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The preparation and characteristic of poly (3,4-ethylenedioxythiophene)/reduced graphene oxide nanocomposite and its application for supercapacitor electrode

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ABSTRACT

Here we demonstrate a facile electrochemical polymerization and laser induction process to fabricate poly (3,4-ethylenedioxythiophene)/reduced graphene oxide (PEDOT/rGO) nanocomposite, which can be used as supercapacitor electrode material. Firstly, a PEDOT film is deposited on ITO substrate using an electrochemical polymerization method and a graphene oxide (GO) film is successively deposited on as-prepared PEDOT film through a spin-coating method. Then, by using a laser-writing method, the GO film is transformed into the rGO and a PEDOT/rGO nanocomposite is obtained. The resulting nanocomposite shows high areal capacitance about 43.75 mF/cm^2, which is nearly 3 times higher than that of the PEDOT film at a current density of 0.2 mA/cm^2. The PEDOT/rGO nanocomposite exhibits excellent cyclic stability, which can retain 83.6% of its initial capacitance after 1000 charge-discharge cycles. Furthermore, this nanocomposite can be deposited on varied substrates as electrode materials, which shows promising application to prepare high performance energy storage materials.

1. Introduction

The research of novel, low-cost, environmentally friendly, and high performance energy storage systems has been under an increasing demand as a result of the growing exponential number of wearable electronics and microelectronic devices [1–4]. The supercapacitors have aroused tremendous attentions as the complement to energy storage devices because of their excellent size compatibility and suitable electrochemical performance.

The electrode materials play the critical role in the supercapacitor performance. From a materials perspective, the carbon materials [5–8] based on electric double layer capacitors (EDLC) mechanism, transition metal oxides [9], and conducting polymers [10–12] based on pseudo-capacitance mechanism have been investigated for using as electrodes in supercapacitors [13]. Recently, as supercapacitor electrode materials, graphene is an emerging class of ultrathin carbon electrode materials due to its high electrical conductivity, large theoretical specific surface area (2630 m^2/g), superior bendability, and good chemical stability. However, the graphene with the easy agglomeration properties is relatively expensive because of lacking the large-scale production technology until today. As a promising method, graphene-like materials from inexpensive graphene oxide (GO), easily made from low-cost and abundant graphite, have been investigated widely. The hydrazine reduction process, hydrothermal reduction, high temperature heat treatment reduction, and laser-writing method as the general methods are utilized to reduce the GO into the reduced graphene oxide (rGO) [14–16]. However, the toxic agents and high temperature condition are needed in most of these methods, which can increase the cost and the preparation process [17–20]. Among these reduction methods, the laser-writing method is a new and facile induction process to prepare high performance rGO, and the large areas of GO films can be directly patterned and effectively transformed into rGO by a simple low-power, inexpensive infrared laser [1,21,22].

Recently, combination of conducting polymer with graphene-like materials as high performance supercapacitor electrode has attracted more attentions due to the synergistic effect of EDLC capacitance and pseudo-capacitance in these composites. Among the conductive polymers, poly (3,4-ethylenedioxythiophene) (PEDOT) [23–26] is a suitable material for supercapacitor electrode

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because of its good conductivity, excellent processability and low cost. The facile way to composite PEDOT with graphene materials with proper structures, which can produce excellent synergistic effect between PEDOT and graphene, is crucial to obtain high specific capacitance composite electrode with excellent cycling stability.

In our work, we fabricate a PEDOT/rGO nanocomposite as electrode material via a facile electrochemical polymerization and laser-writing induction process. The good coverage of high conductivity rGO onto PEDOT layer is obtained by the laser-writing method [27–30]. As expected, the obtained composite electrode shows significantly improved electrochemical properties compared with rGO or pristine PEDOT electrode materials. This PEDOT/rGO nanocomposite exhibits an areal capacitance about 43.75 mF/cm^2 at a current density of 0.2 mA/cm^2, and almost 83.6% of its initial value is retained after 1000 charge/discharge cycles. The morphology, the synthetic conditions, the chemical structure and electrochemical properties of PEDOT/rGO nanocomposite are investigated in detail. Our method is also a valuable way to deposit the conducting polymer/graphene composite films on varied substrates and has the potential to simplify the manufacturing process of supercapacitor.

2. Experimental

2.1. Materials

The 3,4-ethylenedioxythiophene (EDOT) monomer was made by Bayer AG. The GO nanosheets and $LiClO_4$ powder were purchased from Pioneer Nanomaterials Technology and all were used as received. The sulfuric acid (98% H_2SO_4), ethanol, acetone, and other reagents were analytical reagent grade and all the chemicals were directly used without further purification or treatment.

