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Polyethylenedioxythiophene and molybdenum disulfide nanocomposite electrodes for supercapacitor applications

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ABSTRACT

An innovative nanocomposite electrode was chemically synthesized using molybdenum disulphide (MoS_2)- polyethylenedioxythiophene (PEDOT) to understand the charge mechanism in a symmetric supercapacitor. The MoS_2-PEDOT nanocomposite was produced at various ratios of MoS_2 to ethylenedioxythiophene (EDOT) in an aqueous medium of polyanions polystyrene sulfonate (PSS) and cetyltrimethylammonium bromide (CTAB) at controlled conditions. The morphology, crystallinity, and optical properties of MoS_2-PEDOT nanocomposite materials were characterized using scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, particle size analyzer, Raman spectroscopy, X-ray-diffraction, and transmission electron microscopy (TEM) techniques, respectively. The electrochemical properties of the supercapacitor were investigated using cyclic voltammetry, charging–discharging at constant current and electrochemical impedance spectroscopy (EIS) techniques. The specific capacitance, power and energy densities of the supercapacitor were estimated using cyclic voltammetry (CV), charging–discharging, Nyquist and Bode plots. The specific capacitance was estimated to be 361 Farad/gram (F/g) for the 1:2 weight ratio of MoS_2 to the EDOT monomer in the MoS_2-PEDOT nanocomposite based electrodes. Nevertheless, this study provides a fundamental aspect of synthesis of nanocomposite material for optimum attainment supercapacitive properties based on the MoS_2-PEDOT nanocomposite electrode for practical energy storage applications.

1. Introduction

Electrochemical supercapacitors have become a new and revolutionized energy storage field due to their specific capacitance, charging-discharging characteristics, compactness, power density and energy density applications [1,2]. The recent advancement has shown that 2D-nanomaterials such as metal dichalcogenide nanosheets of MoS_2 or others could replace graphene as candidate for obtaining high energy based supercapacitor electrode material [3–5]. The 2D-dichalcogenide MoS_2 reveals high specific capacity and cycle stability when used as anode in lithium ion battery [6]. The 2D-layered MoS_2 shows double layer charge storage capacity, and provides excellent supercapacitive properties due to the large surface area [7–9]. MoS_2 also displays pseudo-capacitance properties similar to ruthenium dioxide (RuO_2) due the +2 to +6 oxidation states of Mo in the structure [8,10]. Various conducting polymers (polyaniline 'PANI', polypyrrole 'PPY', polyethenedioxythiophene (PEDOT) and polythiophene 'PTh') have been used for supercapacitor applications due to their superior redox properties, high electrical conductivity and environmental stability [11–16]. PEDOT possesses fast redox reactions, charging-discharging characteristics and stable conducting polymer, and it is used as an electrode material in various electrolytic solutions for supercapacitor applications [17,18].

However, conducting polymers also illustrate poor stability and recyclability due to the Ohmic polarization in several solvents for supercapacitors applications [19]. The stability and recyclability of conducting polymers has been resolved by formation of nanocomposite with RuO_2, TiO_2, carbon nanotubes, graphite, activated carbon, graphene, etc. [19–22]. MoS_2 composites with conducting polymer (CP) have also been used as an electrode for supercapacitor applications [23–25]. The PEDOT/MoS_2 composite electrode materials are synthesized using exfoliation of MoS_2 and in-situ polymerization technique, and applied for supercapacitor and lithium battery applications [26,27]. The surface analysis of the MoS_2-CP nanocomposites has shown high porosity

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and active surface area [28]. MoS_2 is a hydrophobic material, and its immiscibility in water creates an issue for the successful synthesis of nanocomposites in aqueous media. We have exploited the surface chemistry by using CTAB as surfactant for the presence of MoS_2 in the aqueous solution. The use of CTAB allowed MoS_2 to disperse uniformly in the resulting EDOT based polymerizing solution. The EDOT was dissolved in the aqueous solution in presence of PSS polyanions. As demonstrated in this work, MoS_2-PEDOT nanocomposite materials were successfully synthesized using modified MoS_2 in aqueous media using surfactant. The simplistic synthesis, superior electrochemical redox properties and higher specific capacitance of electrode material are key in the foundation of practical supercapacitor applications for energy storage applications.

2. Experimental

2.1. Synthesis of MoS_2-PEDOT

The MoS_2-PEDOT was obtained by chemical oxidative polymerization technique using the monomer 'ethylenedioxythiophene (EDOT)' dissolved in a solution of 1 M HCl containing 2 mg/ml of polystyrene sulfonate salt. The MoS_2 was dispersed in water using surfactant CTAB before combining with dual oxidants containing a solution of 0.05 M ammonium peroxydisulfate [$(NH_4)_2S_2O_8$)] and 0.05 iron chloride ($FeCl_3$) under controlled conditions. Fig. 1 shows 1:1 MoS_2-PEDOT, 2:1 MoS_2-PEDOT, and 1:2 MoS_2-PEDOT, nanocomposites which were synthesized by varying the ratio of EDOT to MoS_2. The reaction proceeded by mixing EDOT monomer with three ratios of MoS_2 in 1 M HCl containing PSS solution for two hours. The ice bath was used to compensate the heat of exothermic reaction of EDOT polymerization to PEDOT. The synthesized MoS_2-PEDOT nanocomposite was vacuum filtered, and washed thoroughly using deionized water, methanol °C [12,29].

