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Enhanced capacitance and rate capability of graphene/polypyrrole composite as electrode material for supercapacitors

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ABSTRACT

Graphene and polypyrrole composite (PPy/GNS) is synthesized via in situ polymerization of pyrrole monomer in the presence of graphene under acid conditions. The structure and morphology of the composite are characterized by X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectrometer (FTIR), X-rays photoelectron spectroscopy (XPS) and transmission electron microscope (TEM). It is found that a uniform composite is formed with polypyrrole being homogeneously surrounded by graphene nanosheets (GNS). The composite is a promising candidate for supercapacitors to have higher specific capacitance, better rate capability and cycling stability than those of pure polypyrrole. The specific capacitance of PPy/GNS composite based on the three-electrode cell configuration is as high as 482 F g^{-1} at a current density of 0.5 A g^{-1}. After 1000 cycles, the attenuation of the specific capacitance is less than 5%, indicating that composite has excellent cycling performance.

1. Introduction

With the challenges ahead, including reducing environmental pollution and dependence on fossil fuel energy, the great efforts to revitalize the energy industry bring with it a valuable opportunity for us to provide a more stable and secure energy resource. Among them, energy storage is a key technology to enable renewable energy source deployment, and greatly reduce wasted energy. Supercapacitors, the energy storage devices between secondary batteries and traditional capacitors, have attracted considerable attention over the past decades for higher power density, longer cycle life, lower of cost and better environmental friendliness than secondary battery. With the unique advantages, they have been widely utilized in portable electronics, collecting intermittent energy, mobile communications and electrical vehicles [1,2]. Energy storage mechanisms of supercapacitors predominately include two ways: electric double layer effects and pseudocapacitance [3,4]. Commonly, porous carbon materials are the electrodes of double-layer capacitors, while transition metal oxides and conducting polymers are corresponding to pseudocapacitors [5]. In order to exploit the potential of supercapacitors, many efforts have been devoted to studying the carbon materials [6,7] and conducting polymer such as polyaniline (PANI) [8,9], polypyrrole (PPy) [10], and polythiophene (PT) [11]. With the intrinsic electrical conductivity and high capacitance as reported [12], polypyrrole is a promising electrode material for supercapacitors with unusual doping/dedoping processes, lower of cost, and simple synthesis. However, it also exhibits poor stability and rate capability, which limit its wide application [13]. Carbon materials such as activated carbon (AC), mesoporous carbon (MC), and carbon nanotubes (CNTs) usually display good stability. Recently, Jurewicz et al. obtained higher specific capacitance supercapacitors from carbon nanotube/polypyrrole composites electrode than pure samples because of the synergistic effects between these components [14]. However, attractive CNTs are still very expensive and their double-layer capacitance is low [15,16].

More recently, graphene, a single atomic plane of graphite [17], is expected to be an excellent electrode material for supercapacitors due to its superior electrical conductivity, high specific surface area, and chemical stability. It has been demonstrated that graphene-based supercapacitors have high specific capacitance (135–264 F g^{-1}) [18–22]. More importantly, graphene can also be easily incorporated with conducting polymers as precursor [23–25] to improve the electrochemical properties of composite by the synergistic effects, because the ultrathin flexible graphene layers cannot only increase the conductivity of the composite, but also effectively improve the stability of the polymer during charge/discharge process. Yan et al. prepared a graphene/polyaniline composite by in situ polymerization with a high specific capacitance of 1046 F g^{-1} at a scan rate of 1 mV s^{-1} compared to 115 F g^{-1} for the pure PANI [23]. However, the capacitance was mainly dominated by the pseudocapacitance from

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the PANI. On this basis, Zhang et al. also developed another method to prepare the graphene/polyaniline composite, and the specific capacitance reached 480 F g^{-1} at a current density of 0.1 A g^{-1}. However, the specific capacitance retention at higher charge–discharge current densities (210 F g^{-1} at the current density of 1 A g^{-1}) and cycling stability of this composite should be improved [15]. Although some efforts have been made on the composite of graphene with conducting polymer, it is still a challenge to synthesize graphene/conducting polymer composite as electrode materials with the high capacitance and good rate performance for supercapacitors.

Herein, we report a facile strategy to synthesize graphene and PPy composite (PPy/GNS) using an in situ polymerization method. We also describe charge storage properties of the resulting composite in 1 M H_2SO_4 aqueous electrolyte. The high specific capacitance of 482 F g^{-1} is obtained from galvanostatic charge–discharge at a constant current density of 0.5 A g^{-1}, which is much larger than that of each pristine component. This composite not only achieves high specific capacitance properties of PPy, but also keeps the advantage of an excellent conductivity in the single layer network of graphene.

2. Experimental

2.1. Preparation of samples

All the chemicals were of analytical grade and were used without further purification. GNS was prepared by reduction of graphene oxide with hydrazine hydrate according to the literature [26]. Nanocomposite was synthesized using in situ polymerization in the presence of GNS suspension and pyrrole with different ingredient mass ratios from 9:1 to 5:5 for pyrrole and graphite oxide. The nanocomposite synthesized from different ratios is signed as PGratio. Here we take the $PG_{9:1}$ composite as an example, indicating that the mass ratio of pyrrole and graphite oxide is 9:1. Firstly, 0.45 g pyrrole monomers were added into 50 mL of 1 g L^{-1} graphene aqueous suspension and sonicated for 30 min. Then, an equal volume of 6.7 mM $FeCl_3$ solution (solvent: 0.1 M HCl) was slowly added into the above mixture and kept at 0–4 °C for 24 h. Finally, the reaction mixture was filtered, and washed with deionized water and ethanol, and then the product was dried at 60 °C for 24 h. For comparison, the pure polypyrrole was prepared without graphene by the similar procedure.