2.2. Synthesis of the PEDOT/rGO, PEDOT, and rGO electrode materials

Fig. 1 shows a schematic for the synthetic process of PEDOT/rGO nanocomposite electrode. Starting with a 4.6 wt% $LiClO_4$ powder in deionized water, 0.34 wt% EDOT monomer was added and mixed under magnetic stirring for 2 h to form a uniform precursor solution. Next, the solution was poured into the container to obtain the PEDOT film deposited on ITO substrate using an electrochemical polymerization method, and the PEDOT film was annealed in vacuum drying oven at 80 °C for 20 min. The obtained sample was then successively coated by GO through a spin-coating method at 2000 rpm for 30 s. Subsequently, By using the 788 nm infrared laser (power output = 100 mW), the drive converted the golden GO into black rGO at precise locations, then the desired computer-designed circuit was etched onto the film to produce PEDOT/rGO nanocomposite. The obtained PEDOT/rGO nanocomposite was thoroughly washed with acetone and alcohol to remove the unreacted impurity before being left to dry. The PEDOT film and rGO film were also fabricated in order to compare with the PEDOT/rGO nanocomposite.

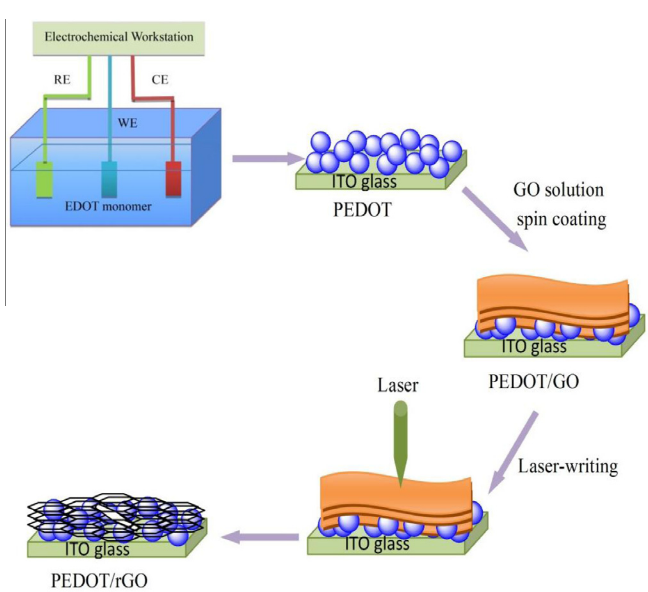

Fig. 1. Schematic of the fabrication process of PEDOT/rGO nanocomposite.

2.3. Characterization and electrochemical measurements

The PEDOT/rGO nanocomposite, PEDOT film and rGO film were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and Raman spectroscopy. The electrochemical properties of electrode materials and Sandwich structure supercapacitor were investigated in 3-electrode configuration and 2-electrode configuration, respectively. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed on a CHI660D electrochemical workstation (Chenhua, Shanghai) at ambient temperature. A pure platinum wire and an Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The working electrodes were PEDOT/rGO, PEDOT, and rGO, all with a working surface area of 0.5 cm^2. Impedance spectroscopy measurements were performed at open circuit voltage with ±5 mV amplitude. PVA/H_3PO_4 gel electrolyte and 1 M H_2SO_4 aqueous solution were used as the electrolytes, and the voltage window during the electrochemical test was $-0.2\sim0.8$ V.

3. Results and discussion

3.1. Morphology and structure of the PEDOT/rGO, PEDOT/GO, PEDOT, and rGO electrode materials

The morphology of PEDOT, PEDOT/GO and PEDOT/rGO nanocomposite was characterized by SEM, which are shown in Fig. 2. Fig. 2a shows the SEM image of as-prepared PEDOT deposited on substrate by electrochemical polymerization, which exhibits an interconnected network of granular structure. Additionally, many irregular and continuous PEDOT particles are observed in Fig. 2b.

Fig. 2c–f show the SEM images of PEDOT/GO nanocomposite before and after the laser-writing treatment with different magnification, respectively. The surface of as-prepared PEDOT is covered by continuous and wrinkled rGO nanosheets (as shown in Fig. 2e). It also can be clearly observed that the crumpled flakes embedded in the PEDOT polymer matrix is formed in the composite structure (as shown in Fig. 2f). These images indicate that the PEDOT/rGO composite can provide an open structure, increasing the specific surface area of electrode film [31].

Fig. 2g and h show the TEM images of PEDOT/rGO nanocomposite and rGO, respectively. Fig. 2h reveals the ripple-like wrinkled structures of the rGO flakes. It can be seen that there are many granular PEDOT embedded in rGO flakes rather than core shell structure in Fig. 2g, which is consistent with the Fig. 2f results. Therefore, the abundant exposed surface and full utilization of PEDOT/rGO nanocomposite could be expected, which are beneficial for obtaining high electrochemical performance of electrode materials. The morphological characterization of PEDOT/rGO nanocomposite after cycling test (in Fig. 2i) are almost the same