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Synergistic effect of reduced graphene oxide, CNT and metal oxides on cellulose matrix for supercapacitor applications

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ABSTRACT

In this paper, a hybrid nanocomposite of cellulose fiber/multi-walled carbon nanotube (MWCNT)/reduced graphene oxide (rGO)/Cobalt oxide (Co_3O_4)/tin oxide (SnO_2) is synthesized via a hydrothermal method for supercapacitor applications and characterized for their electrochemical performance and thermal stability. The morphology of the nanocomposites was characterized by using scanning electron microscope (SEM) and transmission electron microscope (TEM). Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Raman spectroscopy were used to determine the chemical groups and crystal structure. Energy dispersive X-ray spectroscopy (EDX) confirmed the constitutional proportions of various elements in the composite. The electrode was fabricated from the nanocomposite and characterized by cyclic voltammetry (CV) that showed good cyclic stability with 88% capacitance retention after 1000 cycles and a capacitance of 215 F g^{-1} and 181 F g^{-1}at a current density of 0.2 A $g^{-1}$and 0.4 A g^{-1}, respectively. The hybrid nanocomposite showed higher thermal stability than cellulose fiber/MWCNT and cellulose fiber/MWCNT/rGO composites. This simple, scalable and low-cost approach could open new opportunities for next-generation energy storage devices.

1. Introduction

The wide increase in the energy demand and less availability of the non-renewable energies have driven a significant research in the development of novel and more efficient energy storage devices. Electrochemical storage devices, for example, secondary batteries and supercapacitor have generated great interest as an alternative for portable electronics and automobile applications. Supercapacitor has higher power density and charge-discharge cycles as compared to secondary batteries but the storage density of the supercapacitor is lower than that of the secondary batteries. A high-performance electrode material is required in order to develop supercapacitor device with improved storage density and high power density and a large number of charge-discharge cycles [1].

In supercapacitor, the capacitance is defined by electric double layer capacitance and pseudocapacitance. In electric double layer capacitors (EDLC), energy is stored due to the charge separation at the electrode/electrolyte interface. In EDLC, carbon allotropes (carbon nanotubes, graphene) are used as the electrode material. While in pseudocapacitors, energy storage takes place through reversible redox reaction and transition metal oxides, metal sulfides and polymers (natural and artificial) are used as the electrode material [2–5]. In previous studies, reduced graphene oxide (rGO), CNT and conductive polymer were used for supercapacitor application but there are less published studies on rGO, CNT and transition metal oxide used together in a biopolymer matrix [3,5,6]. Supercapacitor electrode offers exceptional properties as compared to the traditional solid dielectrics and it is one of the crucial parts of designing the advanced energy storage devices.

Graphene and carbon nanotubes (CNT) are one of the most extensively discussed carbon allotropes as a material for an electrode in EDLC applications as they offer exceptional properties. To investigate the effect of graphene/CNT coating on electrical properties Yeon et al. synthesized GO/CNT hybrid materials and coated on carbon fiber surfaces by electrophoretic deposition followed by thermal treatment. In another study, Yaming Wang and his co-workers synthesized a flexible supercapacitor with reduced graphene oxide/carbon black hybrid film and high rate response was observed [7–9]. Carbon nanotubes possess exceptional properties for example high surface area (1600 m^2 g^{-1}), high electrical conductivity (105 S cm^{-2}) and high strength. However, nanotubes suffer from limited performance due to microspores and internal resistance [6,10]. High surface area of CNT is explored by deposition of conducting polymers/metal oxides that facilitate the efficiency of ion diffusion phenomenon and shows higher specific capacitance as compared to pristine CNT. The properties of the graphene

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such as superior electrical conductivity (~10^6 S cm^{-2}), high surface area (~2600 m^2 g^{-1}), mechanical strength (~1 T pa), fracture strength (125 GPa) and excellent chemical stability make graphene a perfect electrode material in EDLC applications [11–14]. It is observed that graphene layers tend to re-stack even after the exfoliation process and display the reduced magnitude of capacitance and need to be paired with some transition metal oxide/hydroxide/sulfides or conductive polymer so that it can be used in the supercapacitor applications [15,16].

Many transition metal oxides (SnO_2/Co_3O_4/RuO_2)/reduced graphene oxide (rGO) polymer nanocomposites have been extensively studied in the literature [2,13,17–19]. Co_3O_4 is one of the most investigated transition metal oxide for electrode material due to its high theoretical specific capacitance of 3560 F/g and controllable nanostructure [20,21]. Transition metal oxide (Co and Ni) have been studied for supercapacitor applications because of their characteristics of high capacity, stable structure, and low cost. Due to the variable transition state, metal oxides can be used for fabrication of faradic charge storage electrodes [22–24]. Shravan Suresh et al. synthesized four types of RGO- MFe_2O_4 and showed significant improvement in the specific capacitances of the composites. Debananda Mohapatra et al. showed the importance of the composites microstructure and metal oxide-matrix interaction in the performance of supercapacitor electrodes [25–27]. Yet transition metal oxides demonstrated the high magnitude of capacitance but their commercial use is still limited due to the weak transport of the electrolyte ions within the metal oxide matrix [28,29]. It is observed from the literature that introducing a conductive filler in the metal oxide matrix would lead to increase in the electrical conductivity due to the availability of a continuous path for the transport of the electrolyte ions.

