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Graphene/polypyrrole intercalating nanocomposites as supercapacitors electrode

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ABSTRACT

Hierarchical plush polypyrrole (PPy) layers intercalated graphene sheets have been prepared by in-situ intercalative chemical polymerization. The as-prepared graphene/PPy nanocomposites have been successfully characterized in terms of composition, morphology, and electrochemical properties. It was found that the chemically modified graphene nanosheets and in-situ polymerized PPy layers formed uniform nanocomposites with homogeneous PPy layers intercalated between the graphene substrates. Such uniform nanostructure together with the observed high conductivities (the highest 1980 S m^{-1}) afforded the graphene/PPy composites with high specific capacitance and good cycling stability during the charge–discharge process when used as supercapacitor electrodes. The graphene/PPy (with optimized composition 10:1) based supercapacitors display intriguing performance with a maximum specific capacitance of 650 F g^{-1} at 0.45 A g^{-1} current density, a highest energy density of 54.0 W h kg^{-1} at 1 mA current, and a highest power density of 778.1 W kg^{-1} at 5 mA current. Furthermore, the graphene/PPy supercapacitor exhibits an excellent cycling stability with 95% specific capacitance retained after 5000 cycles. The impressive results presented here may open the window for grapheme/PPy composites for their promising applications in high energy density storage system.

1. Introduction

Energy storage has attracted considerable attention in recent years with the global appeal for renewable energy production and the growing demand for portable devices and hybrid electrical vehicles [1]. For this purpose, supercapacitors, also known as electrochemical capacitors or ultracapacitors, are exhibiting greater advantages over secondary batteries. Featuring faster and higher power capability, long life, wide thermal operating range, and lower maintenance cost [2], supercapacitors can provide instantaneously higher power density than batteries and higher energy density than conventional dielectric capacitors [3–5]. They are considered as the most important technology tailoring for the next-generation energy storage devices [1,6].

Energy storage mechanisms via supercapacitors can be concluded as electric double layer (EDL) effect and pseudocapacitance [3]. Featuring large surface area and good stability, carbon-based materials such as activated carbon, mesoporous carbon, and carbon nanotubes (CNTs) are usually used for EDL capacitors. However, these materials are very limited in capacitance due to the inherent microstructure [7,8]. On the other hand, metal oxides and conducting polymers such as polyaniline (PANI) [9–11], polythiophene [12], polypyrrole (PPy) [13–15] are used for pseudocapacitors, due to their fast and reversible faradic redox reactions [3]. Though high capacitance displayed by conducting polymers, they are limited in applications due to the poor mechanical properties and performance stability during charge/discharge process [9]. To achieve a synergetic combination of both high capacitance, conductivity and mechanical properties, hierarchical composite materials based on carbon-based materials and conducting polymers have thus been explored in supercapacitors, which worked in devices as expected [16,17]. However, the high cost of CNTs and its maximum EDL capacitance up to only 80 F g^{-1} [18] have forced researchers to look for new carbon materials.

Graphene (GE), a two-dimensional all-sp^2-hybridized carbon have has recently attracted wide attention due to its outstanding electric, high specific surface area and excellent mechanical properties [8,18–20]. Graphene-based composites with metal oxides and conducting polymers have been explored for supercapacitors, with tens to 480 F g^{-1} specific capacitance achieved in recent years [9,15,21]. By chemical polymerization of pyrrole onto graphene nanosheets, the as-prepared graphene/PPy composites achieved a maximum specific capacitance of 482 F g^{-1} at 0.5 A g^{-1} current density [15] and 267 F g^{-1} at 0.1 A g^{-1} current density [22]. By using

