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Flexible polypyrrole/copper sulfide/bacterial cellulose nanofibrous composite membranes as supercapacitor electrodes

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ABSTRACT

Polypyrrole (PPy) and copper sulfide (CuS) have been successfully deposited on bacterial cellulose (BC) membranes to prepare nanofibrous composite electrodes of PPy/CuS/BC for flexible supercapacitor applications. The introduction of CuS remarkably improves the specific capacitance and cycling stability of BC-based electrodes. The specific capacitance of the supercapacitors based on the PPy/CuS/BC electrodes can reach to about 580 F g^{-1} at a current density of 0.8 mA cm^{-2} and can retain about 73% of their initial value after 300 cycles, while the PPy/BC-based device could retain only 21.7% after 300 cycles. This work provides a promising approach to fabricate cost-effective and flexible nanofibrous composite membranes for high-performance supercapacitor electrodes.

1. Introduction

Recently, wearable electronics and their associated technologies have been envisioned in an array of applications, thus greatly boosting the developments of flexible and wearable energy storage systems (Jost, Dion, & Gogotsi, 2014). Flexible supercapacitors have received considerable attention due to their desirable advantages, such as high energy density, good cycling stability, fast charge/discharge rate, and environmental safety (Firoz Babu, Siva Subramanian, & Anbu Kulandainathan, 2013; Liang et al., 2013; Xu et al., 2013; Li, Huang, Yang et al., 2014; Li, Huang, Zhang et al., 2014; Liu, Yu, Yan, Li, & Zheng, 2015; Qin et al., 2015; Xu, Wang, & Fan, 2015; Xu, Wang, Yuan, Wei, & Duan, 2015; Xu, Wang, Yuan, Wei, & Gu, 2015; Zhu et al., 2014). On the basis of the energy-storage mechanisms and the used electrode materials, supercapacitors can be divided into electrical double layer capacitors (EDLCs) and pseudocapacitors. The energy stored in EDLCs mainly results from the charge separation at the electrode/electrolyte interface, and the electrode materials used in EDLCs are carbon materials. Usually, carbon materials have good rate capability but exhibit a relatively small specific capacitance. The main electrode materials used for pseudocapacitors are transition metal oxides/sulfides and conducting polymers (CPs, e.g. polypyrrole (PPy), polyaniline, polythiophene and their derivatives). Pseudocapacitor materials have relatively large capacitance values because the energy is stored through a reversible redox reaction.

Among the abovementioned electrode materials, CPs have promised the most for high-performance flexible supercapacitor applications due to their high conductivity, high intrinsic flexibility, various preparation methods and nontoxicity (Gholami, Nia, & Alias, 2015; Liu, He, Fan, Miao, & Liu, 2014; Lü, Chen, Lin, & Yu, 2015; Mensing, Wisitsoraat, Phokharatkul, Lomas, & Tuantranont, 2015; Ramya, Sivasubramanian, & Sangaranarayanan, 2013; Snook, Kao, & Best, 2011; Wang, Li, Ni, Dai, & Lu, 2015). On the basis of low cost and environmental stability, PPy and PPy-based composites used for flexible supercapacitors have been intensively studied. For example, Firoz Babu et al. (2013) investigated the influence of the fabric substrates on electrochemical performance and reported a specific capacitance of 235 F g^{-1} for their viscose-based PPy electrode. Zhao and coworkers (Zhao, Shu, Wang, Gambhir, & Wallace, 2015) demonstrated the performance of PPy-graphene-coated nylon lycra textile electrode in supercapacitor application, showing a specific capacitance of 114 F g^{-1} at a scan rate of 5 mV s^{-1}. Liu, Cai, Zhao, Zhao, & Ge, 2016 fabricated a

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PPy/multi-walled carbon nanotube (MWCNT)/cotton flexible electrode, which exhibited a specific capacitance of 535 F g^{-1} at a very low scan rate of 1 mV s^{-1}. Despite the attractive electrochemical performance and potential of CNTs and graphene, the relatively high price of CNTs and elaborate procedures to obtain graphene would impede their further development in large-scale fabrication.

Transition metal sulfides (e.g., CuS, NiS, CoS, and VS) have been considered as one of the most promising pseudocapacitor materials with respect to their specific capacitance and cost effectiveness (Feng et al., 2011; Hsu, Chen, & Lin, 2014; Peng et al., 2015; Raj et al., 2014; S. Liu et al., 2015; Zhu, Xia, Zhou, & Lou, 2012;). In the recent past, CuS have been extensively investigated due to their good electronic conductivity and high energy capacitance. For example, Zhu et al. (2012) utilized the template-engaged chemical conversion route to prepare CuS nanoneedles on carbon nanotube as electrode, which exhibited a specific capacitance of 122 F g^{-1} in KOH electrolyte. More recently, Hsu et al. (2014) have fabricated a CuS nanowire (NW) array with a hierarchical nanoarchitecture on copper foil using a simple liquid-solid reaction, achieving a specific capacitance of 305 F g^{-1} at a current density of 0.6 mA cm^{-2}. Combining PPy with CuS to form composite electrode materials for flexible supercapacitors is an effective route to further improve the electrochemical properties of supercapacitors. However, to the best of our knowledge, composite materials of PPy and CuS for flexible supercapacitors have rarely been reported.

