Materials Chemistry and Physics 219 (2018) 120–128

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

One-step potentiostatic electrodeposition of polypyrrole/graphene oxide/multi-walled carbon nanotubes ternary nanocomposite for supercapacitor

Muhammad Amirul Aizat Mohd Abdah[a], Nurnaili Syahirah Mohd Razali[a], Pei Teng Lim[a], Shalini Kulandaivalu[a], Yusran Sulaiman[a,b,*]

[a] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia
[b] Functional Devices Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia

HIGHLIGHTS

- Ternary composite PPy/GO/MWCNT was fabricated via one step electropolymerization.
- PPy/GO/MWCNT exhibited specific capacitance of 358.69 F g^{-1}.
- PPy/GO/MWCNT showed superior specific energy and cycling stability.

ARTICLE INFO

Keywords:
Ternary nanocomposite
Supercapacitor
Polypyrrole
Graphene oxide
Carbon nanotube

ABSTRACT

A ternary nanocomposite consisting of polypyrrole (PPy), graphene oxide (GO) and multi-walled carbon nanotube (MWCNT) for supercapacitor was prepared via facile one step potentiostatic technique. Field emission scanning electron microscopy (FESEM) images displayed a randomly entangled nanostructure of MWCNT with rough wrinkle surface of GO incorporating with PPy granular structure represent the morphology of PPy/GO/MWCNT nanocomposite. The ternary nanocomposite was further justified its chemical composition by using Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. PPy/GO/MWCNT exhibited a high specific capacitance of 358.69 F g^{-1} at a scan rate of 100 mV s^{-1} in 1 M Na_2SO_4, which is comparatively higher than both binary nanocomposites, PPy/MWCNT (207.52 F g^{-1}) and PPy/GO (139.03 F g^{-1}). The PPy/GO/MWCNT nanocomposite also possessed much longer charge-discharge time and excellent cycling stability (88.69%) with the specific energy of 40.45 Wh/kg and specific power of 441.24 W/kg. Therefore, PPy/GO/MWCNT nanocomposite is a potential electrode material for high-performance supercapacitor.

1. Introduction

Supercapacitors have attracted much attention among energy storage devices due to high specific power, rapid charging and discharging and longer cycle life [1]. There are three different types of supercapacitors determined by their charge storage process and electrode configuration i.e. electric double layer capacitor (EDLC), pseudocapacitor and a hybrid supercapacitor. The EDLCs involves non-Faradaic mechanism which occurs due to charge separation at the electrode/electrolyte interface [2]. Carbon-based materials such as graphene, graphene oxide (GO), multi-walled carbon nanotubes (MWCNT) and activated carbon are widely used as an electrode of EDLC. In contrast, pseudocapacitors undergo faradaic charge transfer and the electrode materials regularly being used are metal oxides and conducting polymers [3,4]. Polypyrrole (PPy), polyaniline (PAni), polythiophene (PTh) and derivatives of polythiophene are some examples of conducting polymers used in pseudocapacitors [5]. The electrochemical performance of the electrode can be enhanced by fabricating hybrid nanocomposites [6,7] where the electrodes store the charge through both faradaic and non-faradaic [8], thus producing high specific capacitance and high the specific energy [9]..

The most extensively used conducting polymer is PPy due to its high conductivity, good redox properties and non-toxicity [10]. PPy can be prepared via chemical oxidation [11–15], electrochemical polymerization [16,17] and modified oxidative template assembly methods [18]. GO is one of the derivatives of graphene, planar carbon sheet with sp^2 hybridization and has a large amount of oxygenated functional groups (carboxyl, hydroxyl, and epoxy groups) on its edges and basal

* Corresponding author. Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400, UPM Serdang, Selangor, Malaysia.
E-mail address: yusran@upm.edu.my (Y. Sulaiman).

https://doi.org/10.1016/j.matchemphys.2018.08.018
Received 5 February 2018; Received in revised form 12 June 2018; Accepted 7 August 2018
Available online 09 August 2018
0254-0584/

plane [19] which shows a good solubility in aqueous medium [20]. Moreover, GO also has good mechanical properties [21] which can enhance the cycling stability performance. MWCNT is another carbon material that has been widely studied in supercapacitor application as this electrode has high conductivity and excellent chemical stability. MWCNT consists of a thin amorphous layer, a narrow distribution size as well as the unique mesoporous network which can give a better charge accumulation [22]. MWCNT is able to provide conducting pathway during charge and discharge thereby enhancing a fast electrochemical kinetic process [23]. Hence, fabrication of PPy/carbon composite as supercapacitor electrode could contribute to the enhancement of electrocapacitive performance. For example [12], demonstrated high specific capacitance of 225.6 $F g^{-1}$ PPy/graphene using cathodic electrophoretic deposition (CED) approach. For PPy/CNT, the use of different types of anionic dopants like pyrocathechol violet (PV), eriochrome cyanine R (ECR), acid fuchsin (AF) [15] and ponceau S (PS) [13] can improve the electrical conductivity of PPy. In addition, PPy/CNT based composites such as two-dimensional graphene (GN)-PPy/CNT [24], Tiron-doped PPy/CNT [11], cellulose nanocrystal (CNC)-MWCNT aerogels/PPy [25] deliver specific capacitance of 211.0 $F g^{-1}$, 60.0 $F g^{-1}$ and 43.7 $F g^{-1}$, respectively.

