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Helically coiled carbon nanotube electrodes for flexible supercapacitors

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ABSTRACT

Novel highly flexible electrodes consisting of helically coiled carbon nanotubes (HCNTs) have been developed for flexible supercapacitors (SCs). Hierarchically mesoporous HCNTs are synthesized on unidirectional carbon fiber (UCF) by catalytic chemical vapor deposition. Free-standing HCNTs grown on UCF (HCNTF) is further used as electrode cum current collector for fabricating flexible SCs. Highly bendable UCF serves both as the substrate for the synthesis of HCNTs and as current collector for the SC. No separate secondary current collector is used in this study. The microstructure and surface morphology of the HCNTF hybrid is characterized by scanning electron microscopy and transmission electron microscopy, the chemical structure is determined by Raman spectroscopy, the chemical bonding states are examined by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy and the surface area is measured by Brunauer–Emmett–Teller surface area measurement. The electrochemical properties of HCNTF SC are examined by cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge/discharge measurements. The HCNTF hybrid exhibits open mesoporous nanostructure with an average pore size of 3.8 nm. The bendability of HCNTF SC is tested by carrying out the galvanostatic charge/discharge measurement by bending the SC at different angles and the study reveals that the SC is highly bendable. The HCNTF SC exhibits a maximum gravimetric capacitance of 125.7 F g^{-1} with an area specific capacitance of 145.3 mF cm^{-2} at a current density of 0.28 mA cm^{-2}. The supercapacitive performance of the HCNTF SC is found to be superior to that of the SCs utilizing straight-CNTs based electrodes. The present study opens-up the successful development of novel carbonaceous electrode with helical nanostructure for application particularly in SCs.

1. Introduction

Supercapacitors (SCs) or electrochemical capacitors have several advantages when compared to that of the conventional dielectric capacitors, such as high energy and power densities, high rate charge/discharge capabilities, long cycle life, safe operation, etc. The performance of a SC is mainly dependent on the type of electrode material used and the effective surface area and the pore structure of the electrodes. Carbon nanomaterials such as carbon nanotubes (CNTs), graphene, onion-like carbon, mesoporous carbon, etc. have been used as electrode materials in SCs with high-performance. Among these, CNTs have achieved much importance due to various reasons such as large surface area, good electronic conductivity, low density, good chemical and environmental stabilities, good electrochemical properties and availability of easy production methods [1].

Nowadays, the advanced flexible electronic devices are in urgent need of highly flexible energy storage devices to supply them power. In this aspect, SCs are the suitable energy storage devices as they possess high energy and power densities simultaneously along with high flexibility. Flexible and ultra-thin SCs can be easily integrated into various portable electronic devices such as electronic papers, roll-up and bendable displays, wearable multimedia, etc. [2–4]. CNTs and graphene are found to be the best candidates for the preparation flexible SCs due to their excellent bending strength [5,6]. Flexible SCs have been developed with fibrous electrodes in the recent past. Fibrous materials including Kevlar fiber [7], metal

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fiber [8], carbon fiber [9], CNT fiber [10], graphene fiber [11], etc. are successfully used as flexible SC electrodes with high-performance. But for the processing of such fibrous flexible electrodes, sophisticated machineries are required and hence the production cost of these SCs is very high. In order to eradicate this problem, the present study proclaims the use of hierarchically mesoporous 3D electrodes consisting of helically coiled CNTs (HCNTs) for the development of highly flexible SCs. Coiled-CNTs are the fascinating nanostructures in the CNT family in which they possess exceptional electrical and magnetic properties when compared to that of straight nanotubes [12,13]. Coiled-CNTs are formed by the periodic incorporation of pentagon and heptagon pairs within the hexagonal carbon network [14]. These are found to exist in two different forms namely helical and toroidal nanostructures. The synthesis of coiled-carbon nanostructures on various metallic substrates is reported in various literatures [15–17], but the synthesis of free-standing HCNTs on unidirectional carbon fiber (UCF) substrate is not yet reported. Among the various other methods available, chemical vapor deposition (CVD) is the best and efficient method used for the synthesis of coiled-CNTs [18,19]. The coiled-carbon nanostructures are found applications in microwave absorbers [20], field emission displays [21], semiconducting infrared detection elements [22], sensors [23], etc. But the coiled-carbon nanostructures are not yet explored in the area of flexible SCs. In the present study, we report the development of flexible lightweight SC by using free-standing HCNTs grown on UCF (HCNTF) as electrode cum current collector. To the best of our knowledge and belief, this is the first report on the use of HCNTF hybrid as electrode cum current collector in flexible SCs. In this study, the uncoated portion of the UCF is used as the current collector and no separate current collector is used. The unique way of preparing flexible SC by using HCNTF hybrid electrode cum current collector helps in reducing the weight of the SC when compared to that of those utilizing massive metallic current collectors.

