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Flexible and freestanding electrode based on polypyrrole/graphene/bacterial cellulose paper for supercapacitor

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ABSTRACT

A simple and low-cost approach toward flexible and freestanding electrode is developed. The method involves coating the polypyrrole (PPY) encapsulated graphene (RGO) composites on bacterial cellulose, from which large mass loading of 8.93 mg cm^{-2} is obtained. Benefiting from the well structural features, the flexible PPY/RGO/BC paper can be directly acted as supercapacitor electrode without metallic current collectors, binder and additives, and achieves a high areal capacitance (2100 mF cm^{-2} at 2 mA cm^{-2}), good rate performance (1570 mF cm^{-2} retention at 50 mA cm^{-2}) and high flexibility (suitable for arbitrary angles, even 180°). Moreover, the assembled symmetric supercapacitor delivers as high as 790 mF cm^{-2} of areal capacitance and 0.11 mWh cm^{-2} of energy density. Therefore, this strategy provides a facile method for design of flexible supercapacitor electrodes with high areal capacitance.

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1. Introduction

Flexible energy storage devices have attracted tremendous attention in recent years, the potential applications of which ranging from wearable electronics, stretchable electronics, collapsible displays to on-body sensors [1–5]. Among various types of energy storage devices, supercapacitors are widely recognized as an important class due to high power density, fast dynamic response, moderate energy density, good operational safety, and long life cycle [6–9]. However, restrained by the lack of flexibility and lightweight of conventional supercapacitors, one of the key challenges is to fabricate flexible and freestanding electrodes with high capacitance and good mechanical properties [10].

To date, considerable efforts have focused mainly on improving the gravimetric capacitance of the flexible electrodes, but for wearable and portable electronics, areal and volumetric performance are at a premium [11]. In general, supercapacitors can be classified into two categories based on charge-storage mechanism, namely the electrochemical double-layer capacitors (EDLCs) and pseudo-capacitors (PDCs). Carbon based freestanding film including RGO paper and carbon nanotubes paper are very popular to be employed for flexible electrodes in EDLCs due to the high conductive property and large surface area, and the charges are electro-statically stored by reversible ion adsorption at the electrode/electrolyte interface [12–14]. Despite these carbon based flexible paper has shown long cycle life and good gravimetric capacitance, the areal capacitance (<100 mF cm^{-2}) is rather low due to the small mass loading (<1 mg cm^{-2}) [15]. PDCs, based on fast reversible faradic reactions at the surface of electroactive materials, using conducting polymers or metal oxides as active materials provide them with several times higher specific capacitance than the non-faradic EDLCs. PPY, as a kind of traditional conducting polymer, is particularly promising pseudocapacitive electrode material for supercapacitors owing to its high energy storage capacity, high electrical conductivity in doped states, ease of low cost synthesis and low environmental impact [16–18]. Nevertheless, poor cycling stability induced by large volumetric swelling and shrinking during charge/discharge and weak flexibility of PPY limit its use in flexible supercapacitors. A number of methods have been demonstrated to overcome these drawbacks by coupling PPY onto flexible supporting substrates such as office paper, RGO paper, and carbon nanotube film. Therefore, directly electro-polymerization or chemical polymerization PPY onto carbon-based electrical

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conductivity substrates is the main approach. However, the mass loading of these electrodes is generally still very low, resulting in the low areal capacitance, despite that they have obtained high electrical conductivity, good gravimetric performance and rate capability [19].

As has been described recently, porous textiles are also used as alternative substrate. In comparison to printing paper and carbon conductive paper, they can provide three-dimensional (3D) porous network structure, and therefore enable high mass loading. As an interesting ecofriendly biomaterial cellulose, BC is produced by fermentation of bacteria (*Acetobacter xylinum*, *E. coli*, etc.). With so many unique properties such as specific ultrafine network structure, good mechanical strength and high water holding capability, BC could be designed and applied in supporting substrates. Furthermore, while great efforts have been devoted to develop high capacitive devices, relatively fewer attentions have been paid to its mechanical properties. Designing efficient, low-cost flexible electrode that can achieve both good electrochemical properties and high mechanical integrity upon bending or folding, tensile strength and lightweight property is highly required [15]. In this point of view, BC membrane can strongly bind with PPY and carbon materials due to the many hydroxyl groups, meanwhile, the stretchable and compressible properties of these structures can be helpful for mechanical properties of flexible electrode.

Herein, we demonstrate a simple and low-cost "polymerization and vacuum-filtering" method to fabricate the PPY/RGO/BC flexible electrode. The as-constructed flexible electrode exhibits good electrochemical performance and mechanical properties. The as-fabricated paper with high mass-loading (~8.93 mg cm^{-2}) shows a high areal capacitance of 2100 mF cm^{-2}, good rate performance (75% retention at 50 mA cm^{-2}) and good cycling stability with ~64.7% of its initial capacitance after 5000 cycles. By direct coupling of two paper electrodes, symmetric supercapacitor can offer large areal capacitance (790 mF cm^{-2}), high energy density of 0.11 mWh cm^{-2} and power density of 15 mW cm^{-2}. Therefore, this strategy opens up new opportunities for development of high performance flexible energy-storage devices.

