Journal of Power Sources 328 (2016) 195–202

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Physicochemical and electrochemical properties of carbon nanotube/graphite nanofiber hybrid nanocomposites for supercapacitor

Nurul Infaza Talalah Ramli [a], Suraya Abdul Rashid [a, b, *], Yusran Sulaiman [a, c], Md Shuhazlly Mamat [d], Syazwan Afif Mohd Zobir [b], Shutesh Krishnan [e]

[a] Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[b] Department of Chemical & Environment Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[c] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[d] Department of Physics, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[e] Graphene Nanochem Sdn. Bhd., Level 9, WORK@Clearwater, Changkat Semantan, Off Jalan Semantan, Damansara Heights, 50490 Kuala Lumpur, Malaysia

HIGHLIGHTS

- The specific capacitance is raised to 174 F g^{-1} (87%) with 20 wt% of CNT addition.
- Excellent electrochemical performance is achieved even at low mass loading (50 μg).
- High specific energy of 14.3 WhKg^{-1} and specific power of 512 kWkg^{-1} is attained.
- CNT:GNF ratio of 29:80 shows outstanding thermal stability.
- Significant enhancement in supercapacitance is attributed to synergistic effects.

ARTICLE INFO

Article history:
Received 7 April 2016
Received in revised form
26 July 2016
Accepted 27 July 2016

Keywords:
Carbon nanotube
Graphite nanofiber
Supercapacitors
Physicochemical
Electrochemical characterization

ABSTRACT

This work reports the combination of graphitic nanofibers (GNF) and carbon nanotubes (CNT) as the electrode material for supercapacitors. The hybrid CNT/GNF was prepared via a synthesis route that involved simple sonication and stirring. The loading of CNT was varied from 5 to 40% weight percentages. A specific capacitance of 174 Fg^{-1} has been obtained for 20 wt% CNT loading at 50 mV F g^{-1}th 1 M H_2SO_4 aqueous solution as the electrolyte. The addition of 20 wt% CNT raised the specific capacitance by 87% more than the GNF electrodes. Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscope (TEM) reveals the random entanglement of CNT and GNF that create diffusion paths for ion transportation. Conformational changes were monitored by Raman spectroscopy, where two dominant peaks (D and G) showed strong intensities and sharp profiles. X-ray Diffraction spectroscopy (XRD) confirmed the purity of CNT/GNF hybrid nanocomposites. 20 wt% of CNT addition also shows an outstanding thermal stability. The marked improvement of the hybrid performance was attributed to the high conductivity of the two constituent materials, coupled with sufficient accessible active sites for electrochemical reactions that resulted in a synergistic behavior of the materials.

1. Introduction

Energy storage is one of the necessities for human daily activities. Energy storage devices are essential for various electronic appliances including mobile phones and vehicles. Supercapacitors are one of the energy storage devices that have the ability to overcome the disadvantages possessed by other types of devices. Supercapacitors have greater specific energy and power compared to the existing batteries and capacitors [1]. The gradual decrease of natural sources for energy storage applications has prompted many researchers to find new alternatives. Therefore, innovative and renewable sources have become the target in order to combat the extinction of natural sources. Extensive research has been performed in the development of supercapacitors to replace the existing energy storage sources [2–4]. Supercapacitors possess most of the important properties that are needed for an energy

* Corresponding author. Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia.
E-mail address: suraya_ar@upm.edu.my (S. Abdul Rashid).

http://dx.doi.org/10.1016/j.jpowsour.2016.07.110
0378-7753/

storage device. It operates with long cyclic life (>100000 cycles), low maintenance cost and fast dynamics of charge propagation [2]. However, due to the demand for even longer storage life, existing supercapacitors still need to be improved in terms of its specific capacitance that determine its capability to store energy.

Carbon nanomaterials including graphite, graphene and carbon nanotubes (CNT) have extensively shown their potential in a wide range of applications [2–7]. CNT is among the most popular material that is being used in recent research. It has shown to have superior properties in energy storage applications. CNT has a nanotubular structure, with highly accessible surface area, high conductivity, and excellent stability [5]. Another material that is also a very interesting carbon material is graphitic nanofibers (GNF). GNF was reported to have a unique structure where it has virtually open edges and large interlayer spacing [6]. However, there are relatively limited studies that have been conducted on GNF applications, although its potential characteristics have been reported [8,9]. GNF can typically be classified into four main types which are platelet (PGNF), herringbone (HBGNF), tubular (TGNF), and stacked-cup (SCGNF) [9]. Of all these types, herringbone GNF was reported to be very unique as it has enhanced field emission that is caused by the open edges sites, and the localized states at the Fermi level may give rise to materials with novel electronic and magnetic properties [10].

