Vacuum 122 (2015) 135–142

Contents lists available at ScienceDirect

Vacuum

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

Fabrication and application of carbon nanotubes/cellulose composite paper

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ARTICLE INFO

Article history:
Received 5 June 2015
Received in revised form
13 September 2015
Accepted 14 September 2015
Available online 16 September 2015

Keywords:
CNTs
Cellulose
Composite
Electrochemical
EMI

ABSTRACT

A kind of flexible carbon nanotubes (CNTs) paper was investigated. Cellulose fibers were used as matrix and CNTs were used as conductive additive. The CNT papers were made by suction filtration method. The size and conductivity of the CNT paper can be arbitrarily tailored. The CNT papers show good electrical conductivity, electrochemical and electromagnetic interference (EMI) shielding properties. The electrical conductivity and (EMI) shielding effectiveness (SE) of CNT papers were enhanced with an addition of CNTs in the paper. The electrical conductivity increased from 9.92 S m^{-1} to 216.3 S m^{-1} and SE improved from 15 dB to 45 dB with a loading of CNTs from 10 wt% to 71 wt%. The CNT papers also show excellent applications for lithium ion battery, supercapacitors and zinc-manganese batteries. The testing results show that the capacity of supercapacitor reached 46 F/g at a scan rate of 5 mV/s. The reversible discharge capacity reached 474.0 mAh/g with the paper as anode current collector of lithium ion battery. The discharge capacity of Zn–Mn battery increased 100% when CNT paper replaced the graphite collector as current collector.

1. Introduction

Recently, electrical devices are becoming increasingly popular in many areas. The tiny and smart devices that based on nanotechnology are gaining prominence for novel information-processing devices. Many researchers consider that nanodevices, for instance, quantum dot devices, single-electron circuit devices, magnetic-flux quantum circuit devices, and so on, will be devices which have several functions [1].

Papermaking is an ancient art that plays an important part in human history, and it is still very relevant in today's economy. By incorporating specific fillers with cellulose fibers, paper can take on properties of conductive [2], magnetic [3], photoluminescent [4,5], catalytic [6], antimicrobial [7,8], acoustic dampening [9], or flame retardant [10,11], which open the doors to myriad new potential applications. High performance flexible cellulose electrical paper are researched broadly and deeply which can be used for the antistatic package [12], electromagnetic shielding [13], foldable energy storage device [14–17] and electrical smart brands [18].

Since their discovery, carbon nanotubes (CNTs) [19] have attracted much attention in areas such as electronic devices, biosensors, field emission displays, hydrogen storage, and composites, on account of their extraordinary electrical, physical, chemical, and structural properties [20–23]. The CNT films can be used in energy storage devices were reported in recent research [24–26]. Many studies have been performed on CNT/cellulose composite paper, that was fabricated by dispersing carbon nanotubes into cellulose papers [27–30], followed by papermaking process. The paper can exhibited high electrochemical activity [15] and electromagnetic shielding effectiveness (EMI SE) [31–34]. However, the CNTs of CNT/cellulose composite paper will be lost during the papermaking process. The content of CNTs of the conductive paper cannot be controlled in most researches, so

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http://dx.doi.org/10.1016/j.vacuum.2015.09.020

the systematic research of the electrical property of CNT/cellulose paper is difficult.

In this study, CNTs were absorbed and embedded in cellulose pulp and followed by infiltration. Different with papermaking process which was reported recently [31–33], the content of CNTs can be accurately controlled by infiltration method. The cellulose and CNTs were deposit on filter paper. The filter paper can guarantee the cellulose and CNTs not loss when the paper was made. Therefore, series of researches for different content of CNTs in paper can be studied. What's more, the measure using thermogravimetric analysis (TGA) to determine the amount of CNTs adsorbed in the cellulose [29,32] is unnecessarily. Systematic research was made to compare EMI SE of CNT paper with different CNTs content. And the electrochemical activity of CNT paper was tested with an exact CNT content 50 wt%. The result show that CNT paper not only can perform a high electrochemical activity as an electrode in a supercapacitor and lithium battery, but also can be good current collector for zinc-manganese battery in this paper.

2. Experimental

2.1. Fabrication of CNT-cellulose composite paper

Carbon nanotubes (CNTs) were synthesized by chemical vapor deposition and graphitized at 3000 °C for 10 h in Acheson graphitization furnace. The purity of the CNTs were tested by thermogravimetric analysis (TGA) under a open atmosphere at temperatures up to 1000 °C. The TGA pattern of the raw CNTs and graphitized CNTs were shown in Fig. 1. The purity of the as-grown CNTs was 95.6% and the purity of graphitized CNTs was improved to 99.8%.