Bacterial cellulose (BC) is a fascinating natural nanofibrous material with a three-dimensional and interconnected network structure, which can be produced on industrial scales through microbial fermentation process. The average diameter of its ribbon-like fibrils is lower than 100 nm, while the length can be larger than 100 μm. The specific structure and numerous hydrogen bonds endow BC with sufficient porosity and high specific surface area, which can serve as a matrix to support other functionalized materials and a template to form different nanostructures (Hu, Chen, Yang, Zhe, & Wang, 2014; Tang, Han, Jiang, Chen, & Wang, 2015). For example, CdS and CdSe nanoparticles have been prepared on the BC nanofibers using in situ precipitation method (Li et al., 2009; Yang et al., 2012). PPy (Müller, Rambo, Recouvreux, Porto, & Barra, 2011; Müller, Rambo, Porto, Schreiner, & Barra, 2013; Wang, Bian, Zhou, Tang, & Tang, 2013) and PANI (Lee, Chung, Kwon, Kim, & Tze, 2012; Marins et al., 2011; Müller et al., 2012) nanoparticles have been synthesized on the BC nanofibers via in-situ polymerization. Recently, Tang et al. prepared the polysiloxane-coated PPy/BC nanocomposite membranes with amphiphobicity by in situ oxidative polymerization of PPy and then infiltrated with polysiloxane solution (Tang et al., 2015). In our previous work (Xu et al., 2013), we have successfully fabricated the PPy/BC nanofibrous membranes with core-sheath structure for the application of flexible supercapacitor electrodes, which exhibited an initial capacitance of 459.5 F g^{-1} at 0.16 A g^{-1} current density. More recently, the PPy/NiS/BC membranes were prepared in our group (Peng et al., 2016), which had a relatively high initial capacitance of 713 F g^{-1} at 0.8 mA cm^{-2} current density. However, the capacitance was decreased dramatically during the charge/discharge cycles, with the remaining capacitance of 258 F g^{-1} (only 36.2% of the initial value) and 172 F g^{-1} (24.2%) after 100 and 300 cycles, respectively. CuS could provide good cycling durability due to the crystallinity of CuS (Raj et al., 2014). To improve the cycling performance of the BC-based electrodes, herein, we report the fabrication of flexible PPy/CuS/BC nanofibrous composite membranes, which exhibited a high specific capacitance as high as 580 F g^{-1} and good cycling performance (the retention 73% of initial specific capacitance after 300 cycles) at a current density of 0.8 mA cm^{-2}.

2. Experimental

2.1. Materials

BC membranes (food-grade, degree of polymerization $\approx 5.18 \times 10^3$) were purchased from Hainan Yide Foods Co. Ltd. (China) and treated as the previous report (Xu et al., 2013). Other chemicals were supplied by Sinopharm Chemical Reagent Co. Ltd. (China) and used as received. Ultrapure water used in the experiments with resistivity of 18 MΩ cm was produced a Milli-Q Advantage system.

2.2. In situ synthesis of CuS on BC nanofibers

In a typical procedure, the purified BC membrane (4 × 4 cm) were immersed into a beaker with a magnetic stirring bar containing 50 mL aqueous solution of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) for 8 h. Then it was taken out and soaked into a 50 mL aqueous solution of sodium sulfide (Na_2S) with the same concentration as $CuSO_4$ solution for 1 min. It was observed that the BC membrane changed to a dark green color. Finally, the membrane was washed with pure water for several times and dried in a vacuum oven at 60 °C for 12 h. The BC membranes treated by the solutions of $CuSO_4 \cdot 5H_2O$ with different concentrations of 10, 50, 100 mM were named as CuS/BC-10, CuS/BC-50 and CuS/BC-100, respectively.

2.3. Fabrication of PPy/CuS/BC composite membranes

PPy was deposited on the CuS/BC membranes through in-situ oxidative polymerization as previously reported (Xu et al., 2013). The CuS/BC membranes were soaked in a pyrrole aqueous solution (1.0 M) and stirred for 1 h. An aqueous solution of iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 0.5 M) was added to initiate the polymerization. After 2 h at 5 °C, the obtained samples were cleaned thoroughly with alcohol and pure water and dried in a vacuum oven at 40 °C for 12 h. The composites prepared on different CuS/BC membranes were coded as PPy/CuS/BC-10, PPy/CuS/BC-50 and PPy/CuS/BC-100, respectively. The control sample obtained by using purified BC membrane without CuS was named as PPy/BC.

2.4. Characterization

The mass of active materials was determined by the weight difference before and after the deposition of CuS and PPy. The microscopic features of the samples were characterized on a JSM-6510LV scanning electron microscopy (SEM) microscope (JEOL, Japan). Energy dispersive X-ray spectroscopy (EDS) was examined on a HORIBA X-ACT spectrometer. Fourier transform infrared (FTIR) spectra were recorded by a TGA-FTIR spectrometer (Tensor 27, Bruker, