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Poly(3,4-ethylenedioxypyrrole) Enwrapped Bi_2S_3 Nanoflowers for Rigid and Flexible Supercapacitors

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ABSTRACT

A hybrid material composed of poly(3,4-ethylenedioxypyrrole) or (PEDOP) enwrapped Bi_2S_3 nanoflowers was synthesized for the first time for use as supercapacitor electrodes. The Bi_2S_3 nanoflowers were enveloped by a sheath of PEDOP, during the course of electropolymerization and uniform coatings of PEDOP/Bi_2S_3 hybrid were deposited on rigid and flexible current collectors. Asymmetric supercapacitors were constructed using the PEDOP/Bi_2S_3 hybrid and graphite (Gr) as working and counter electrodes. The electrochemical specific capacitance of the hybrid based cell (201 F g^{-1}) was found to be 3.58 times greater than that of the pristine polymer (56 F g^{-1}), at the same current density of 1 A g^{-1}. The PEDOP/Bi_2S_3-Gr cell delivered energy and power densities of 100.5 Wh kg^{-1} and 0.5 kW kg^{-1} respectively. The Bi_2S_3 nanoflowers also furnish a robust support to PEDOP, which was reflected in an excellent rate capability, for the hybrid sustains high currents, without incurring a significant loss in capacitance, and good durability upon repeated switching between doped and dedoped states. A flexible supercapacitor was also fabricated with the PEDOP/Bi_2S_3 hybrid and it delivered a capacitance of 329 F g^{-1} (at 0.4 A g^{-1}), thus indicating the promise the hybrid holds for realizing scalable, but lightweight high performance supercapacitors.

1. INTRODUCTION

Hybrid nanostructured materials have spurred considerable scientific interest in the last decade, particularly, with regard to their application in energy storage devices. Among the two dominant energy storage solutions, batteries and supercapacitors, the latter devices have driven significant research efforts, due to long cycle life, greater safety, larger power density compared to batteries and higher energy density relative to conventional dielectric capacitors [1,2]. Supercapacitors are categorized into two subgroups according to their charge storage mechanism, electrical double layer capacitors (EDLCs) and redox capacitors (pseudocapacitors) [3–5]. EDLCs are based on a non-Faradaic surface charge induced at the electrode/electrolyte interface and pseudocapacitors rely on the ability of the electroactive material (e.g. conducting polymers and transition metal oxides) to store/release charge by undergoing reversible Faradaic reactions. These redox processes are accompanied by mass transfer: ions at the conducting polymer or oxide/electrolyte interface and electrons at the current collector/conducting polymer or oxide interface [6,7]. Conducting polymers are promising electrode materials for pseudocapacitors due to low toxicity, low cost, light weight, highly reversible redox states, moderate conductivities, ease of synthesis and good chemical stability of the doped form [8].

A simple approach to further increase the charge uptake capability of a conducting polymer involves the incorporation of an electrically conductive and electrochemically stable nanostructured additive (such as multiwalled carbon nanotubes (MWCNTs) or graphene) in the conducting polymer matrix. This strategy has been fairly successful for developing high performance supercapacitors. In the past, a novel super capacitor fabricated by use of a pyrene functionalized polyfluorene as an adhesive inter-layer between poly(3,4-propylenedioxypyrrole) (PProDOP) and single walled carbon nanotubes (SWCNTs) delivered a specific capacitance (SC) of 122 F g^{-1} [9]. Rigid supercapacitors constructed with poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS)-SWCNT bucky paper showed a maximum SC of 133 F g^{-1} at a current density of 0.67 A g^{-1} [10]. In another study, a SC of 180 F g^{-1} was obtained for a PANI/porous carbon composite electrode [11]. To date, the bulk of scientific reports have focused on developing hybrid supercapacitors encompassing composites of conducting polymers with either carbonaceous nanostructures

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such as CNTs, graphene, carbon fibers [12,13] or metal oxides (RuO_2, MnO_2, V_2O_5, Co_3O_4 etc) [14–18]. Recently, some transition metal sulfides such as CoS [19], NiS [20] and Sb_2S_3 [21] were also used in redox capacitors due to their intrinsic properties: good performance and cost effectiveness relative to the high cost of RuO_2. But their usage as replacements for carbon nanostructures in conducting polymer/carbon hybrid based supercapacitors is extremely limited.