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in-situ oxidation polymerization of pyrrole monomers in aqueous graphene oxide (GO) solutions, followed by chemical reduction using ethylene glycol (EG), graphene/PPy composites were prepared with large specific capacitance, high rate performance, and good charge–discharge stability [23]. Zhang et al. [24] further prepared graphene/polypyrrole/carbon nanotube (GN/PPy/CNT) ternary composites using the in-situ polymerization method. The prepared GN/PPy/CNT composite with GN:CNT =8:1 (8GCPPy) exhibits a large surface area of 112 $m^2 g^{-1}$ and a current density of 0.2 $A g^{-1}$ (361 $F g^{-1}$), which is much higher than that of pure PPy (176 $F g^{-1}$) and binary composites of CNT/PPy (253 $F g^{-1}$) and GN/PPy (265 $F g^{-1}$). By electropolymerization of polypyrrole onto electrophoretically deposited graphene, the graphene/PPy composites were reported to exhibit a specific capacitance of 1510 $F g^{-1}$ [25]. The capacitance of graphene/PPy nanocomposites is found to be strongly dependent upon the preparation methods of graphene and PPy, as well as the morphology of the composites. It is intriguing to us whether morphology-controllable graphene/PPy composites can be prepared as electrode for high-performance supercapacitors.

Inspired by our recent study on the development of excellent supercapacitor electrodes based on bacteria cellulose/PANI or PPy nanocomposites with controlled conducting polymers nanostructures [10,14], a facile strategy was proposed to prepare graphene/PPy composites via in-situ polymerization of given mass ratio of pyrrole onto well chemically modified graphene sheets. The in-situ "one-pot" proparation approach realized the reduction of graphene oxide and intercalation of PPy into GE sheets in sequence to avoid the aggregation of graphene. With controlled morphology and optimized composition, the graphene/PPy composites exhibited the highest electrical conductivity of 1980 $S m^{-1}$ and specific capacitance of 650 $F g^{-1}$ at 0.45 $A g^{-1}$ current density for supercapacitor applications.

2. Experimental

Preparation of graphene oxide (GO). Graphene/PPy (GE/PPy) with different mass ratio was prepared via in-situ polymerization of Py self-assembled on the homogeneously dispersed individual graphene sheets, while graphene was obtained by the reduction of graphene oxide with hydrazine hydrate [26,27]. For a complete oxidation of graphite, graphene oxide (GO) was prepared from natural graphite powder via a two-step oxidation, i.e., a pre-oxidation [28] and a followed Hummers oxidation [29]. For the pre-oxidation, natural graphite powder (325 mesh, 20 g) was first added into an 80 °C solution of concentrated H_2SO_4 (30 mL), $K_2S_2O_8$ (10 g) and P_2O_5 (10 g). After 6 h reaction at 80 °C, the resultant dark blue mixture was thermally isolated and cooled to room temperature. Towards the mixture was then carefully added with deionized water (DI water) for dilution. The mixture was filtered and washed with DI water until the pH of the rinse water became 7. The product was dried overnight at 60 °C in vacuo. This pre-oxidized graphite was then subjected to a further Hummer oxidation. To a solution of concentrated H_2SO_4 (450 mL) in ice bath was added with the pre-oxidized graphite (20 g), and then $KMnO_4$ (60 g) was slowly added under vigorously stirring. The rate of addition was carefully controlled to keep the reaction temperature lower than 20 °C. After the addition of $KMnO_4$, the reaction was heated to 35 °C for 3 h and then to 95 ~ 100 °C for 30 min by adding small amount of DI water. The reaction was terminated by the addition of DI water (2.8 L) and H_2O_2 (30 mL). The reaction mixture was filtered and the solid was washed 10% HCl solution (5 L). The GO product was then subjected to dialysis for a week to remove all metal ions and acids. The GO dispersion was centrifuged and dried over vacuum to obtain a grey powder (60% yield).