Biopolymers such as cellulose, lignin, and gelatin have attracted much attention as they are biodegradable, renewable and emit fewer greenhouse gases as compared to the synthetic polymers [30]. Cellulose is one of the most abundant organic biopolymers and offers properties such as biocompatibility, flexibility, high mechanical strength, and biodegradability. Cellulose can be obtained from plants and bacteria and due to its unique properties, it has the possibility to be used as a renewable separator for supercapacitor [31]. In previous studies, bacterial cellulose (BC) was integrated with inorganic phases such as metal oxide-BC, metal sulfide-BC and metal nanoparticles-BC in the electrochemical and photocatalysis applications [32,33]. Recent researches also mentioned that tuning the properties of cellulose by carbon nanomaterials such as graphene would improve the functionality of supercapacitor electrode by offering improved conductive network and capacitance [34,35]. In literature, fabrication of cellulose/GO composites is reported for the applications of different sensors (chemical/temperature/proximity) and energy storage devices [36–40]. Some studies demonstrated bacterial cellulose (BC) as a favorable substrate for flexible and aqueous supercapacitor electrode having three-dimensional porous networks and hydrophilicity [41–43]. However, there are very few discussions on the reinforcing effects of MWCNT and rGO in natural biopolymers such as cellulose, lignin, and chitosan because of the difficulties of the dispersion of these nanomaterials in the solvents, used for biopolymers [44]. Usefulness of cellulose for supercapacitor electrode can be improved after altering its properties by inorganic nanomaterials such as graphene and carbon nanotubes [34,45].

In this study, we have synthesized a nanocomposite (cellulose/rGO/MWCNT/SnO_2/Co_3O_4) and demonstrated the synergistic effect of carbon nanomaterial (reduced graphene oxide and CNT) and metal oxide (SnO_2 and Co_3O_4) in the cellulose fiber matrix for supercapacitor application.

2. Experimental method

2.1. Materials and methods

The cotton cellulose (MVE, Degree of polymerization: 7450) was purchased from Buckeye Technologies Co. (USA). N, N-Dimethylacetamide (DMAc), Lithium chloride (extra pure grade), Multi-walled carbon nanotubes (MWCNT), graphene oxide (GO), cobalt (II) chloride ($CoCl_2.6H_2O$), tin (II) chloride ($SnCl_2.2H_2O$), potassium hydroxide (KOH) and aminopropyl triethoxysilane (γ-APTES) were purchased from Sigma Aldrich (USA).

2.2. Synthesis of MWCNT and graphene oxide

The hybrid nanocomposites of MWCNT and GO were synthesized according to the literature [46]. At first, the measured amount of MWCNTs (1 g) was sonicated with 20% hydrochloric acid for 3 h and filtered with Millipore membrane. After filtration, the reaction mixture was transferred to a flask and shocking for 8 h, followed by cooling to the ambient temperature. The reaction mixture was then filtered (pore diameter 0.22 μm) and the residue was washed repeatedly by de-ionized water until the pH of the filtrate became neutral. The residue was then dried in a vacuum oven at 90 °C for 3 h. The sample so formed was termed as MWCNT-COOH.

Graphene oxide was synthesized via modified Hummer's method [46]. This modified process of synthesis involves both oxidation and exfoliation of graphite sheets due to the thermal treatment. First, the graphite flakes (2 g) and $NaNO_3$ (2 g) were mixed in 90 ml of H_2SO_4 (98%) in a volumetric flask with continuous stirring at 300 rpm in the ice bath (0–5 °C). Then the reaction mixture stirred for 4 h and potassium permanganate (12 g) added slowly to the suspension, keeping the temperature of the reaction mixture below 5 °C. The reaction mixture was then diluted slowly by adding 200 ml of water and kept stirring for 4 h at the same temperature. The ice bath was then removed and the mixture was stirred at 40 °C for 2 h. The above mixture was refluxed at 95 °C for 30 min and a brown colored solution was obtained which on treatment with 40 ml H_2O_2 gives a bright yellow color solution. The final mixture was washed repeatedly with 20% HCl and then with deionized (DI) water until gel-like substance (neutral pH) was formed. After washing, the sample was vacuum dried at 80 °C for 12 h and graphene oxide (GO) powder was obtained.

2.3. Preparation of reduced graphene oxide (rGO) via chemical process

100 ml of an aqueous suspension of graphene oxide (0.1 mg/ml) and 50 mg of ammonium hydroxide with hydrochloric acid (50% of NH_4OH) were added to three neck round bottom flask. The reaction mixture was then heated at 95 °C under constant stirring (500 rpm). The color of the reaction mixture was changed from yellow-brown to black, indicating the reduction of graphene oxide (rGO). The rGO so formed was filtered and washed repeatedly with distilled water followed by drying and stored in the closed container.

2.4. Preparation of cellulose fiber/MWCNT nanocomposites

At first, the stoichiometric amount of cellulose fiber (0.5 wt%) and MWCNT (0.2 wt%) were dispersed in DMAc (10 ml) and stirred for 2 h. Then, γ-APTES was added along with water and HCL, followed by heating for 12 h at 90 °C. After heating, the solution was dried in the vacuum oven at 90 °C for 12 h followed by repeated washing of water and ethanol. Then the washed nanocomposite sample was dried and characterized.

2.5. Preparation of cellulose fiber/MWCNT/rGO nanocomposites

Cellulose/MWCNT/rGO nanocomposite was synthesized as reported