

Improved electrochemical performance of electrochemically designed layered poly(3,4-ethylenedioxythiophene)/graphene oxide with poly(3,4-ethylenedioxythiophene)/nanocrystalline cellulose nanocomposite



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ABSTRACT

A bilayer hybrid nanocomposite, poly(3,4-ethylenedioxythiophene)/graphene oxide with poly(3,4-ethylenedioxythiophene)/nanocrystalline cellulose (PEDOT/GO|PEDOT/NCC) was prepared through electrochemical deposition using layer-by-layer assembly. Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and field emission scanning electron microscope (FESEM) techniques were used to study thoroughly the structure and morphology of nanocomposites. The as-prepared bilayer showed good performance with high specific capacitance (129.03 F/g at 25 mV/s), good capacity retention, remarkably low charge transfer resistance (4.02 Ω) and good specific power and specific energy compared to its individual binary hybrid nanocomposites (PEDOT/NCC and PEDOT/GO). The as-mentioned electrochemical performance of bilayer could be related to its well-structured morphology and synergistic effect provided by the individual binary hybrid nanocomposites.

1. Introduction

Electrochemical capacitors (or ultracapacitor) are considered as one of the favorable energy storage devices and the demand for the electrochemical capacitors is extremely high especially for its high specific capacitance, high specific power and long life cycle [1–3] compared with batteries and fuel cells. The overall performance of supercapacitor depends on the performance of the electrode material and it is possible to improve the electrochemical performance of supercapacitor by modifying the electrode materials. To date, conducting polymers are employed as the active material for supercapacitor due to its low-cost synthesis and high conductivity [4,5]. Among the variety of conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has drawn drastic interest as an electrode material for supercapacitor due to its excellent stability in the oxidized state [6], good thermal stability and environmental stability [7]. Interestingly, it was found that the characteristics of PEDOT could be tuned accordingly depends on the type of dopants, for instance, carbon-based materials [8,9].

On the other hand, carbon-based materials are well-known for their intriguing properties such as large surface area, excellent electrical, mechanical and electrochemical properties [10,11]. Being an advanced material from carbon-based material family, graphene oxide (GO) has attracted much interest for the development of supercapacitor due to its

distinctive characteristics such as high mechanical strength, high surface area [12], low fabrication cost and nature-friendly [13]. Nevertheless, its poor conductivity [14] constrains the use of GO in many energy storage applications. Another carbon material, nanocrystalline cellulose (NCC) has been investigated and described widely for the last few years. Typically, NCC which is in rods-, needle- or ribbon-like structure possesses few interesting properties such as extreme strength, high surface area, renewability and low density. NCC is not only available most abundantly, but also could be extracted from various sources through acid hydrolysis and environmentally benign [15,16]. The comparatively poor electrical conductivity of NCC than other carbon-based materials is a known fact. However, NCC can be modified with GO and resulted in enhanced electrical conductivity along with exceptional mechanical strength [17,18]. Despite this, there is still a lack of exploration on NCC for supercapacitor studies.

Taking into account the advantages of layer-by-layer (LBL) technique, such as inexpensive and versatile method, straightforward approach and uniformity of the film, [19], it is an impressive way to prepare a hybrid electrode material consisting of a conducting polymer, PEDOT and carbon materials, NCC and GO through LBL assembly. There are different combinations of carbonaceous and conducting polymers have been studied lately in order to produce electrode material with enhanced properties for supercapacitor. Lee, et al. [20] have

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prepared multilayered polyaniline with graphene nanosheets thin film and achieved a gravimetric capacitance of 375.2 F/g at 0.5 A/g. In another study, three-layered PEDOT|polypyrrole|PEDOT film has been prepared by Aradilla, et al. [21] with a specific capacitance of 150 F/g, the specific energy of 15.7 Wh/kg and specific power of 2136 W/kg. Therefore, to develop a better supercapacitor electrode with great properties by tuning the materials, preparation conditions, has been our underlying purpose of this study.

Herein, we report on a novel electrode material, PEDOT/GO|PEDOT/NCC prepared via a simple electrochemical deposition method. Unlike other reported electrode materials, in this work, we have introduced a PEDOT doped NCC composite layer assembled on top of PEDOT doped GO composite layer. The prepared layered hybrid nanocomposite film was then measured its electrochemical performance as an electrode material for supercapacitor. Based on the above-mentioned advantages, the combination of PEDOT with carbon materials (NCC and GO) produces a hybrid nanocomposite with enhanced electrochemical properties. With loose microstructure and compact underneath layer, the as-formed bilayer exhibits hydrogen bonding and electrostatic interaction between the layers ensure efficient charge transfer. Moreover, the bilayer electrode was prepared via a simple method which produces a high specific capacitance with good electrical conductivity, is promising for a large-scale production.

2. Experimental section

2.1. Materials

Nanocrystalline cellulose, NCC (University of Maine), 3, 4-ethylenedioxythiophene, EDOT monomer (Sigma-Aldrich) and graphene oxide, GO (Graphenea) were purchased for fabrication purpose. Potassium chloride and lithium perchlorate were supplied by Fischer Scientific and Sigma-Aldrich, respectively. Indium tin oxide (ITO, $7 \Omega \text{sq}^{-1}$) coated glass substrates were obtained from Xin Yan Technology Limited. ITO pieces of 1cm^2 were sectioned from the glass substrate and were cleaned using acetone (System), ethanol (HmbG chemicals) and deionized water under sonication for 15 min. Deionized water, DI ($18.3 \text{M}\Omega \cdot \text{cm}$ @ 25°C) was used throughout the experimental section. All the reagents were analytical grade and were used as received without further purification.

