



Reduced graphene oxide and vertically aligned carbon nanotubes superhydrophilic films for supercapacitors devices

H. Zanin^{a,b,*}, E. Saito^a, H.J. Ceragioli^b, V. Baranauskas^b, E.J. Corat^a

^a Associated Laboratory of Sensors and Materials of the National Institute for Space Research, Av. dos Astronautas 1758, Sao Jose dos Campos CEP 12227-010, SP, Brazil

^b Departamento de Semicondutores, Instrumentos e Fotônica, Faculdade de Engenharia Elétrica e Computação, Universidade Estadual de Campinas, UNICAMP, Campinas 13083-970, Brazil

ARTICLE INFO

Article history:

Received 28 May 2013

Received in revised form 14 September 2013

Accepted 19 September 2013

Available online 4 October 2013

Keywords:

A. Nanostructures

B. Vapor deposition

C. Raman spectroscopy

D. Electrochemical properties

D. Energy storage

ABSTRACT

Reduced graphene oxide (RGO) and vertically aligned carbon nanotubes (VACNT) superhydrophilic films were prepared by chemical vapor deposition techniques for electrical energy storage investigations. These electrodes were characterized in terms of their material and electrochemical properties by scanning electron microscopy (SEM), surface wettability, Fourier transform infrared spectroscopy (FTIR), energy dispersive and Raman spectroscopies, cyclic voltammetry (CV) and galvanostatic charge–discharge. We observed several physical structural and electrochemical similarities between these carbon-based materials with particular attention to very good specific capacitance, ultra-high energy storage and fast power delivery. Our results showed that the main difference between specific capacitance values is attributed to pseudocapacitive contribution and high density of multiwall nanotubes tips. In this work we have tested a supercapacitor device using the VACNT electrodes.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Supercapacitors are energy storage devices able to store and deliver energy at high rates, compared with those best accessible batteries [1–5]. One of the most promising applications for supercapacitor is in electric vehicles to deliver high power needed during acceleration and to recover energy during braking [6]. However, the application possibilities of those devices are endless such as instantaneous electric charge of cell phone, cameras, laptop, etc.

These supercapacitors have two main mechanisms of energy storage; known as (i) double-layer capacitance, which capacitance comes from the charge accumulated at the electrode/electrolyte interface and (ii) pseudocapacitance, which capacitance comes from the charge accumulated at reversible Faradic redox reactions [6–8]. The typical time response of pseudocapacitors is significantly longer than those of double-layer capacitors. Strong pseudocapacitance phenomena may have a restrictive heterogeneous rate constant

and, consequently, components correspond to a longer time response and higher capacitance decay rate, which is usually undesired [9–11]. Up to date, different materials have been extensively researched for supercapacitor applications [12–15]. Especially, various carbon materials, mixed metal oxides and conducting polymers have attracted attention. Particularly, carbon – in its various structures, e.g. charcoal, amorphous carbon, nanotubes, graphene – has been used as electrode materials for supercapacitors, due to their high specific capacitance combined with high power density [16]. Among the carbon-based materials, graphene and carbon nanotubes have outstanding performance.

Graphene-based and carbon nanotubes electrodes show very good properties for supercapacitor devices, such as high surface area, good electrical conductivity and controlled pore size distribution [17–19]. These superb properties combined with the adequate surfaces treatment can provide high electrical energy storage and ultrafast power density delivery [20,21]. In most cases, the surface functionalization is the key to allow the effective permeation of the electrolyte to establish both electrical double layers and pseudocapacitance [22,23]. Basically, the oxidation of the carbon-based materials surface promotes the ready wetting by electrolyte. For instance, a hydrophobic surface, which has poorly electrochemical activity, could be changed to superhydrophilic by acid or plasma etching [24]. This improves access and decreases the electrolyte contact impedance of electrode/electrolyte interface. It

* Corresponding author at: Associated Laboratory of Sensors and Materials of the National Institute for Space Research, Av. dos Astronautas 1758, Sao Jose dos Campos CEP 12227-010, SP, Brazil. Tel.: +55 (12) 3208-6000.

E-mail addresses: HUDSONZANIN@GMAIL.COM, HUDSON.ZANIN@BRISTOL.AC.UK (H. Zanin), ESAITO135@GMAIL.COM (E. Saito), HELDERJC@GMAIL.COM (H.J. Ceragioli), VITOR@DSIF.FEE.UNICAMP.BR (V. Baranauskas), CORAT@LAS.INPE.BR (E.J. Corat).

has been reported that the heteroatoms and functional groups on the carbon sheets may improve the wettability of electrode, due to the increased number of hydrophilic polar sites [16], and thus enhance the overall capacitor performance.

Just few works [25] studied the plasma effects in carbonaceous materials for energy storage applications. In this work, we prepared RGO and VACNT-O by oxygen plasma to obtain superhydrophilic samples for electrochemical studies. Surprisingly these materials present several structural similarities and close electrochemical response.

2. Experimental

2.1. Synthesis of graphene-based films

Prior the deposition, 10 mm × 10 mm titanium substrates were immersed in 1 ml polyaniline diluted in 2 ml of dimethylformamide and then dried for 2 h at room conditions. After that, 0.2 ml of nickel nitrate diluted in 1 ml of acetone were dropped onto its surface. The graphene oxide films were produced from catalytic conversion, using hot-filament chemical vapor deposition (HFCVD) reactor feedstock by (1:1:1) camphor/acetone/citric acid vapor solution, which were dragged by hydrogen flow. The catalytic conversion is conducted under 20 Torr pressure and in 150 sccm of N₂ and 40 sccm of O₂ gases atmosphere. The deposition temperature was measured at the backside of the substrate and kept constant at 450 °C along the 30 min catalysis. The growth temperature was kept for 1 min in only hydrogen atmosphere in order to reduce the graphene oxide. The reactor was cooled suddenly in hydrogen flux [26].

