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Polypyrrole/graphene oxide deposited on two metalized surfaces of porous polypropylene films as all-in-one flexible supercapacitors

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ABSTRACT

Sandwich-structured composite films with two conductive surface separated by porous insulator have been fabricated after the two sides of porous polypropylene films (PPF) have been covered with gold films *via* electroless plating method. Subsequently, the composite of polypyrrole-graphene oxide (PPy-GO) has been electrochemically deposited on the two conductive sides *via* galvanostatic method to form the sandwich structured PPy-GO/PPF/PPy-GO composite films. After gel electrolyte of H_3PO_4/polyvinyl alcohol being coated on the composite films of PPy-GO/PPF/PPy-GO, the integrated flexible supercapacitors (SCs) of PPy-GO//PPF//PPy-GO are fabricated, and the optimal SCs exhibits excellent cycling stability (84.9% capacitance retention after 10000 cycles). Based on the one side electrode, the optimal SCs exhibit relatively high areal specific capacitance (108.0 mF cm^{-2} at 2 mV s^{-1} scanning rate). The integrated SCs exhibit excellent flexibility, the capacitance retention can reach 93.4% after 2000 bending cycles and 80.0% after 5000 bending cycles. Furthermore, this kind of integrated flexible capacitors can be conveniently connected in series without further wires due to their special structure. As a result, they display great potential in flexible and solid integrated energy storage systems.

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1. Introduction

The research related to energy storage devices is becoming more and more important [1–5] with the development and utilization of the clean energy for sustainable development. Among various energy storage devices, supercapacitors (SCs) have attracted great attention because of their high energy density, high power density and long cyclic life [6–11]. Recently, with the rapid development of personal consumer electronics, it is becoming imminent to design and develop SCs with lightweight, flexible and high performance to match these electronic products [1,12–15]. For instance, the flexible SC based on activated carbon electrodes [16], activated carbon cloth electrodes [17], polypyrrole (PPy)/paper electrodes [18], activated reduced graphene oxide (rGO)/PPy nanotube paper electrodes [19], carbon nanotube-GO/PPy electrodes [20] have been fabricated and the integrated SC-sensor system [21] has also been designed.

Generally, SCs are assembled into a sandwich-structure by using two activated electrodes and a diaphragm, in which the diaphragm lies in the middle of the two electrodes and allows electrolyte ions to conduct electricity while prevents electron conduction as much as possible [22,23]. However, the sandwich-structure assembled by the separated electrodes and diaphragm will bring additional ineffective mass or volume in SCs devices, for instance, the current collectors have to be used. This multilayer stacking structure is also prone to splitting between layers during the bending process, which will seriously affect the bending resistance of the flexible SCs. Furthermore, separately assembled structure will make the flexible SCs connected in series difficult, and make SCs unable to maintain a compact structure to meet the requirements of future flexible electronic devices.

As commonly used conductive polymer material, PPy is considered as a kind of promising electrode materials for flexible SCs with light weight because it is easy to be synthesized, and has good conductivity, relatively high specific capacitance (C_s) and intrinsic polymeric flexibility [24–33]. However, PPy exhibits a poor cyclic stability because its structure may be destroyed during the continuous doping and dedoping process [34–38]. On the other

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hand, the electrolyte ions can only diffuse into thin PPy layer easily, therefore thick layer or the dense structure of PPy will lead to decrease of the capacitance due to the limited diffusion of ions [35]. In order to improve the electrode's performance, materials with porous three-dimensional (3D) structure have aroused widespread concern. So far many efforts have been devoted to design PPy films with porous 3D structure [20]. For example, the porous 3D composites of PPy with carbon nanotubes, metal oxide nanoparticles or insulating polymers have been designed to overcome the shortcomings of pure PPy [39–41].

Two-dimensional (2D) GO sheets exist high specific surface area (SAA) and contains oxygen-containing groups which make it easy to disperse in water and form composites with other components [42–46]. For example, the large SAA of GO can effectively disperse the formed PPy and limit the uncontrollable growth of the PPy because the oxygen-containing groups of GO can act as partial counter ion to interact with the formed PPy chains, so as to provide the nucleation sites for depositing PPy [47]. Considering the above reasons, the GO sheets can act as the scaffold to form 2D PPy-GO sheets which may further assemble into 3D porous composites.

In order to fabricate flexible SCs with a compact structure and good resistance to repeated bending, here we have used the porous polypropylene films (PPF, a kind of lithium-ion battery separator) as the substrate directly to fabricate the integrated flexible SCs. First, the conductive gold layers are deposited on the two sides of the PPF *via* electroless plating to form the sandwich-structure with two conductive sides separated by middle porous insulator. Then PPy-GO composites are electrochemically deposited on the two conductive sides of the sandwich-structure to form the integrated flexible SCs after the gel electrolyte has been coated on the composite films. This strategy not only eliminates the assembly steps, but also effectively reduces the distance between the two active electrodes. It can be expected this kind of SCs have good capacitive properties, flexibility and bending resistance.