2.2. Preparation of electrodes

A two-step approach was employed for fabrication of the PEDOT/GO|PEDOT/NCC bilayer by a simple electrochemical deposition. In the first step, PEDOT/GO was deposited on the surface of ITO. PEDOT/NCC was then deposited on the top of PEDOT/GO coated ITO. The solution for electrodeposition was 10 mM EDOT in 1.0 mg/ml GO (or 10 mM EDOT in 1.0 mg/ml NCC). For each deposition step, 1.2 V vs. Ag/AgCl for 15 min was applied. As a comparison for electrochemical studies, a single layer of PEDOT/GO and PEDOT/NCC films were also prepared using a similar method.

2.3. Fabrication of supercapacitor device

Symmetrical supercapacitor device was fabricated by assembling two identical modified electrodes facing each other. A filter paper soaked overnight in 1.0 M KCl was placed in between the electrodes as a separator and clamped with a clip.

2.4. Material characterization

The morphology of the prepared films was analyzed using a field emission scanning electron microscope (FESEM, JEOL JSM-7600F) at an acceleration voltage of 5.0 kV. Raman spectra were recorded by using Alpha300 R microscopic confocal Raman spectrometer (WITec

GmbH) with an excitation 532 nm. The Fourier transform infrared (FTIR) measurements were carried out with Perkin Elmer's FTIR spectrometer designed with Universal Attenuated Total Reflectance (UATR) accessory. The X-ray diffraction (XRD) patterns were recorded with a Shimadzu X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$).

2.5. Electrochemical measurements

All the electrochemical measurements were performed using a potentiostat/galvanostat (Autolab 101) equipped with NOVA software. Cyclic voltammograms were recorded at different scan rates in a range of 25 mV/s–200 mV/s. Galvanostatic charge-discharge tests were conducted at five different current densities (0.5–5.0 A/g). Both analyses were conducted in a potential window between 0 V to 1.0 V to avoid electrolysis of aqueous electrolytes components. The electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 0.01 Hz–100 kHz with an amplitude of 5 mV at open circuit potential.

3. Results and discussion

3.1. FTIR spectroscopy

FTIR spectroscopy was used to determine the presence of the functional groups in each composite. Examination of FTIR spectra reveals the functional groups present in PEDOT, GO, NCC, PEDOT/GO, PEDOT/NCC and bilayer composites as illustrated in Fig. 1. The assignments for the peaks are summarized in Table 1. Fig. 1a shows the FTIR spectrum recorded for PEDOT deposited at 1.2 V for 15 min. The PEDOT spectrum shows a peak at 618 cm^{-1} which is assigned to the C–S vibration of the thiophene and a peak at 1080 cm^{-1} indicates the presence of C–O–C deformation in the ethylenedioxy group [22,23]. The stretching vibration of C–C is appeared at around 1364 and 1418 cm^{-1} . Additionally, peaks at 1510 and 1627 cm^{-1} are assigned to the symmetrical and asymmetrical of C=C vibration of the thiophene ring, respectively [24,25]. The peak at 1194 cm^{-1} indicates the ethylenedioxy group stretching [26]. A broad absorption band centered at around 3335 cm^{-1} in the GO spectrum (Fig. 1b) indicates the presence of O–H stretching vibration. The characteristic bands of the carboxylic group (C=O stretching), C–OH and C–O vibrations of epoxy groups in GO are observed at 1758, 1453 and 1096 cm^{-1} , respectively [27]. NCC

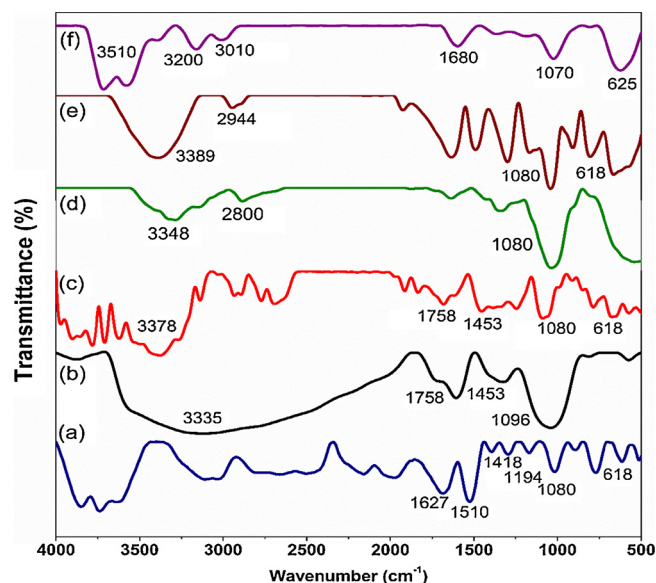


Fig. 1. FTIR spectra of (a) PEDOT, (b) GO, (c) PEDOT/GO, (d) NCC, (e) PEDOT/NCC and (f) PEDOT/GO|PEDOT/NCC.

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