2.2. Synthesis of vertically aligned carbon nanotubes films

The VACNT films were produced as thin film, using a microwave plasma chamber at 2.45 GHz, as reported elsewhere [27]. Prior deposition, as purchased titanium substrates were polished and exposed to pre-heating (in air/480 °C) to grow a TiO₂/TiN barrier for catalyst. 10 mm × 10 mm polished titanium substrates were covered by a 10 nm nickel layer deposited from e-beam system. Inside the MWCVD reactor, the substrates were initially preheated for nickel film nucleation, which are the catalyst for VACNT growth. The pre-treatment was carried out during 5 min in plasma of N₂/H₂ (10/90 sccm). After pre-treatment, CH₄ (14 sccm) was inserted in the chamber at a substrate temperature of 750 °C for 5 min. The reactor was kept at a pressure of 30 Torr during the whole process [28].

2.3. Functionalization of VACNT

The incorporation of oxygen-containing groups (–OH, –COOH, =O) was performed in a pulsed-DC plasma reactor with an oxygen flow rate of 1 sccm, at a pressure of 85 mTorr, –700 V, at a frequency of 20 kHz [26,28]. After this functionalization the VACNT samples are named vertically aligned carbon nanotube oxide (VACNT-O).

2.4. Materials characterization

The samples were characterized by Fourier transform infrared spectroscopy (FTIR), surface wettability, scanning electron microscopy (SEM), Energy dispersive and Raman spectroscopies. We employed Raman Scattering Spectroscopy (Renishaw 2000 system), with excitation by Ar⁺-ion laser ($\lambda = 514.5$ nm) in backscattering geometry to analyze the structural changes on samples. The curve fitting and data analysis software Fityk [29] assigned the peak locations and corresponding fitting of all spectra.

We used energy dispersive X-ray spectrometer (EDS) for chemical analysis, operating with a Si (Li) detector with an energy resolution of 126 eV coupled with the scanning electron microscope. Morphological images were performed using a field emission scanning electron microscope (FEI Inspect F50) to evaluate structural arrangements and monitor modifications details on the surface morphology. A Krüss Easy Drop system in sessile drop method measured the contact angle (CA) using high purity deionised water at room temperature to evaluate the wettability of RGO and as-grown and superhydrophilic VACNT films.

Fourier transform infrared spectroscopy (FTIR: Spotlight 400 – Perkin-Elmer) was used to identify the oxygen content of the samples in chemical bonds. All measurements were conducted at room temperature.

2.5. Electrochemical assays

The electrodes were characterized by cyclic voltammetry (CV) and galvanostatic charge–discharge (g-C/D). First electrochemical analyses were performed in a classical three-electrode cell system with high purity platinum helicoidal wire as a counter electrode and Ag/AgCl (3 M) as reference electrode. We have also performed the measurements in two electrodes cell, as a simple supercapacitor device. An Autolab PGSTAT302N potentiostat was used with electrochemical cell at room temperature in 0.5 M H₂SO₄ aqueous electrolyte solution. All electrochemical experiments were carried out exposing a fixed geometric area of 0.13 cm² of working electrode. The cyclic voltammetry (CV) measurements were carried out from 10 to 100 mV s^{–1} and between 0 and 1.0 V. The charge–discharge measurements were performed between 0 and 1.0 V using three different electric current density (0.25, 1.25 and 2.5 A g^{–1}).

3. Results and discussion

3.1. Material characterization

The typical SEM images of the reduced graphene oxide (RGO) and the vertically aligned carbon nanotubes oxide (VACNT-O) films are presented in Fig. 1(a–f). The top view (Fig. 1a) of RGO films shows that the sample has porous microstructures composed by entangled wires. High resolution images (Fig. 1b and c) revealed that those wires have ~1 μm of outer diameter and graphene nanosheets along the outer tube surfaces.

Fig. 1(d) shows a side view image of vertically aligned carbon nanotubes, presenting a high density of the tubes and the film thickness of around 40 μm. Fig. 1(e) is a top view of these carbon nanotubes, showing its carpet-like organization. High resolution images reveal high crystallinity of these nanotubes and the effect of oxygen plasma treatments. The VACNT films have high tube crystallinity, low residues of amorphous carbon content and no catalyst metallic particles outside the tubes, as we reported elsewhere [30]. We observed that the oxygen plasma exfoliated the carbon nanotubes tips, opening its walls and exposing its fundamental structure: graphene (Fig. 1f).

There are some alternatives to produce graphene by carbon nanotubes exfoliation [31–34], but the inconvenience is usually the strong chemical oxidants manipulation and its inadequate discards. In this direction, the oxygen plasma etching is a simple, low cost and green methodology for graphene production. Even more, we reported elsewhere [26] the efficiency of the oxygen plasma treatment on VACNT surfaces, revealing the transition from superhydrophobic to superhydrophilic behavior [35].

The comparison of surface wettability of as-grown reduced graphene oxide, VACNT and VACNT-O was investigated using a

Download English Version:

<https://daneshyari.com/en/article/1488641>

Download Persian Version:

<https://daneshyari.com/article/1488641>

[Daneshyari.com](https://daneshyari.com)