2. Experimental

2.1. Preparation of PPY/RGO

RGO suspension (0.5 mg ml^{-1}) was obtained by a modified Hummers method and referred to the previous papers [15,20]. PPY/RGO composite was prepared by the in situ polymerization of pyrrole monomer and RGO aqueous dispersion in the presence of $FeCl_3$ as an oxidant and $C_7H_8O_3S{\cdot}H_2O$ (*P*-TSA) as a dopant. Typically, 0.2 ml pyrrole monomer and 532 mg *P*-TSA were added into the 50 ml RGO suspension with strong mechanical stirring for 1 h in an ice-water bath. 778 mg ferric chloride was dissolved in 30 ml deionized water and added dropwise into the pyrrole/RGO suspension with constant stirring for 1 h at 0–5 °C to obtain PPY_1/RGO suspension. The other samples of PPY_2/RGO, PPY_4/RGO, PPY_6/RGO and PPY_8/RGO were conducted by prolonging the polymerization times for 2, 4, 6 and 8 h.

2.2. Preparation of PPY/RGO/BC hybrid membrane

To obtain a uniform BC suspension, BC pellicle (Hainan Yide Foods Co. Ltd.) was first neutralized with deionized water, and then cut into small slices, followed pulped with a mechanical homogenizer at the speed of 10,000 r min^{-1}. The collected suspension (200 ml, 0.7 mg ml^{-1}) was drained on a nitro cellulose filter membrane (porous size of 0.22 μm) to get a uniform BC paper by vacuum filtration. Subsequently, the as-prepared PPY_x/RGO (x = 1, 2, 4, 6 and 8) suspension was poured onto the BC paper to obtain a filter cake and dried at 60 °C overnight, and then peeled off to get the freestanding PPY_x/RGO/BC film. The active materials of PPY_1/RGO, PPY_2/RGO, PPY_4/RGO, PPY_6/RGO and PPY_8/RGO were 5.78, 6.74, 7.81, 8.93 and 9.14 mg cm^{-2}, respectively.

2.3. Characterization and electrochemical measurements

The morphology and microstructure of the samples were characterized through scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscope (TEM, JEM-2100 F). The functional group distribution was investigated by Fourier transform infrared spectroscopy analyzer (FT-IR, PerkinElmer Spectrum 100 Model) and X-ray diffraction (XRD, Rigaku 2500) equipped with Cu Kα radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS, VG ESCALABMK II) was carried out to investigate the surface elemental compositions. Electrochemical studies were performed with a CHI660E electrochemical workstation. The single electrode was tested in a three-electrode system in 1 M $NaNO_3$ aqueous solution with active carbon and a saturated calomel electrode (SCE) as the counter electrode and reference electrode, respectively. Symmetric supercapacitor was measured in two electrode configuration using both flexible PPY/RGO/BC hybrid paper as electrodes, which separated with diaphragm.

3. Results and discussion

Synthetic procedure of PPY/RGO/BC is presented in Fig. 1. The PPY/RGO was first prepared through in situ polymerization using pyrrole and *P*-TSA as the monomer and dopant, respectively. The grown PPY thickness is roughly tunable with polymerization time. Then, the PPY/RGO composite was poured onto the prepared BC paper, black active materials spontaneously dispersed into the 3D porous network to form a hybrid paper with large mass loading. The flexible paper can be directly acted as supercapacitor electrode without metallic current collectors, binder and additives.

Fig. 2 presents the typical morphology and microstructure of BC, RGO, PPY_6/RGO and PPY_6/RGO/BC composites. The BC pellicle (Fig. 2a) shows a water rich morphology due to a large number of hydrophilic groups along its network. The SEM image illustrates that the BC consists of continuous nanofibers to form a porous and interconnected network structure (Fig. 2b). Further characterization by TEM demonstrates that the diameter of BC nanofibers is 20–60 nm (Fig. 2c). The BC with porous network serves as a substrate to provide a large surface area for active materials, while high hydrophilicity of BC can effectively enable the contact between active materials and aqueous electrolytes and reduce the diffusion distance of electrolyte ions during the charge/discharge process. The SEM image of RGO in Fig. 2d reveals a wrinkled and crumpled features, which could be identified in Fig. 2e. Fig. 2f shows the SEM image of PPY_6/RGO/BC paper, it is observed that highly uniform PPY grown on the surface of RGO nanosheets, and then assembles into BC to form the freestanding electrode. It is worth noting that PPY_6/RGO/BC paper retains the porous nanoarchitectures, which can be help for electrolyte transport and active-site accessibility. Moreover, such freestanding paper (0.28 mm thickness) exhibits high flexibility and can be bended for a large angle (Fig. 2i), which enables the practical applications on flexible and lightweight energy storage devices. Further observation from the TEM of PPY_6/RGO (Fig. 2g) indicates that the RGO is distinctly enwrapped with gauze-like PPY. Moreover, the high resolution TEM image exhibits direct evidence that randomly orientated PPY is assembled along the RGO nanosheets (Fig. 2h). The RGO is uniformly sandwiched between PPY, which forms two potential benefits for flexible electrode. First, this architecture could act as a buffering layer to prevent the severe

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