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Research paper

One step electrodeposition of poly-(3,4-ethylenedioxythiophene)/graphene oxide/cobalt oxide ternary nanocomposite for high performance supercapacitor

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ABSTRACT

Poly-(3,4-ethylenedioxythiophene)/graphene oxide/cobalt oxide (PEDOT/GO/Co_3O_4) nanocomposite was prepared using a single-step electropolymerization technique via chronoamperometry at 1.2 V. Field emission scanning electron microscopy (FESEM) images revealed the presence of Co_3O_4 nanoparticles on the wrinkled-sheets of PEDOT/GO. The presence of Co_3O_4 particles in the ternary nanocomposite was proven using Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. Ternary PEDOT/GO/Co_3O_4 nanocomposite electrode displayed better capacitive performances than pure PEDOT and hybrid PEDOT/GO nanocomposite. The ternary nanocomposite electrode exhibited a specific capacitance of 535.60 F g^{-1} and excellent cycle stability with the capacitance retention of 92.69% after 2000 cycles. PEDOT/GO/Co_3O_4 possessed much smallest charge transfer resistance (R_{ct}) and equivalent series resistance (ESR) indicating that the ternary nanocomposite has low charge transfer resistance and excellent electronic conductivity. Thus, PEDOT/GO/Co_3O_4 could be recommended as an excellent electrode material for high-performance supercapacitor.
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1. Introduction

In order to meet the challenge of the increasing depletion of fossil fuels and global warming, researchers are trying to enhance the performances of the current energy storage and conversion devices by developing new electrodes for multifunctional applications. Batteries, fuel cells, supercapacitors and conventional capacitors are the examples of energy storage and conversion devices which are currently being used nowadays. Supercapacitor channels conventional capacitor and batteries through their high specific power and energy with excellent cycle life, environmental friendly and economical cost which makes supercapacitor considered as the foremost option in the energy world [1].

In general, there are three types of supercapacitors, determined by their electrode configuration and charge storage mechanisms i.e. electric double layer capacitor (EDLC), pseudocapacitor and hybrid supercapacitor. In EDLC, the charges are stored electrostatically between the interface of electrode and electrolyte. Carbon-based materials such as carbon nanotubes [2], graphene [3] and carbon nanofibers [4] are widely used EDLC electrodes due to their large surface area and good electrochemical stability. Meanwhile, pseudocapacitor materials such as conducting polymers and transition metal oxides store the charge via chemical redox reaction on the surface of the electrode that can remarkably improve the amount of energy stored. However, the specific power and the cycling stability of the pseudocapacitorsare simultaneously sacrificed. Hybrid supercapacitors store the charge through the combination of electrostatic and redox reaction, thus produce high specific capacitance. Great electrochemical results can be obtained from hybrid supercapacitor due to their synergistic effect and reduction of diffusive path length by increasing the specific surface area [1]. Hence, the recent studies are now concentrating on the preparation of hybrid electrodes for supercapacitors [5].

Poly-(3,4-ethylenedioxythiophene) (PEDOT) is a conducting polymer that drawing much interest as an electrode material for supercapacitor due to its great chemical stability and conductivity [6]. PEDOT can be prepared through electrochemical polymerization in which only a low quantity of the monomer is required and well-adhering films on various electrode substrates could be

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obtained. However, PEDOT suffers from poor cycling stability as a result of low mechanical strength [7]. Hence, by combining PEDOT with carbon-based materials with high mechanical strength could improve the cycling stability of PEDOT. Among the carbon materials, graphene has attracted massive attention as an electrode material for EDLCs due to its excellent conductivity, high surface area, good mechanical and electrochemical stabilities [8]. These great properties allow graphene and graphene-based materials to find applications in high-performance structural nanocomposites, electronics and environmental protection and energy devices including both generations of energy and storage. In addition, the specific capacitance of PEDOT is expected to be higher with the incorporation of metal oxides. Of all the transition-metal oxides, cobalt oxide (Co_3O_4) is known as the great electroactive material due to its outstanding stability, high theoretical capacitance (3560 Fg^{-1}) and also environmental friendliness [8]. Incorporation of Co_3O_4 could also enhance the faradaic response through fast and reversible faradaic redox reactions involving electrons and ions in their charge storage mechanism thus enhancing the performance of supercapacitor [9]. Thus, in this study, PEDOT/GO/Co_3O_4 was fabricated via electrodeposition to study the effect of incorporation of Co_3O_4 into PEDOT/GO on the supercapacitor performance. The supercapacitive performance of the PEDOT/GO/Co_3O_4 nanocomposites was compared with PEDOT/GO and PEDOT. The electrochemical performances of the nanocomposites were studied using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) and stability test. The morphology and the compositions of the nanocomposites were investigated using field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy.

