



Three-dimensional, free-standing polyaniline/carbon nanotube composite-based electrode for high-performance supercapacitors



Rachit Malik^a, Lu Zhang^a, Colin McConnell^b, Michael Schott^c, Yu-Yun Hsieh^a, Ryan Noga^b, Noe T. Alvarez^b, Vesselin Shanov^{a, b, *}

^a Department of Mechanical & Materials Engineering, University of Cincinnati, Cincinnati, OH, 45221, USA

^b Department of Biomedical, Chemical and Environmental Engineering, University of Cincinnati, Cincinnati, OH, 45221, USA

^c Department of Physics, University of Cincinnati, Cincinnati, OH, 45211, USA

ARTICLE INFO

Article history:

Received 20 November 2016

Received in revised form

10 February 2017

Accepted 12 February 2017

Available online 14 February 2017

Keywords:

Carbon nanotubes

Polyaniline

Energy storage

Supercapacitors

Hybrid nanostructures

ABSTRACT

Vertically aligned Carbon Nanotube (CNT) arrays are synthesized directly on CNT sheets used as substrates by plasma enhanced chemical vapor deposition (PECVD) in NH₃ plasma environment. The resulting 3-D nanostructured, N-doped CNT (NCNT) architecture combines high conductivity and superior mechanical properties of CNT sheets with porous structure and high electrochemical activity of CNT arrays. NCNT sheets are then used as scaffolds for polyaniline (PANI) deposited by electrodeposition. PANI coating thickness is optimized to create a core-shell morphology with PANI shell supported by CNT core. Freestanding and flexible PANI/NCNT electrodes are fabricated without using any metal supports/foil or binders with the CNT sheets serving as current collectors. PANI/NCNT electrodes with 56 wt% polymer content demonstrate a gravimetric capacitance of 359 F/g at a current density of 1.56 mA/cm². The electrode also shows high rate capabilities and retains 82% of original capacitance after current density is increased 30-fold to 46.87 mA/cm². PANI/NCNT electrodes are used to assemble a symmetric supercapacitor device with PVA/H₂SO₄ hydrogel as separator and electrolyte. The flexible PANI/NCNT supercapacitor showed a specific capacitance of 128 F/g at 2.47 A/g current density and retained over 92% of initial capacitance after 10000 cycles of charge-discharge at 24.7 A/g current density.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Recent developments in wearable, flexible electronics have created an interest in the development of supercapacitors (SCs) as an alternative to traditional batteries [1,2]. SCs offer the advantage of fast charge speed, high power density and long-term cycling stability that can bridge the gap between traditional capacitors and batteries [3]. The performance of SCs strongly depends on the properties of the electrode materials used which need to be electrically conductive, have a high surface area and be chemically stable. The development of flexible and wearable energy storage devices also demands the electrode materials to be mechanically stable and light weight. Carbon Nanotubes (CNTs) have been a prevalent choice as electrode material and CNT sheets have gained popularity as highly conductive, light-weight and flexible

electrodes [4]. These properties also make CNTs ideal for combining with pseudocapacitive materials such as transition metal oxides [5] and conductive polymers [6], which store charge by undergoing redox reactions or faradaic processes. On their own, these materials provide high specific capacitance, however, due to their relatively poor conductivity and mechanical properties, they are often combined with CNTs and other powdered carbon nanomaterials to form electrodes for SCs. The latter approach is facing some challenges due to the creation of random networks which add more obstacles to a fast charge transfer [7,8]. The creation of electrodes from powdered materials often requires conductive additives and binders [9,10] to be added followed by casting on a current collector, which is typically made of metal that adds further weight.

Vertically aligned CNT arrays, typically grown on metal foils [11–13] have been shown to facilitate better mobility of ions due to their high porosity and specific surface area. The increased porosity of CNT arrays allows greater loading of pseudocapacitive materials while still maintaining uniform diffusion of the electrolyte throughout the electrode area. The use of the CNT growth substrate

* Corresponding author. Department of Mechanical & Materials Engineering, University of Cincinnati, Cincinnati, OH, 45221, USA.

E-mail address: Vesselin.Shanov@uc.edu (V. Shanov).

(metal foil) as current collector allows rapid electron transport to and from the individual nanotubes, which in turn results in an overall improved charge transfer facilitating the SCs to maintain high energy densities at very high power densities. However, the use of a separate metallic current collector adds a tremendous amount of 'parasitic weight' to the SC thereby limiting its application in wearable and flexible electronics. Researchers have attempted to overcome this problem by using light weight carbonaceous substrates for CNT growth and as current collectors. Carbon cloth or fabric [14] have been used as substrates for CNT synthesis and as scaffolds for pseudocapacitive materials [15] to make flexible SCs. The relatively low electrical conductivities of these materials [16] however, can slow down the rate of electron transfer resulting in lower overall charge transfer rate and thus reduced capacitance at high current densities. Aligned CNT sheets with high electrical conductivity have been utilized as current collectors and as scaffolds for pseudocapacitive materials such as MnO₂ [17] and polyaniline [18] to produce light-weight, flexible SCs.

