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Hierarchical Polyaniline Spikes over Vegetable Oil derived Carbon Aerogel for Solid-State Symmetric/Asymmetric Supercapacitor

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ABSTRACT

Herein, we report an environment friendly methodology for the synthesis of carbon aerogel (CA) using bio-mass (mustard oil) as precursor. The synthesis process is highly reproducible and economical yet devoid of any sophisticated procedure and hazardous organic/inorganic chemicals. Exfoliated graphitic planes of carbon beads with enhanced inter-planer spacing are observed in synthesized CA with low bulk density ($0.144\,g\,cm^{-3}$) and high specific surface area ($1032\,m^2\,g^{-1}$). The CA comprises of meso/microporosity with open pore microstructure. Symmetric supercapacitor cell (CA||CA) is fabricated to test the capacitive performance of CA in H_2SO_4-polyvinyl alcohol (H_2SO_4-PVA) gel as electrolyte. The CA||CA cell exhibits nearly symmetrical voltammograms up to working potential window of 2 V and impedance response demonstrates phase angle ~80° indicating highly capacitive behavior. Polyaniline (PANI) spikes are further synthesized over CA using chemical oxidative polymerization route to introduce pseudocapacitive characteristics in addition to double layer capacitance. Solid-state symmetric (CA-PANI||CA-PANI) and asymmetric (CA||CA-PANI) supercapacitor cells are fabricated to examine the electrochemical performance. Fabricated CA||CA-PANI supercapacitor cell exhibits remarkable high power density ($7.9\,kW\,kg^{-1}$) and high energy density ($55.6\,Wh\,kg^{-1}$). The CA||CA-PANI cell is capable to power a light-emitting diode (LED) bulb effectively for 3.5 min by assembling two supercapacitors ($1 \times 1\,cm^2$).

1. Introduction

Ever-increasing worldwide depletion of fossil fuel leads to energy crisis as well as climate injuries which ultimately causes severe impact on public health and economy. To resolve these energy demand issues, energy storage and conversion devices such as batteries, fuel cells, photovoltaic cells, capacitors and supercapacitor cells have attracted much attention from last two decades. Fuel cells and batteries are considered as high-energy devices while the capacitors are the high-power devices. Supercapacitor cells, in addition to optimum energy storage as well as power delivery, have high rate performance with high operational working stability and high cycle life [1–3]. Electrochemical performance of a supercapacitor cell is primarily influenced by the porous morphology and ionic conductivity of electrode material as these govern the diffusion of electrolyte ions and its rate respectively.

Carbon materials exist in variety of forms such as nanotube, activated carbon, aerogel, graphene, graphene nanoribbon, carbide-derived nanocomposites [4–8] etc. Among these, aerogels/aerogel-like structures have shown outstanding characteristics such as 3-D structures with large open pores, very low density, more layer to layer distance (d-spacing) and high surface area [9–11]. Owing to the unique features, carbon aerogels are expected to have potential applications in energy devices (fuel cell, supercapacitors, photovoltaic), sensors, actuators, catalysts, water treatment, optical applications [12–19] etc. Carbon-based aerogels are the promising electrode materials for supercapacitors due to micro/mesoporous 3-D morphology demonstrating outstanding electric double layer (EDL) performance and excellent mass transfer properties. Adequate thermal and electrical conductivity in ultralight weight structures (high volume/mass ratio) make them unique EDL supercapacitor materials for portable electronics.

Usually, the organic and inorganic precursors are employed in synthesizing organic, inorganic and organic-inorganic hybrid aerogels. Carbon aerogels are typically synthesized from various organic precursors such as resorcinol–formaldehyde (RF) [20,21],

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phenolic–furfural [22,23], polymethylmethacrylate/polyacrylonitrile [24], poly (vinyl chloride) [25] etc. followed by pyrolysis. Pekala et al. have reported the first organic aerogel using RF condensation process [26,27]. Aerogel-like morphology can also be synthesized using silica, carbon materials, metal oxides and polymers as precursor [28]. Above reported synthesis approaches made use of expensive and environmental hazardous organic/inorganic precursors.

Several reports are available to cast off these expensive organic/inorganic precursors. Among them, new and common synthetic approach is the direct conversion of renewable and sustainable natural resources such as crude plants [29,30], bagasse, coconut, peanut shells [31–34], cellulose [35], hemp fibers [36], watermelon [13], pollens, seaweeds, D-glucose, polysaccharides [37–41] etc. into carbon materials. An interesting approach to protect environment with clean and efficient energy generation/storage is the utilization of secondary non-biodegradable waste, examples are the utilization of hazardous diesel soot [42], bamboo-based industrial byproduct [43], scrap waste tires [44], cigarette filter [45]. There are scant reports on the utilization of carbon soots in energy storage however in the present article using chemical activation process, formation of the carbon powder aerogel with large surface area is reported for the first time.