2. Experimental

2.1. Chemicals and materials

3, 4-Ethylenedioxythiophene (EDOT, 97%) was purchased from Sigma-Aldrich. Graphene oxide (GO >95%) and cobalt (II) nitrate ($Co(NO_3)_2.6H_2O$, 98.0–102.0%) were obtained from Graphenea and Alfa Aesar, respectively. Potassium chloride (KCl, 99.5%) was supplied by Fischer scientific. Indium tin oxide (ITO) glass was purchased from Xin Yan Technology Limited.

2.2. Electrodeposition of PEDOT/GO/Co_3O_4

The ITO glasses were sequentially washed using acetone, ethanol and deionized water for 10 minutes. PEDOT/GO/CO_3O_4 nanocomposite films were electrodeposited from a solution containing 10 mM EDOT, 1 mg mL^{-1} GO and 5 mM $Co(NO_3)_2.6H_2O$ at a constant potential of 1.2 V for 15 minutes. The electrodepositions were conducted using a potentiostat (Autolab M101) with a three-electrode system. The platinum (Pt) wire, Ag/AgCl and ITO glass were used as the counter, reference, and working electrodes, respectively. PEDOT and PEDOT/GO were also prepared with the same experimental conditions for comparison.

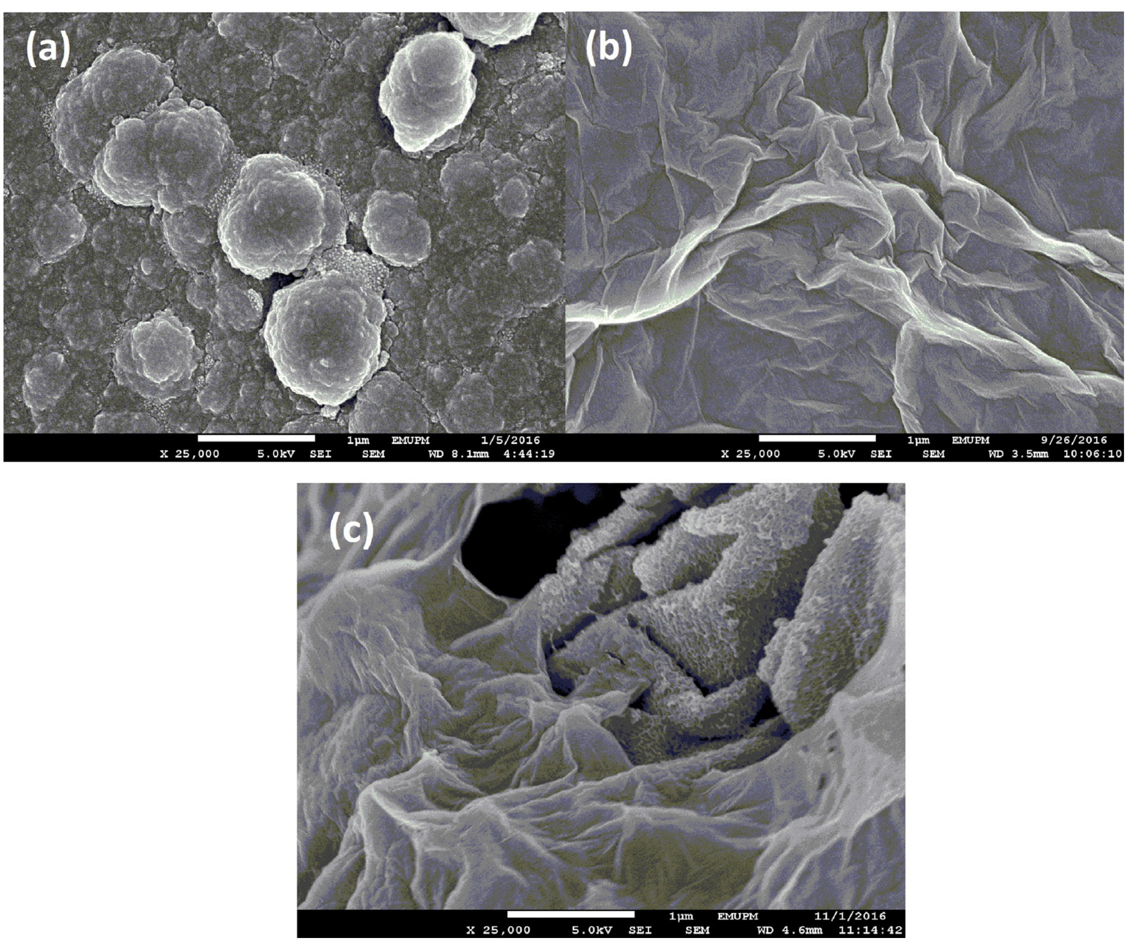

Fig. 1. FESEM images of (a) PEDOT, (b) PEDOT/GO and (c) PEDOT/GO/Co_3O_4.

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