2. Experimental

2.1. Materials

Polyacrylonitrile based UCF (specific gravity ~ 1.8 g cm^{-3}, tensile strength ~ 1900–2750 MPa, diameter ~ 8 μm) was received from M/S Fortafil Industries Inc., U.K. Nickel sulphate hexahydrate ($NiSO_4.6H_2O$, 99%), ammonium chloride (NH_4Cl, 99%), tri-sodium citrate ($Na_3C_6H_5O_7.2H_2O$, 98%), liquor ammonia (NH_3, 25%) were obtained from M/S Qualigens Fine Chemicals, India. Sodium hypophosphite ($NaH_2PO_2.H_2O$, 99%), polyvinyl alcohol (PVA) and potassium hydroxide (KOH, 99%) were obtained from M/S Loba Chemie Pvt. Ltd., India. Thiophene (C_4H_4S) was supplied by M/S Sigma Aldrich, India. Lithium chloride anhydrous (LiCl, 98%) was purchased from Sisco Research Laboratories Pvt. Ltd., India.

2.2. Synthesis of HCNTF hybrid

Free-standing HCNTs with high density were synthesized on UCF substrate by catalytic thermal CVD. UCF with individual fiber diameter of ~8 μm were used as the substrate to grow HCNTs. Nickel is used as the catalyst and an electroless dip-coating mechanism is opted for the deposition of catalyst on UCF [24]. The electroless deposition bath contains nickel sulphate hexahydrate as the nickel salt, sodium hypophosphite monohydrate as the reducing agent, trisodium citrate as the stabilizer, and liquor ammonia for controlling the pH. The concentration of these chemicals used in the electroless coating bath is given in Supplementary Table S1. Heat-treated UCF strands were dip-coated inside the electroless coating bath at an elevated temperature of 85 °C for 10 min, rinsed several times with ethanol and deionized water and then subsequently dried at 85 °C for 24 h in vacuum oven. These nickel-coated UCF was used as substrate for the synthesis of HCNTs by catalytic thermal CVD thereafter. During the catalytic thermal CVD process, the nickel-coated UCF was heated upto 500 °C in a horizontal quartz furnace (1.12 m length with 105 mm diameter) under a continuous N_2 flow (200 ml min^{-1}). In order to prevent the formation of oxides on the nickel nanoparticles, H_2 was introduced at a flow rate of 100 ml min^{-1} for 15 min. The temperature was further increased to 700 °C and acetylene was introduced at a flow rate of 90 ml min^{-1} for 15 min while keeping the N_2 flow fixed at 200 ml min^{-1} throughout and thiophene was introduced simultaneously by heating the thiophene containing round bottom flask at 80 °C on the way of nitrogen flow. The HCNTF thus obtained were collected after cooling down the furnace to room temperature under N_2 flow.

2.3. Fabrication of flexible HCNTF SC

Symmetric type SCs were fabricated with HCNTF hybrid as electrode cum current collector, without any further modification. The dimension of SC electrode was 30 mm (length), 3 mm (width) and 1 mm (thickness). The SC was assembled by arranging two similar pieces of HCNTF strands on both sides of an electrolyte-soaked Whatman® filter paper parallel to each other and then kept in between two highly flexible Teflon® sheets with thickness of 0.4 mm and the entire device is sealed with polypropylene film. A 5 M KOH was used as the electrolyte. In the as fabricated SC, the nickel uncoated portion of the HCNTF strand was used as current collector and no separate current collector was used. The overall process of fabricating flexible HCNTF SC is schematically shown in Fig. 1.

2.4. Fabrication of all-solid-state flexible HCNTF SC

All-solid-state flexible HCNTF SC module was fabricated with all-solid-state HCNTF SCs by using solid-state polymer electrolyte where the electrolyte was consisted of PVA/LiCl gel. Initially, the PVA/LiCl gel electrolyte was prepared in the following manner. PVA (3 g) and LiCl (6.5 g) were mixed together in deionized water (30 ml) and heated at 85 °C for 30 min under vigorous stirring. The HCNTF strands were dipped inside the gel electrolyte and SC cell was fabricated by arranging two electrodes on both side of a Whatman® filter paper and the cell was allowed to solidify at 45 °C thereafter. While dipping the HCNTF strand inside the electrolyte, a small portion was left uncoated and it was used as current collector for the all-solid-state SC. The individual HCNTF SC cells thus prepared were connected in series combination to fabricate the HCNTF SC module in which two similar cells were used.

2.5. Material characterizations

The microstructure and surface topography of the HCNTF hybrids were examined by using a scanning electron microscope (SEM; Carl Zeiss EVO MA 15) and transmission electron microscope (TEM; FEI Technai 20 U Twin TEM). The thicknesses of the hybrid electrodes and the SC were measured by using a thickness gauge (S. C. Dey & Co., India). Raman spectra of the HCNTF hybrids were analyzed with the help of LabRam Micro Raman Spectrometer (Jobin-Yuon HR 800 UV) by using a He–Ne (632.7 nm) laser excitation source. Fourier transform infrared spectroscopy (FTIR) experiments were performed by using an infrared spectrometer (Perkin Elmer Spectrum 1) at the frequency range (4000–400) cm^{-1} in transmission mode spectrum. X-ray photoelectron spectroscope (XPS; PHI 5000 Versa Probe II, FEI Inc.) was employed to