In this study, we used vegetable (mustard) oil [46] as precursor to synthesize an economic carbon aerogel (CA). The CA obtained exhibits micro and mesoporosity with high surface area ($1032\ m^2\ g^{-1}$) and low density value ($0.144\ g\ cm^{-3}$). The electrochemical performance of CA is studied by fabricating symmetric supercapacitor cell (CA||CA) using H_2SO_4-polyvinyl alcohol (H_2SO_4-PVA) gel electrolyte. High energy storage capability can be achieved by synthesizing hybrid aerogel nanocomposites [47–50]. Therefore a nanocomposite of micro/mesoporous carbon aerogel with flexible and conducting polyaniline (PANI) is proposed to introduce pseudo-capacitance. Synergism in the proposed nanocomposite improved the cycling stability and mass transport limitation of polymers due to mass insertion/desertion during redox switching [51]. The polymer CA nanocomposite exhibits short relaxation time constant, fast and reversible adsorption/desorption of electrolyte ions in symmetric (CA-PANI||CA-PANI) and asymmetric (CA||CA-PANI) supercapacitor cells at high current density.

2. Experimental Section

2.1. Synthesis of Carbon Aerogel

The carbon material was obtained by burning the mustard oil in air. The synthesis route is illustrated in Fig. S1. The vegetable oil was kept in ordinary stainless steel lamp and burnt using cotton wick. For the collection of carbonaceous material, inverted petri dish was placed over lamp with the help of tripod stand at a height of two inches so that the flame of the lamp just touched the petri dish. The temperature of flame measured with the help of thermocouple was found to be ~600 °C. The carbon sample obtained was scratched out.

So obtained sample was activated by heating carbon/KOH slurry at 800 °C under N_2 ambient. In brief, 1.0 g of carbon and 7.0 g of KOH were taken in 50 mL round bottom flask. The minimum quantity of water was added to the above reaction mixture and magnetically stirred till the mixture turned into thick slurry-like appearance and kept uninterrupted for 24 hrs so that the KOH adsorbed thoroughly. The KOH soaked mixture was transferred to alumina-crucible and kept at 110 °C till the slurry like mass became solid. The crucible was transferred into a tubular furnace programmed to 800 °C at 10 °C min^{-1} and hold for one hr. The black solid product was filtered and washed with distilled (DI) water till the pH of the filtrate became neutral. The washed product was dried in vacuum oven at 100 °C for 12 hrs.

2.2. Synthesis of CA-PANI Nanocomposite

2.0 mL of aniline and 14.0 mL of H_2SO_4 were added to 140 mL of ethanol (20%). To this solution, 700 mg CA was dispersed under vigorous stirring for 2 hrs. The above reaction mixture was kept in ice bath to control the temperature at 0 °C. Then ammonium persulfate solution (APS, 5.0 mL) was added drop wise while stirring. The product was filtered using 0.45 μm PTFE membrane and washed with DI water and ethanol. Product obtained was dried at 70 °C and is found to be 1.75 g. The content of polyaniline in CA: PANI composite is 1.5 times to that of CA and is abbreviated as CA-PANI nanocomposite.

2.3. Fabrication of Solid-state Supercapacitor

In order to fabricate the supercapacitor electrodes, 20 mg of CA and CA-PANI nanocomposite were separately dispersed in isopropyl alcohol under ultrasonication and spray deposited onto polished graphite sheets. Then H_2SO_4-PVA gel electrolyte was prepared as described in our earlier article [52] and used as gel electrolyte membrane. The solid-state symmetric as well as asymmetric supercapacitor cells were fabricated. In brief, the resulting gel membrane was spread onto 1 cm^2 area of electrode material and dried at room temperature (35–40 °C) for 6 hrs to evaporate the excess water. Finally two spray coated electrodes were assembled together in face to face arrangement to get symmetric supercapacitor cell assembly (CA||CA or CA-PANI||CA-PANI). In the same way, asymmetric supercapacitor cell (CA||CA-PANI) was fabricated where CA was used as negative and CA-PANI was used as positive electrode. Charge storage is balanced ($q_+ = q_-$) with the help of $q = C_{sp} \times \Delta V \times m$ equation [53], where C_{sp} is the specific capacitance, ΔV is the operational potential window after iR drop and m is the total mass on two electrodes. The optimized mass loading ratio for negative to positive electrode is ~2.

2.4. Structural and Electrochemical Characterization

The crystalline structures of CA and CA-PANI nanocomposite were analyzed using powder X-ray diffraction (XRD, Bruker D8 advance X-ray diffractometer) and Raman spectroscopy (Renishaw Invia Reflex Microraman spectrometer, 514 nm laser). Specific surface area (SSA) was estimated from N_2 adsorption/desorption measurements performed at −196 °C and degassed at 300 °C using Brunauer-Emmett-Teller (BET, Micromeritics ASAP 2020, USA) method. High resolution transmission electron microscopy (HRTEM, Phillips Technai T-300 microscope) and Scanning electron microscope with Energy-dispersive X-ray spectroscopy (SEM-EDX, Zeiss Ultra 55 microscope) were employed to study the microstructures. All electrochemical performances were evaluated in two electrode cell assembly using H_2SO_4-PVA gel electrolyte. Cyclic voltammograms (CVs) and electrochemical impedance spectroscopy (EIS) were carried out with the help of CHI 604D electrochemical analyzer. Electrical conductivity was measured by two-probe method using Keithley 6517 B electrometer. Galvanostatic charge/discharge (GCD) and cycling stability measurements were performed employing PARSTAT 4000.

3. Results and Discussion

A brief synthetic procedure is sketched for the preparation of carbon aerogel in Scheme 1. Here concentric spheres corresponding to graphitic planes are observed in vegetable oil derived carbon and the outer graphitic planes of these concentric spheres get