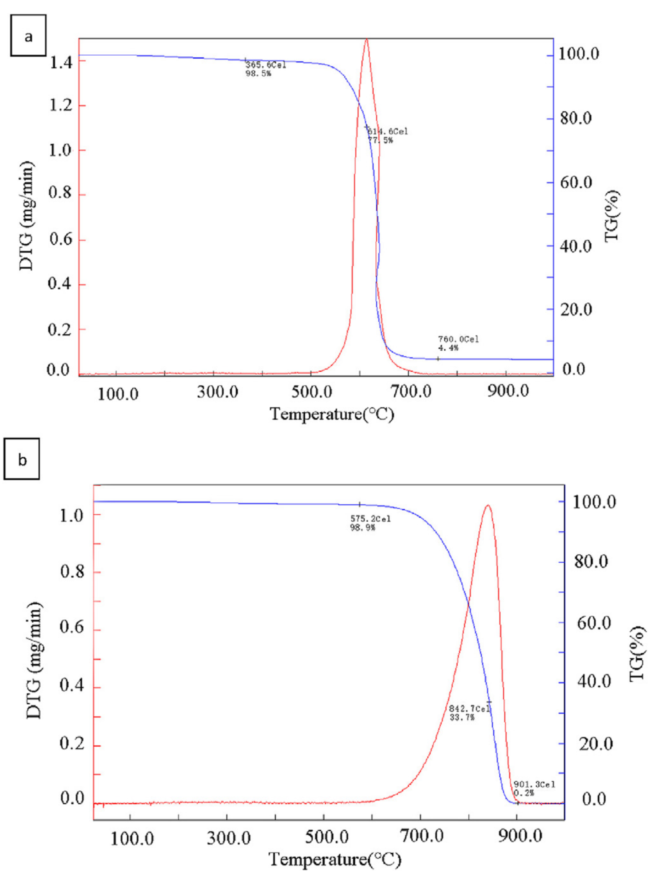

Fig. 1. TGA patterns of raw CNTs (a) and graphitized CNTs (b).

The CNTs were observed (Fig. 2) under scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The as-grown CNTs have large aspect ratios and high degree of crystallinity and line structure. This kind of CNTs which not entangled with each other compared with traditional CNTs (Fig. 2d) which intertwined. So they were easy to be dispersed than traditional CNTs.

The CNTs were characterized by X-ray diffraction (XRD). The XRD pattern of the CNTs (Fig. 3a) revealed the characteristic graphite (002) and (100) diffraction peaks of CNTs at around 26° and 43°. The diffraction peak (002) shows that the CNTs behave high crystallinity and perfect graphitic structure. These mean the CNT have high mechanical and electrical properties. The Raman spectra can be used to analyze the crystalline qualities (crystallinity) of MWCNTs. The intensity ratio of the G-band to the D-band (I_G/I_D) can be used to evaluate the degree of crystalline perfection. The Raman spectrum of the CNTs was shown in Fig. 3b. The D band at 1334 cm^{-1}, the G band at 1576 cm^{-1} and the 2D band at 2656 cm^{-1}. I_G/I_D ratios of CNTs is 4.16. the results reveal that CNTs have high crystallinity. The results of Raman spectra are in line with XRD.

The CNTs powder were dispersed in water by sonication for 2 h followed by high-speed shearing for 2 h, with the addition of sodium dodecylsulfate SDS ($CH_3(CH_2)_{11}OSO_3Na$) as a surfactant. A cellulose pulp was prepared by immersing softwood pulp into water followed by high-speed shearing for 3 h. The CNTs dispersion liquid and the cellulose pulp were mixed to form suspension by high-speed shearing for 3 h. By vacuum filtration, the liquid was infiltrated and a randomly interwoven fiber mat was generated (Fig. 4). The CNT paper was obtained. The paper was then rolled and tailored for following testing and applications.

2.2. Characterization

The morphology of all of the samples was observed using field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6701F). Transmission electron microscopy (TEM) was performed using a JEOL JEM-2010FEF. The X-ray diffraction was measured by a Bruker D8 Focus X-ray diffractometer (Germany) with monochromatized CuKα radiation at an accelerating voltage of 35 kV and an emission current of 20 mA, from 10° to 90° with a step size of 0.02°. Thermal stability of as-grown sample was verified by thermogravimetric analyzer (TG/DTA, PYRIS DIAMOND). Raman spectroscopy (Jobin Yvon, Labram-010) was performed with a 632 nm incident. The sheet resistance was measured by four-probe method using a multi-electrical measurement system (St2258C).

3. Results and discussion

3.1. The CNT/cellulose composite paper and characterization

Fig. 5a shows the obtained homogeneous and stable CNT/cellulose composite paper. The paper's size and thickness depended on the size of the filter cone and the amount of pulp. In this experiment, a 15 cm diameter filter cone was used to fabricate the paper. Fig. 5b shows the flexibility of the composite paper. The flexibility is almost as same as raw paper. Fig. 5c shows the high electrical conductivity of the composite paper by using the paper as an electrical wire for LED. Fig. 5d shows the CNT paper was used as current collector in flexible zinc-manganese battery and can light up a LED. The nice flexible