Preparation of graphene/PPy composites. Graphene was firstly prepared by reduction of hydrazine. A dispersion solution of the above-obtained GO (100 mg) in DI water (100 mL) was ultrasonicated for 1 h to get an exfoliated yellow–brown GO suspension. The suspension was heated to 80 °C before the addition of hydrazine (2 mL). After 24 h reaction, the mixture was filtered and the solid was washed subsequently with ethanol and water several times. The as-prepared graphene was dried overnight at 60 °C in vacuo (70% yield). The GE/PPy nanocomposites with different mass ratios were further prepared via in-situ polymerization of pyrrole onto dispersed graphene sheets. The weight feeding ratio of pyrrole to graphene was varied as 1:1, 5:1, 10:1, 15:1 and 20:1, and the resulting composites were designated as $PG_{1:1}$, $PG_{5:1}$, $PG_{10:1}$, $PG_{15:1}$ and $PG_{20:1}$, respectively. A typical preparation protocol for $PG_{1:1}$ was described as following. The freshly distilled pyrrole (0.21 mL) was injected into a suspension of graphene (0.2 g) in DI water (80 mL). The suspension was ultrasonicated for 40 ~ 60 min prior to cooling in an ice bath. The reaction mixture was bubbled with N_2 to remove the O_2 in the system. The reaction was then slowly added with an equivalent $FeCl_3$ (0.49 g in 0.1 M HCl) solution and allowed to proceed at 0–5 °C for 24 h. After filtration, the title composite was washed subsequently with ethanol and water several times, and the product was dried at overnight at 60 °C in vacuo. All as-prepared composites were kept in cool place for followed characterization.

Characterization methods. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Bomen MB154S spectrometer with KBr pellets. Raman spectra were recorded on a RM 2000 microscopic confocal Raman spectrometer employing a 514 nm laser beam. X-ray diffraction (XRD) analyses were performed on a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation ($\lambda \approx 1.54$ Å) at 40 kV and 30 mA. X-ray photoelectron spectra (XPS) were recorded on a Thermo ESCALAB 250 X-ray photonelectron spectrometer, using Al $K\alpha$ radiation ($h\nu \approx 1486.7$ eV) as the excitation source. Morphological of the as-prepared products were observed on a transmission electron microscopy (TEM, JEOL JEM-2100) at an accelerating voltage of 120 kV and a field emission gun scanning electron microscopy (FE-SEM, Hitachi S4800) at an accelerating voltage of 15 kV.

Conductivity measurement. The conductivity of as-obtained GE/PPy composites was measured with a conventional four-point probe technique (RTS-8, Probes Tech., China) at ambient temperature (20 ± 1 °C, 67% humidity). The flat surfaces of samples were prepared by pressing the composites at 15 KPa. The conductivity of pure PPy disc was determined as ~10^2 $S cm^{-1}$ [17]. According to the four-point probe method, resistivity can be calculated with $\rho = 2\pi S\left(V/I\right)$, where S is the probe spacing (mm) which was kept constant, I is the supplied current in microampere, and the corresponding voltage V is measured in millivolts. Conductivity can be computed using $\sigma = 1/\rho$.

Electrochemical measurement. Cyclic voltammetry analysis was carried out on a CHI660D electrochemical workstation (Shanghai, China) with a three-electrode system. The working electrodes were prepared by mixing the active material with 15 wt% acetylene blank and 5 wt% polytetrafluoroethylene (PTFE, based on the total electrode mass) to form a slurry. Then the slurry was cast on stainless steel, and dried under vacuum at 50 °C for 24 h. A platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The electrolyte was 1 M H_2SO_4 solution. Cyclic voltammetry was performed in the voltage range of − 0.2 ~ 0.8 V at different scan rates. Galvanostatic charge–discharge experiment was carried out in potential range from − 0.2 to 0.8 V with applied current density increased gradually from 0.45 to 3.17 $A g^{-1}$. The electrochemical impedance spectroscopy (EIS) analysis was operated under the condition: AC voltage amplitude 5 mV, frequency range: $1 \times 10^5 \sim 1 \times 10^{-2}$ Hz at 0.5 V.