2. Experimental

2.1. Reagents and materials

Natural graphite powder (325 mesh) was purchased from Tianjin Guangfu Research Institute, and GO was prepared from the natural graphite powder by using a modified Hummers method [48,49]. Pyrrole was purchased from Shanghai Chemical Reagent Co. and stored in a refrigerator (−20 °C). The PPF with an average thickness of about 20 μm was obtained from Taiyuan force of the source battery Co. Ltd. Polyvinyl alcohol (PVA-124), $NaH_2PO_4 \cdot 2H_2O$ and H_3PO_4 were purchased from Hengxing Chemical Reagent Co. Ltd; chloroauric acid ($AuCl_4 \cdot 4H_2O$), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) and trishydroxymethyl aminomethane ($(HOCH_2)_3CNH_2$ >99%) were obtained from Shanghai Baiyan Technology Co. Ltd, dopamine hydrochloride was purchased from Aladdin. And all other reagents were of analytical grade.

2.2. Preparing the sandwich structured Au/PPF/Au via electroless plating

To deposit the continuous gold films on the two sides of the PPF film, the PPF films were first modified with thin layer of polydopamine. Simply, certain amount of dopamine (57.0 mg) was dissolved in the trishydroxymethyl aminomethane buffer solution (120.0 mL, 0.6 mg mL^{-1}) to keep the pH = 8 [50], then the PPF films were immersed in the dopamine solution and stirring for 12–15 h in the aerobic environment, during which the color of the solution changed from colorless to brown, and the surface of PPF films also underwent similar changes, which implied that the films had been coated with a brown layer of poly-dopamine.

Secondly, after being washed with water thoroughly, the modified PPF films were immersed into a solution of $AuCl_4 \cdot 4H_2O$ (1.0 mL, 50 mg mL^{-1}) to adsorb the gold ions, then the PPF films adsorbed with gold ions was immersed into $NaBH_4$ solution (5.0 mg mL^{-1}, 10 mL) to make the adsorbed gold ions reduced and form the gold seeds on the surface. The PPF films loaded with gold seeds were subsequently immersed into the freshly prepared mixture (150 mL) of $AuCl_4 \cdot 4H_2O$ (0.2 mg mL^{-1}) and $NH_2OH \cdot HCl$ (0.025 mg mL^{-1}) under stirring to deposit the gold on the surface after the PPFs were washed by dilute HCl solution and water to remove the unreacted $NaBH_4$ and the non adherent gold seeds. Finally, the sandwich-structured composites with two sides covered with continuous gold films separated by middle insulated layer were obtained and defined as Au/PPF/Au after the samples were washed by water and dried under ambient atmosphere.

2.3. Electrochemically depositing PPy and PPy-GO on Au/PPF/Au

Electrochemical deposition was carried out by using a three-electrode system, the Au/PPF/Au sandwich films were used as working electrode, two Pt foils close to (1.0 cm) both sides of Au/PPF/Au and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. The solution containing pyrrole (0.1 mol L^{-1}) and $NaH_2PO_4 \cdot 2H_2O$ (0.2 mol L^{-1}) was used as deposition solution and treated under ultrasonic condition for 10 min before use. During the electrochemical deposition, the working electrodes' length immersed into electrolyte was kept at 1.0 cm, and the current density was kept at 3.0 mA cm^{-2} (based on the geometric surface area of the two sides). To fabricate different sandwich electrodes, various deposition times were employed to synthesize the PPy on the electrodes. According to the optimized deposition time and the concentration of GO (Fig. S1 and S2), we chose 400 s, 700 s and 1000 s as deposition time to synthesize PPy-GO composites on the Au/PPF/Au electrodes *via* the similar procedure, but the aqueous solution of pyrrole (0.1 mol L^{-1}), $NaH_2PO_4 \cdot 2H_2O$ (0.2 mol L^{-1}) and GO (2.0 mg mL^{-1}) was used as electrolyte. In the presence or absence of GO, the sandwich electrodes prepared at different deposition times were defined as PPy/PPF/PPy (400, 700 and 1000) and PPy-GO/PPF/ PPy-GO (400, 700 and 1000), respectively.

2.4. Preparation of the integrated solid-state SCs

In this manuscript, H_3PO_4/PVA was prepared according to literature [51] and used as gel electrolyte. After the H_3PO_4/PVA was coated on the sandwich electrodes evenly, they were placed into a refrigerator to freeze for 30 min. Finally, the flexible SCs were obtained after they were placed at room temperature to melt (Fig. 1), the integrated SCs fabricated from PPy/PPF/PPy and PPy-GO/PPF/PPy-GO were respectively named as PPy//PPF//PPy and PPy-GO//PPF//PPy-GO.

2.5. Characterization and electrochemical measurements

The morphologies of the samples were observed by using a field emission scan electron microscope (JSM-6701F, JEOL) and a transmission electron microscopy (JEM-2100, JEOL) operating at 200 kV. The infrared spectra of the samples were directly recorded by using an attenuated total reflection Fourier transform infrared spectrometer (ATR-FTIR, Nicolet iS50R, USA) at 400-4000 cm^{-1} with a resolution of 2 cm^{-1}. The X-ray diffraction (XRD) patterns were obtained by using a Bruker D8 Advance Xray diffraction meter with Cu Kα radiation at the scan speed of 5° min^{-1} with a step size of 0.02° and the Raman spectra were recorded with a confocal Raman

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