To date, to the best of our knowledge, electrically conductive and electrochemically stable bismuth sulfide (Bi_2S_3) nanostructures have not been used as alternates to carbon nanostructures in conducting polymer hybrid based supercapacitors. Further, the inclusion of Bi_2S_3 nanostructures in a conducting polymer like poly (3,4-ethylenedioxypyrrole) or PEDOP to form a PEDOP/Bi_2S_3 hybrid for supercapacitor applications also remains unreported until now. In a previous report from our group, Sb_2S_3 nanorods were used [21], but they were prepared at a higher temperature of 180 °C compared to Bi_2S_3 nanoflowers herein, which were prepared at a lower temperature of 120 °C. The electrolyte used for supercapacitor application in the earlier report was a gel [21], whereas here it is a an ionic liquid wetted borosilicate glass membrane, the device configuration is oversimplified in this case. Bi_2S_3, is direct gap semiconductor with a band gap of 1.3 eV (nanowires), and The functional properties of nano-sized Bi_2S_3, are to a very great extent, controlled by their shape, morphology and crystal structure. Syntheses of Bi_2S_3- nanorods [22,23], nanotubes [24,25], nanowires [26,27] and nanoribbons [28,29] are well-reported. Similarly, among various conducting polymers such as PEDOT, PANI, poly (pyrrole) (PPy), poly(thiophene) etc, PEDOP, stands out owing to a low band gap (1.6 eV) compared to PEDOT (2.2 eV), lower oxidation and reduction potentials, and highly conductive and stable doped state [30]. Despite being extremely versatile, it continues to remain severely under-utilized [30]. In this report, Bi_2S_3 nanoflowers were synthesized by a hydrothermal route and then incorporated in PEDOP, during electropolymerization and PEDOP/Bi_2S_3 hybrid coatings were obtained on rigid and flexible substrates. Field emission scanning electron microscopy (FE-SEM), Raman spectroscopy, high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) methods were used for the structural characterization of the materials. The electrochemical charge-discharge characteristics of the novel PEDOP/Bi_2S_3 hybrid were evaluated by constructing asymmetric cells with graphite and compared with the performance of the pristine PEDOP and the role of Bi_2S_3 nanoflowers in greatly enhancing the electrochemical activity of the hybrid was unraveled. A flexible supercapacitor was also constructed with the PEDOP/Bi_2S_3 hybrid and a LED illumination was demonstrated. Our studies unambiguously bring out the remarkable ability of hitherto unexplored highly conductive and cost effective Bi_2S_3 nanoflowers, in amplifying the electrochemical specific capacitance of a less studied conducting polymer such as PEDOP, and open up avenues for extending the use of these sulfide nanostructures for developing composites based on other conducting polymers as well.

2. EXPERIMENTAL

2.1. Chemicals

3,4-ethylenedioxypyrrole (EDOP) monomer, thiourea, graphite (particle size: <20 μm) and an ethyl cyanoacrylate epoxy were purchased from Sigma-Aldrich and used as received. 1-Butyl-3-methyl imidazolium trifluoromethanesulfonate (BMITFI), Bismuth nitrate pentahydrate ($Bi(NO_3)_3.5H_2O$), acetone, acetonitrile, and ethanol were purchased from Merck chemicals. Ultrapure water (resistivity 18.2 MΩ cm) was obtained through a Millipore Direct - Q3UV system. SnO_2: F (FTO) coated glass substrates with a sheet resistance of about 14 Ω sq^{-1} were purchased from Pilkington, washed with soap solution, flushed with copious amounts of distilled water and cleaned with acetone prior to use. The carbon fiber fabric was characterized by a sheet resistance of 2.7 Ω cm^{-2}, thickness ~3 mm and weight ~1.8 g $cm^{-2}$was purchased from Alibaba Pvt. Ltd. A GF/D borosilicate glass fiber membrane separator, was procured from Alfa Aesar.