Herein, we report progress in creating of a new 3-dimensional nanostructured electrode architecture which combines the high porosity and better ion diffusion properties of a CNT array with the superior mechanical properties and high electrical conductivity of CNT sheets. Vertically aligned carbon nanotube arrays are synthesized by plasma enhanced chemical vapor deposition (PECVD) directly on a CNT sheet substrate composed of horizontally aligned carbon nanotubes. The result is a free-standing structure (NCNT) consisted of the CNT sheet acting as substrate, also as current collector. The CNT array provides increased porosity and higher surface area to the electrode. This electrode scaffold is then coated with polyaniline (PANI) via an easy electrodeposition process. The result is a truly freestanding electrode manufactured without any metal support, conductive additives or binders. PANI/NCNT electrodes with a core-shell/CNT-PANI morphology deliver a high specific capacitance of 359 F/g at a current density of 4.95 A/g calculated based on the mass of PANI coating. The electrode also shows high rate capability and retains more than 82% of its capacitance even after the current density is increased 30 times to 46.87 mA/cm². A symmetric supercapacitor device comprised of PANI/NCNT electrodes and PVA/H₂SO₄ gel electrolyte was fabricated which revealed a specific capacitance of 128 F/g at high current density of 2.47 A/g. The device is also able to maintain 92% of its initial capacitance after 10000 cycles of charge-discharge at a high current density of 24.7 A/g.

2. Experimental section

2.1. Plasma-enhanced chemical vapor deposition (PECVD) of CNTs on CNT sheet

CNT sheets are fabricated by dry-drawing from 'spinnable' CNT arrays in a process described previously [19,20]. The CNT sheet substrates used in this study are made by winding 100 layers of CNT web while densifying the deposited webs with acetone. The evaporation of acetone creates capillary forces between the nanotubes and brings them closer together resulting in a 'densified' sheet material. After densification, the CNT sheets have thickness of ~4 μm and possess an areal density of 0.24 mg/cm². As-produced CNT sheets comprising of aligned carbon nanotubes are coated with 7 nm Ni catalyst by e-beam evaporation. Ni-coated CNT sheets were then used as substrates for growth by plasma enhanced chemical vapor deposition (PECVD) in an Aixtron Black Magic™ reactor that can accommodate a 4" wafer. Ni-coated CNT sheets were flattened on a TiN coated, boron doped, conductive Si wafer. The latter serves as an electrode in the PECVD process and good electrical conductivity is critical to maintain stable plasma. Further,

the CNT sheet is annealed inside the reactor in a hydrogen atmosphere at 500 °C prior to growth of CNT array. Annealing in hydrogen allows uniform Ni particle formation for CNT synthesis. The growth was carried out for 10 min at 700 °C temperature and 3.7 mBar pressure in an ammonia (NH₃) plasma environment with acetylene (C₂H₂) as the carbon precursor. NH₃ and C₂H₂ are fed at 160 sccm and 40 sccm respectively to maintain a 4:1 ratio considered ideal for CNT growth [21]. The DC plasma electric field also enables vertical alignment of CNTs during growth creating a three-dimensional structure comprised of vertically aligned CNTs extending from horizontally aligned CNTs in the CNT sheet substrates. This electrode design is termed NCNT or NCNT sheet for the sake of identification in this work. For comparison, a pristine CNT sheet was also made on which no CNT growth was carried out. This sample is termed PCNT or PCNT sheet for the sake of identification.

2.2. Fabrication of PANI/NCNT electrode

NCNT sheets were used to create free-standing electrodes by attaching a copper wire using electrically conductive silver epoxy. The connection point is then sealed with conventional epoxy. NCNT electrode was used as working electrode in a 3-electrode configuration connected to a Gamry Interface 1000 Potentiostat/Galvanostat with a Pt wire and Ag/AgCl electrode used as the counter and reference electrode, respectively. Prior to deposition of polyaniline, the NCNT electrodes were treated with 4 M H₂SO₄ for 30 min to remove Ni catalyst from tips of the CNT array synthesized in a tip growth mode. PANI was deposited on the NCNT electrode by cyclic voltammetry (CV). A solution of 0.018 M aniline in 1 M H₂SO₄ was used for deposition and the electrodes were cycled between -0.2 V and 0.8 V at a scan rate of 25 mV/s. The amount of PANI deposited was controlled by changing the number of cycles of CV. The electrodes are named after the number of cycles of PANI deposition by CV as follows: 10PANI/NCNT, 20PANI/NCNT, 30PANI/NCNT, 40PANI/NCNT and 50PANI/NCNT for electrodes coated with 10, 20, 30, 40 and 50 cycles of CV, respectively. NCNT sheet electrode without PANI coating was also prepared for comparative testing and is termed as NoPANI/NCNT electrode. After coating, the electrodes are rinsed three times with D.I. water and dried overnight under vacuum at room temperature. Pristine CNT sheet without any CNT array grown on it was also coated with PANI and tested for comparison. Pristine CNT sheet electrode coated with 30 cycles of PANI deposition is termed as 30PANI/PCNT for identification.

2.3. Assembly of PANI/NCNT || PANI/NCNT capacitor

A symmetric capacitor device was assembled by combining two PANI/NCNT electrodes with PVA/H₂SO₄ solid gel electrolyte sandwiched in between. PVA/H₂SO₄ gel electrolyte was prepared by dissolving 1 g PVA in 10 mL water and 2 mL concentrated H₂SO₄. The mixture was stirred at 90 °C until all the PVA dissolved and the solution became clear. The gel, which remains a viscous liquid, was cooled down to 50 °C and then applied as a thin layer on the PANI/NCNT electrodes. The gel-coated electrodes were dried overnight at room temperature. After drying, the two electrodes were gently pressed together with an additional thin layer of PVA/H₂SO₄ gel applied in between. The device was dried in air overnight. The PVA/H₂SO₄ gel acts as an electrolyte and separator for the device. An illustration of the symmetric capacitor device is shown later in Fig. 8 (a).

2.4. Characterization

Scanning electron microscopy (SEM, FEI SCIOS) and Transmission Electron Microscopy (TEM, FEI CM20, 300 kV) were used

Download English Version:

<https://daneshyari.com/en/article/5432215>

Download Persian Version:

<https://daneshyari.com/article/5432215>

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