Electrochemical characteristics of graphene nanoribbon/polypyrrole composite prepared via oxidation polymerization in the presence of poly-(sodium 4-styrenesulfonate)

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HIGHLIGHTS

- PPy/GNR nanocomposites are synthesized using *in situ* chemical polymerization.
- The notable specific capacitance of 881 F g^{-1} at a current density of 0.5 A g^{-1} is obtained.
- Excellent cyclic stability of PPy/GNR nanocomposites is achieved.

GRAPHICAL ABSTRACT
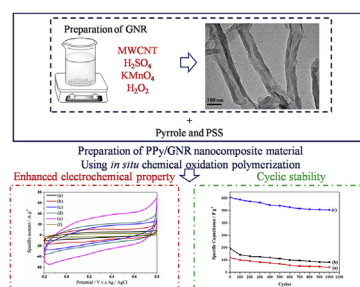
ABSTRACT

Graphene nanoribbon (GNR)/polypyrrole (PPy) composite is synthesized via *in situ* chemical oxidation polymerization in presence of poly-(sodium 4-styrenesulfonate) (PSS) as a surfactant. The morphology of GNR/PPy composites is observed by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The electrochemical properties are characterized using galvanostatic charge—discharge and cycle voltammetry (CV). The specific capacitance of GNR/PPy composites shows the highest value of 881 F g^{-1} that in presence of 9 wt% GNR at a current density of 0.5 A g^{-1}. The GNR/PPy composite also demonstrates the good cycle stability with only 16% decay of initial capacitance that much lower than 64% decay of pure PPy after 1000 cycles.

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1. Introduction

Supercapacitors are a focus of attention in the field of energy storage due to their higher power density, greater cycle stability, and lower cost compared with traditional batteries and capacitors [1]. There are two main types of supercapacitors when considering their energy storage mechanism—electrical double layer capacitors (EDLCs) and pseudocapacitors. The charge storage principle in an EDLC is ascribed to the accumulation of charge at the electrode/electrolyte interface, and the performance of an EDLC is dependent on the specific surface area of the electrode material [2]. Currently, among carbon materials, activated carbon, carbon nanotubes (CNTs), and graphene may provide the high specific surface area required for the accumulation of charge at the electrode/electrolyte interface; consequently, they have attracted significant interest in EDLC research [3—5]. In general, EDLCs exhibit high structural stability, but their capacitance is comparatively low [6]. Charge storage in a pseudocapacitor, on the other hand, is due to fast faradic reactions between the electrode and electrolyte. Fast redox

reaction materials such as intrinsically conducting polymers and transition-metal oxides have the greatest potential for use in pseudocapacitors [7,8]. Unlike EDLCs, most pseudocapacitors exhibit high capacitance, but relatively poor cycle stability [9]. Therefore, to improve the performance of supercapacitors, most studies on supercapacitors are focused on combining EDLC and pseudocapacitor storage mechanisms [10].

Graphene, a two-dimensional monolayer of carbon atoms, can be obtained via the mechanical exfoliation of bulk graphite [11]. Graphene possesses excellent electrical conductivity [12], thermal stability [13], specific surface area [14], and mechanical properties [15,16]. Its result has been used extensively in many energy storage applications during the past few years [17–19]. Intrinsically conducting polymers such as polypyrrole (PPy) have also received significant attention for energy storage applications due to their good electrical conductivity, high specific capacitance, environmental stability, and low cost [20]. However, the poor cycle stability of PPy during repeated charge–discharge processes is the most critical problem limiting its application in supercapacitors.

Recently, to overcome the issue of poor cycle stability, the investigation of conducting PPy and graphene nanocomposites for use in supercapacitors has received much attention. Zhang et al. reported a graphene/PPy nanocomposite that synthesized via *in situ* polymerization had a high specific capacitance of 482 F g^{-1} at a current density of 0.5 A g^{-1} [21]. Meanwhile, Si et al. prepared a three-dimensional graphene/PPy nanocomposite with a high specific capacitance of 285 F g^{-1} at a current density of 0.5 A g^{-1} and a long cycle life (greater than 90% of its initial capacitance was retained after 1000 cycles) [22]. Liu et al. synthesized a ethylene glycol reduced graphene oxide/PPy nanocomposite that exhibited a specific capacitance as high as 420 F g^{-1} at a current density of 0.5 A g^{-1} [23]. In addition, Qian et al. prepared a reduced graphene oxide/PPy composite through electrostatic interaction and π-π accumulation with a high specific capacitance of 557 F g^{-1} at current density of 0.5 A g^{-1}. The capacitance of this material decreased by approximately 15% after 1000 cycles [24]. All of these results demonstrate that the combination of PPy and graphene has the potential to effectively enhance electrochemical capacity and cycle stability. However, a practical method for the production of high-performance supercapacitors with durable cycle stabilities remains a critical challenge and objective in the energy storage field.