2.2. Characterization methods

X-ray diffraction (XRD) analyses were performed using a X' Pert Pro system with Cu Kα radiation (λ = 1.54060 Å) operated at 40 kV and 40 mA. Raman spectra were obtained on a RM 2000 microscopic confocal Raman spectrometer (Renishaw in Via Plus, England) employing a 514 nm laser beam. Fourier transform infrared spectroscopy (FTIR) spectra were measured using a Nicolet IR 750 spectrometer with pure KBr as the background. X-rays photoelectron spectroscopy (XPS) analysis was recorded on a PHI Quantear SXM (ULVAC-PH INC) which used Al as anode probe in 6.7×10^{-8} Pa. C, H and N microanalysis was recorded on an Elementar Vario El elemental analyzer. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were carried out using a JEOL JSM-2010 operating at an accelerating voltage of 200 kV. Electronic conductivity was measured on compacted pellets by standard four-probe resistance using Physical Property Measurement System (PPMS).

2.3. Electrochemical measurements

The electrode performance was measured in a beaker-type electrochemical cell equipped with the working electrode, a platinum sheet as the counter electrode, and a standard calomel electrode (SCE) as the reference electrode. The working electrode was prepared by mixing 70 wt% active material, 20 wt% acetylene black, and 10 wt% poly(vinylidene fluoride) in N-methyl-2-pyrrolidone and the slurry was spread onto a titanium plate with 1 cm^2 geometry area. The electrode was heated at 120 °C for 2 h to evaporate solvent. The electrolyte was 1 M H_2SO_4.aqueous solution. Cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) were measured by a CHI 660C electrochemical workstation. CVs were carried out at the scan rates ranging from 2 to 500 mV s^{-1} within the potential range of −0.2 to 0.7 V (vs. SCE). Galvanostatic charge–discharge was carried out at current densities ranging from 0.5 to 5 A g^{-1}. EIS was recorded under the following condition: AC voltage amplitude 5 mV, frequency range from 0.1 to 10^5 Hz at 0.4 V.

3. Results and discussion

3.1. Structure and morphology studies

Fig. 1a shows the XRD patterns of GNS, pure PPy and PPy/GNS samples with different ingredient mass ratios. For GNS, the diffraction peaks at $2\theta = 24.5°$ and 42.8° can be attributed to the graphite-like structure (0 0 2) and (1 0 0), respectively. A characteristic peak of amorphous for pure PPy appears at about $2\theta = 26°$ [27]. As the GNS percentage increases in the composite, the broad peak also shifts from $2\theta = 26°$ to 24.8° and the peak at 42.8° does not obviously appear, implying that the PPy and GNS have been completely interacted. Here, we can calculate that the value of interplanar spacing is about 0.34 nm for the broad peak about at $2\theta = 25°$, which is identical to the π–π stacking distance. As a result, we can speculate that there probably exists π–π stacking between the PPy chains and the graphene planes, further supported by the HRTEM images [28]. Raman spectroscopy is as shown in Fig. 1b, which is widely used to obtain structural information about carbon-based materials. The Raman spectroscopy of all samples exist two prominent peaks at about 1590 and 1350 cm^{-1}, which correspond to the G and D bands, respectively (Fig. 1b). The G and D bands are significantly broadened with the introduction of GNS, suggesting that the nanocrystal size decreases due to the phonon confinement [29]. Additionally, there are a broad peak at 1051 cm^{-1} and two small peaks at 933 and 981 cm^{-1} for pure PPy and PGratio composite, which are the characteristic peaks of PPy.

The FTIR absorption spectra of the PPy and $PG_{9:1}$ are shown in Fig. 1c. From the top of spectrum, the characteristic polypyrrole peaks are located at 1529 cm^{-1} and 1446 cm^{-1}, which are due to the antisymmetric and symmetric ring-stretching modes, respectively [30]. Strong peaks near 1144 cm^{-1} and 887 cm^{-1} indicate the doping state of polypyrrole, and a broad band at 3000–3500 cm^{-1} describes N–H and C–H stretching vibrations. Furthermore, the bands at 1030 and 1284 cm^{-1} are attributed to C–H deformation vibrations and C–N stretching vibrations, respectively [31–33]. Compared with the pure PPy, it is clearly observed that most of the marked peaks are shifted left when the graphene was introduced into the synthesis process of PPy. This reveals that the groups from graphene are associated to the nitrogenous functional groups of PPy backbone via the same doping process into the PPy backbone, just as the normal dopant of Cl^- [34]. Herewith, there probably exist interactions such as π–π stacking between polypyrrole backbone and graphene or hydrogen bonding for the residual oxygen functional groups on graphene.

Similar phenomenon is also observed by N 1s XPS core-level spectra for $PG_{9:1}$. From Fig. 2, the peaks are reasonably decomposed into three Gaussian peaks with the binding energy of 398.2, 399.9 and 401.2 eV, respectively. The peak at 398.2 eV related to the neutral and the imine-like structure (>C=N–) can be used to