The development of ternary composites consisting of metal oxides, conducting polymers and carbonaceous materials is one of the approaches that can combine the advantages of EDLC and pseudocapacitors which can enhance the electrical conductivity and the stability performance of the electrode [26]. The combination of all materials is expected to give high-performance electrode materials due to the unique advantages of each component which lead to the synergistic effect between them. Both PPy/rGO/ZrO_2 based supercapacitor electrodes [27] and ternary nanocomposite of PPy, Prussian blue (PB), and GO [28] have shown an improvement of electrochemical performance compared to their binary nanocomposites.

Herein, this paper reported a successful fabrication of PPy/GO/MWCNT ternary nanocomposite via potentiostatic approach for supercapacitor. The PPy/GO/MWCNT ternary nanocomposite was then characterized using electrochemical analysis, field emission scanning electron microscopy (FESEM), Fourier transforms infrared (FTIR), and Raman spectroscopy. GO was selected as it contains an abundance of hydrophilic groups, which makes the GO well-dispersed in aqueous suspensions [29]. The presence of the MWCNT offers a unique porous network that allows the electrolyte diffuse through the material, resulting in an increase of the conductivity and charge-transfer behaviour of the nanocomposites [30].

2. Experimental

2.1. Materials

GO, ethanol (95.0%), and acetone (99.5%) were obtained from Graphenea, ChemAr and HmbG Chemicals, respectively. Both pyrrole (Py, 98%) and sodium sulfate (Na_2SO_4, 99.0%) were purchased from Merck. Py was distilled under reduced pressure and stored in a refrigerator at 4 °C. Other reagents such as sulfuric acid (96.0%) and nitric acid (65.0%) were supplied by Fisher scientific and directly used without further purification. MWCNT and indium tin oxide glass substrates (polished, 7Ω/sq) were supplied by Aldrich and Xin Yan Technology Limited. Deionised water (resistivity, 18.2 MΩ cm) from a Merck Millipore-Q system was utilised throughout the experiments.

2.2. Functionalization of multi-walled carbon nanotube (MWCNT)

A mixture (100 ml) of concentrated HNO_3 and concentrated H_2SO_4 (volume ratio of 1: 3) was added to 200 mg MWCNT. The mixture was then sonicated and left for 24 h at ambient temperature. The resulting mixture was thoroughly washed with distilled water until pH 7 was obtained followed by drying the functionalized MWCNT in an oven at 60 °C.

2.3. Preparation of ternary nanocomposite of PPy/GO/MWCNT

ITO glasses were washed using acetone, ethanol and deionised water for 15 min sequentially. To prepare ternary nanocomposite, 0.1 M PPy, 1 mg/ml GO, and 0.3 mg/ml MWCNT were mixed into deionised water. The flask containing this mixture was then wrapped with aluminium foils to prevent Py from unintended oxidation. PPy/GO/MWCNT nanocomposite film was then electrodeposited onto ITO glass (1 cm^2) at +0.8 V for 10 min. The electrodeposition was performed using a potentiostat (Autolab M101) at ambient temperature using a three-electrode configuration where the platinum wire (Pt), Ag/AgCl and ITO glass were utilised as the counter electrode, reference electrode and working electrode, respectively. The binary nanocomposites of PPy/MWCNT and PPy/GO were prepared under the same experimental conditions for comparison.

2.4. Material characterisation

The functional groups of the nanocomposites were analysed by using the Perkin-Elmer FTIR Spectrophotometer. and WITec Raman Microscope. The morphological structure and structure of samples were characterized by field emission scanning electron microscopy (FESEM, JEOL JSM –T600F) at 5.0 kV.

2.5. Electrochemical characterisation

Electrochemical behaviours of PPy/GO, PPy/MWCNT and PPy/GO/MWCNT were evaluated using a half-cell configuration (three electrode system); Pt wire as a counter electrode and Ag/AgCl as a reference electrode. The fabricated electrodes were then further tested using two-electrode configuration (full cell) consisting of two electrodes sandwiched together, separated by a filter paper immersed with 1.0 M Na_2SO_4. The cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were carried out using Autolab M101 potentiostat. The CV analyses were performed in 1 M Na_2SO_4 from 0 to +1.0 V. GCD analysis were measured at various current densities. The impedance spectra (EIS) were recorded using 5 mV ac potential amplitude with a range frequency from 0.01 Hz to 100 kHz. The mass loading for ternary PPy/GO/MWCNT composite is approximately 0.1 mg/cm^2.

3. Results and discussion

3.1. Field emission scanning electron microscopy (FESEM)

The surface morphology of PPy/GO, PPy/MWCNT and PPy/GO/MWCNT nanocomposites were studied using FESEM. Fig. 1a displays a compact and crumbled surface of PPy/GO, indicating PPy is homogenously incorporated with GO. In addition, the GO nanosheets are interconnected to each other resulting to a domination of GO in PPy/