Graphene nanoribbons (GNRs), strip of graphene with high length-to-width ratios and straight edges, represent a new graphene morphology that has attracted significant attention over the last few years. Due to their unique physical properties, GNRs are used in many electronic devices such as transistors [25], sensors [26], and solar cells [27]. Recently, nanocomposites composed of conducting polymers and GNRs have been synthesized, and their uses in supercapacitors with high specific capacitance and good cycle stability have been investigated [28–30].

Herein, we have reported the synthesis of GNR/PPy composites via *in situ* chemical oxidative polymerization in the presence of poly-(sodium 4-styrenesulfonate) (PSS) as a surfactant. The combination of PPy and one-dimensional GNR with a high length-to-width ratio was expected to play a key role in achieving a supercapacitor material with a high specific capacitance and an excellent cycle life for use in electrode applications. The morphology and electrochemical and capacitance properties of the GNR/PPy composites were examined.

2. Experimental

2.1. Materials

Multi-wall carbon nanotube was obtained from XinNano Materials. Pyrrole monomer (98%, Aldrich Chemical Co.) was purified by distillation under reduced pressure. Other reagents, including potassium permanganate ($KMnO_4$), ammonium peroxodisulfate (APS), poly-(sodium 4-styrenesulfonate) (PSS), were used without further purification.

2.2. Preparation of GNR

GNR was prepared by the chemical oxidation method that in presence of strong oxidation agent and strong acid. 0.1 g MWCNT with the average diameter of 60 nm was mixed with 100 mL H_2SO_4 (98%) and the mixture was stirred for 2 h at room temperature. 0.5 g $KMnO_4$ was added slowly into the mixture and reacted for 1 h at room temperature. Then, the solution was heated at 85 °C and reacted for 1 h. After reaction, the solution was added into 5% H_2O_2 solution and kept it for 24 h. The product was then filtered and washed several times with 20% HCl solution and DI water until the solution became acid free. Finally, the products were dried under vacuum at 60 °C for 24 h.

2.3. In situ polymerization of GNR/PPy composite

GNR/PPy composites were synthesized using *in situ* chemical oxidative polymerization in presence of PSS as a surfactant. 0.05 g PSS powder was added into 40 mL DI-water and stirred for 30 min at room temperature. The different weight ratio of GNR (1, 5, 7, and 9 wt%) were added into the PSS solution and sonicated for 30 min. Then, the solution was cooled down to 0–5 °C. 0.512 mL pyrrole monomer was added into the dispersed GNR solution and stirred for 10 min. The 2.04 g of APS was first dissolved in 10 mL DI-water and then was dropped into the GNR/pyrrole monomer solution. The polymerization was carried out for 3 h at 0–5 °C. After reaction, the GNR/PPy product was added into large amount of methanol to stop reaction. Finally, the product was filtered and washed with methanol for several times. Then, the product was dried in vacuum at 40 °C for 24 h.

2.4. Characterization

Fourier transform infrared (FTIR) spectra were characterized by a Perkin–Elmer Spectrum One spectrometer with the resolution of 4 cm^{-1}. The samples were pressed into tablets with potassium bromide (KBr). Raman spectra were recorded on a Jobin Yvon TRIAX 550 spectrometer with the scan range 1000–2000 cm^{-1} using He–Ne laser having a wavelength 633 nm. The morphology of nanocomposite was observed by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). FESEM measurements were conducted at 3 kV using a JEOL JSM-6700F field emission instrument. TEM experiments were performed on a JEOL JEM-2000EX instrument with an accelerating voltage of 200 kV. The samples for TEM measurement were prepared by casting a drop of the sample suspended in ethanol on a copper grid covered with carbon.

2.5. Electrochemical measurements

All electrochemical measurements were carried in a three-electrode cell system using CHI 6271D electrochemical analysis instrument. The samples were prepared according to the following steps. 5 mg nanocomposite was dispersed in 10 mL ethanol, which mixed by sonication for 1 h. Then, 0.02 ml suspended solution was dropped onto the glassy carbon electrode and dried at 60 °C before electrochemical analysis and using 1 M H_2SO_4 solution as an electrolyte. Then, the potential range of CV testing was measured from −0.2 V to 0.8 V (vs. Ag/AgCl) and the platinum was used as