2.2. Synthesis of Bi_2S_3 nanoflowers

$Bi(NO_3)_3.5H_2O$ (1.94 mM) was dissolved in ultrapure water (30 mL) and magnetically stirred for 10 min, which was followed by addition of thiourea (2.9 mM) at room temperature. The mixture was stirred for another 30 min. It was then transferred into an autoclave of 100 mL capacity and heated for 12 h at 120 °C. A black precipitate was obtained, which was filtered and washed with deionized water and ethanol, mixed in a 1:1 v/v ratio. The precipitate was heated in an oven at 60 °C. The resulting Bi_2S_3 product was stored in a vacuum dessicator. This product is referred to as Bi_2S_3 nanoflowers.

2.3. Fabrication of electrodes and cells

A clear solution of the monomer: EDOP (0.1 M) was prepared in acetonitrile (30 mL) to which the ionic liquid, BMITFI (0.1 M) was added. A three electrode cell was used for the deposition of PEDOP or PEDOP/Bi_2S_3 hybrid films. FTO coated glass or a carbon fiber fabric (of area 1 × 2 cm^2) was employed as the working electrode and another FTO coated glass plate was used as the counter electrode. Ag/AgCl/KCl was used as the reference electrode. Pale blue-black colored films of PEDOP were obtained by the application of a dc potential of +1.0 V to the working electrode with respect to an Ag/AgCl/KCl reference electrode for 500 s, under potentiostatic conditions at room temperature in chronoamperometric mode. The Bi_2S_3 nanoflowers (50 mg) were added to the monomer bath solution (containing the IL) and the resulting formulation was sonicated for 30 min. This dispersion was used as the medium in a three electrode cell, similar to the one described for the preparation of pristine PEDOP. Upon applying +1.0 V to the working electrode (FTO coated glass or C-fiber fabric), with respect to Ag/AgCl/KCl reference electrode PEDOP/Bi_2S_3 films were obtained on the working electrode. A graphite coating was electrophoretically deposited on the C-fabric, using the same experimental conditions which were employed for coating FTO/glass substrates. The PEDOP/Bi_2S_3 hybrid was electropolymerized onto the C-fabric. The weight of the active material was determined utilizing a TA Instruments' Discovery Thermo Gravimetric Analyzer's microbalance with a 0.001 μg resolution.

A dispersion of graphite (0.1 g) in ethanol (30 mL) was prepared by ultrasonication for 15 min. By using a two electrode configuration with FTO coated glass or carbon fiber fabric as the working electrode and another FTO coated glass as counter electrode, graphite coatings were obtained on the working electrode by electrophoresis; by application of a constant potential of 20 V for 5 min with a Tarsons MC-01 electrophoresis power supply. Graphite electrodes were washed in water, dried in air and have been labeled as Gr. Both asymmetric and symmetric supercapacitor cells were fabricated. In symmetric configuration, both the working and counter electrodes were made of the same electroactive material and the IL, BMITFI as the electrolyte: PEDOP-BMITFI-PEDOP and PEDOP/Bi_2S_3-BMITFI-PEDOP/Bi_2S_3. In the asymmetric configuration, the working electrode was PEDOP/Bi_2S_3 or PEDOP and the counter electrode was Gr, to yield the following cells: PEDOP-BMITFI-Gr and PEDOP/Bi_2S_3-BMITFI-Gr. A PEDOP/Bi_2S_3-BMITFI-Gr cell with carbon fiber as the current collector was also constructed, a borosilicate glass fiber membrane