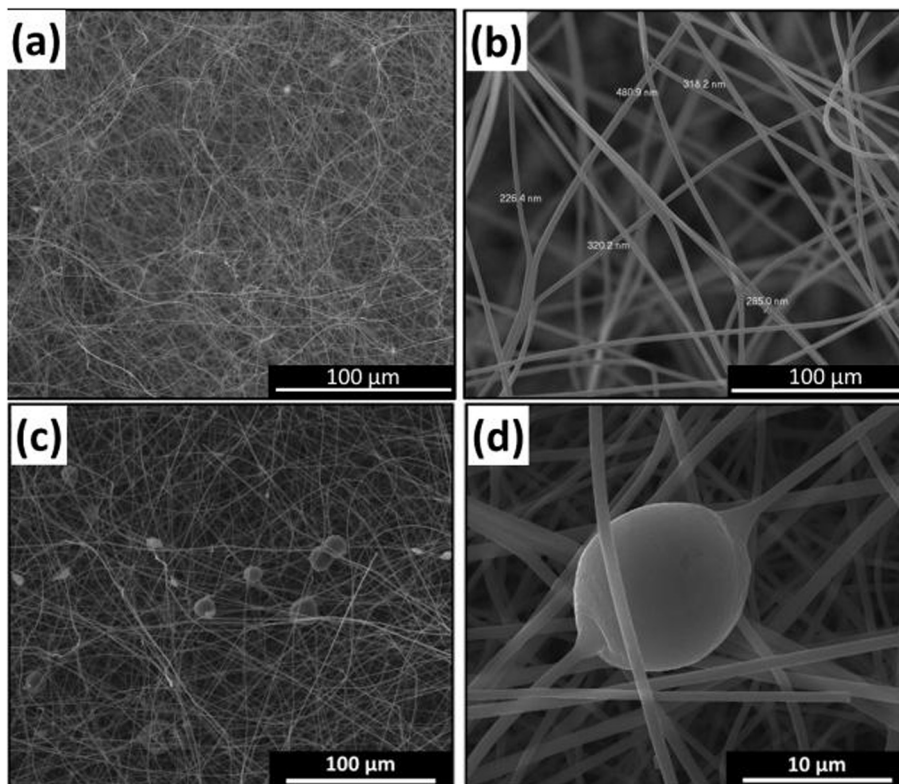

Fig. 1. FESEM images of (a) CNF, (b) magnified image of CNF, (c) CNF-GnP 1 mg ml^{-1} and (d) magnified image showing GnP suspended within a nanofiber strand.