2.2. Optical Characterizations of Films

The nanocomposite at various ratios containing MoS_2-PEDOT were optically characterized using FTIR "Perkin Elmer spectrum one" and Raman "Renishaw inVia micro-Raman spectrometer" techniques. A potassium bromide pellet was made with MoS_2-PEDOT nanocomposite powders for FTIR measurement while the Raman Shift bands were measured for MoS_2-PEDOT nanocomposite film on a silicon substrate.

2.3. Surface/Structure Characterization

Field Emission Scanning Electron Microscopy (FE-SEM, S-800, Hitachi, Japan) was used to understand the surface morphology of the nanocomposites. TEM (Tecnai F20 high-resolution transmission electron microscopy (HRTEM)) measurement was used on various nanocomposite samples deposited on copper grid required for the measurement. The crystalline structure was studied using Powder X-ray diffraction (XRD) technique (PANalytical X'Pert Pro MRD system with Cu Kα radiation (wavelength = 1.5442 Å) operated at 40 kV and 40 mA).

2.4. Electrode Fabrication

The supercapacitor electrodes were made by mixing 1.5 mg of MoS_2-PEDOT powder with a 2–3% nafion solution using a pastel and motor. Graphite, FTO and silicon substrates were used to deposit the nafion mixed MoS_2-PEDOT nanocomposite. The MoS_2-PEDOT with nafion coated substrates with defined area were dried at 100 °C before insulating for any non-deposited substrate area. The symmetric MoS_2-PEDOT electrodes were used for supercapacitor study in both 2 M hydrochloric acid 'HCl' and 2 M sulfuric acid 'H_2SO_4' as electrolytes.

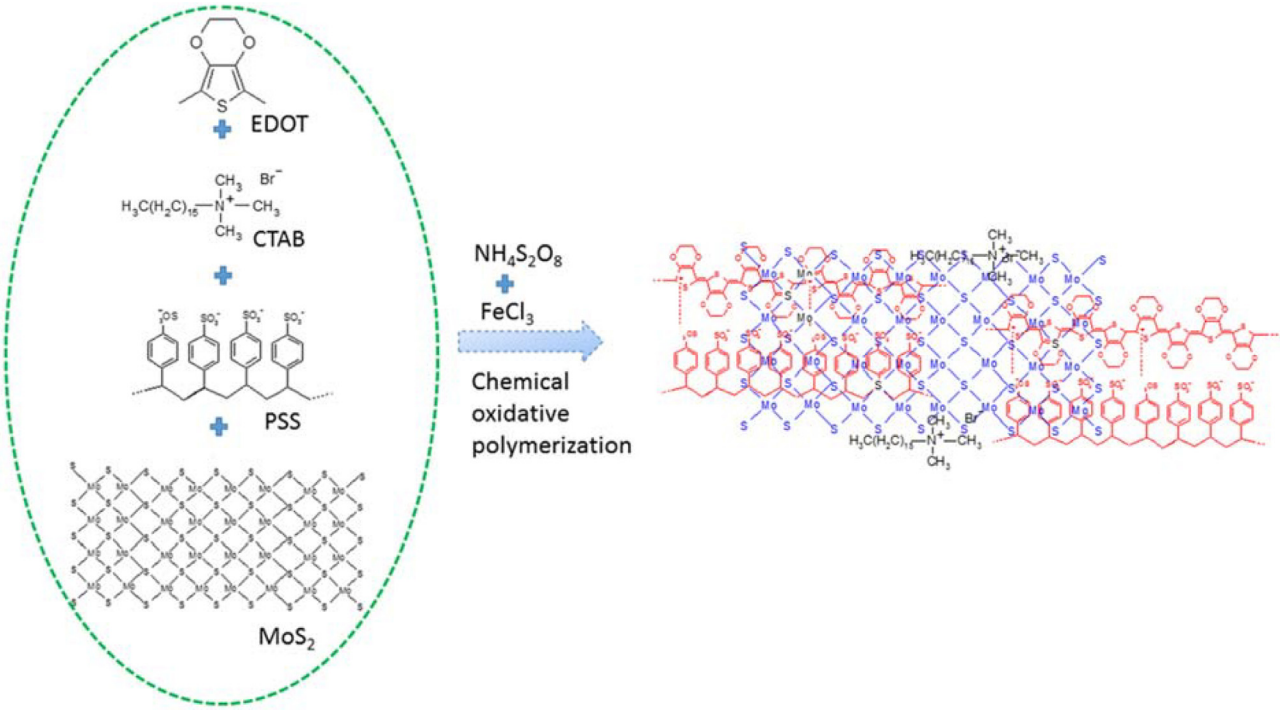

Fig. 1. Schematic structures of molybdenum disulphide, PSS, EDOT and MoS_2-PEDOT nanocomposite.