Different materials have different supercapacitor performance. Carbon materials such as CNT, graphene, and activated carbon for supercapacitor materials have been vastly studied [11–14]. However, studies on GNF material for energy storage applications is very limited. In 2011, Lu et al. [13] produced a flexible graphene/multi-walled CNT film that displayed an excellent specific capacity of 265 F g^{-1} at 0.1 A g^{-1} current density. Veerappan et al. [12] reported a simple route combining mixing and stirring process to synthesize three-dimensional graphene oxide-CNT and graphene-CNT hybrids. A maximum specific capacitance of 251 F g^{-1} was achieved at 5 mV^{-1}. Zhao et al. [11] reported a synthesis of graphene/single-walled CNT by using chemical vapor deposition (CVD). The specific capacitance obtained was 98.5 F g^{-1} at a scan rate of 10 mV^{-1}, and it retained 78.2% of its initial capacity as the scan rate was increased to 500 mV^{-1}. Various other types of carbon-based hybrids with good capacitances were also reported in the literature. Ezeigwe et al. [14] reported a one-step green synthesis of graphene/ZnO via the solvothermal method. In their study, an improved capacitive performance of 236 F g^{-1} at a scan rate of 10 mV^{-1} was obtained.

In this study, we attempted to improve the supercapacitance performance of GNF and CNT by forming its hybrid which has never been reported in literature. Open edges and large interlayer spacing GNF will act as a substrate for the CNT networks. Incorporated CNT are believed to provide greater area for the ions to adhere to. Moreover, the entanglement of CNT will form a mesoporous network that will channel the ion into the composite active sites. The qualities that are possessed by both GNF and CNT are predicted to enhance the electrochemical performance of the hybrid by synergistic effects. The physicochemical and electrochemical properties of CNT/GNF hybrid nanocomposites were carefully examined to determine the performance of the hybrid material for the application of supercapacitor.

2. Materials and methods

2.1. Materials

GNF and CNT-COOH were supplied from Graphene Nanochem Sdn. Bhd. Sulfuric acid H_2SO_4 (98%), nitric acid HNO_3 (65%), and Triton X-100 (10%) were purchased from J.T Baker. Deionized water (DI) from the Millipore system was used throughout the experiment.

2.2. Purification and functionalization of CNT

The CNT were first purified and functionalized through an acid treatment process. The CNT were treated with 3:2 ratio of H_2SO_4 and HNO_3 and sonicated for 5 h. The purified CNT were then suspended in 50 ml Triton X-100 solution with 50 ml DI water, and followed with sonication for another 1 h. The CNT was washed with DI water several times, and dried at 40 °C in a conventional oven to ensure that any residual surfactant was removed before further use.

2.3. Preparation of hybrid GNF/CNT

The GNF-CNT hybrid nanocomposites were prepared via chemical mixing and stirring at different weight ratios of CNT:GNF (Table 1). The weight ratios ranged from 5 wt%-40 wt% of CNT addition to GNF samples. The samples are named as CNTGNF5, CNTGNF10, CNTGNF20, CNTGNF30 and CNTGNF40 accordingly. A certain amount of GNF was dispersed into 100 ml of DI water and sonicated for 1 h to obtain a stable suspension. Varying amounts of purified CNT was then added into the GNF suspension and sonicated for another hour. The sonication process was followed by 24 h of stirring by using magnetic stirrer. The sample was then dried in a conventional oven at 40 °C.

3. Characterizations

The electrochemical measurements were conducted by using a three electrode system, operated using Autolab PGSTAT204 N potentiostat. Glassy carbon electrode (GCE) drop-casted with CNT-GNF hybrids served as the working electrode, Ag/AgCl as the reference electrode, a platinum wire served as the counter electrode and 1 M H_2SO_4 aqueous solution as the electrolyte. CNT/GNF sample was drop-casted onto 3 mm diameter glassy carbon electrode with loading mass of ~50 μg. Cyclic voltammetry (CV), galvanostatic charge-discharge cycles (GCD) and electrochemical impedance spectroscopy (EIS) were analyzed by using the same setup. CV tests were performed between −0.2–0.8 V potential window at different scan rates ranging from 10 to 100 mV^{-1}, while the galvanostatic charge-discharge cycle test at 1 A g^{-1} to 4 A g^{-1} current densities [15]. The impedance analysis were carried out at 1–100 kHz frequency ranges with 5 mV AC voltage amplitude, taking 50 points per decade. The as-prepared samples were characterized by WITec Raman microscope model Alpha 300R with He-ne laser at 532 nm excitation wavelength. The morphology and microstructure of the samples were investigated by viewing the sample under Nova Nanosem 230 FESEM and Tecnai G2 20 TEM. Thermogravimetric analysis (TGA) of CNT-GNF nanostructures was performed by using Mettler Toledo (model TGA/DSC 1 H T) at a heating rate of 10 °C min^{-1} over a temperature range of 30–900 °C under a nitrogen atmosphere to study the thermal stability of the samples [14–16].

Table 1
Different weight ratios of CNT to GNF to form CNT/GNF hybrid nanocomposites.

Sample	Weight of CNT (g)	Weight of GNF (g)
CNTGNF5	0.15	2.85
CNTGNF10	0.30	2.70
CNTGNF20	0.60	2.40
CNTGNF30	0.90	2.10
CNTGNF40	1.20	1.80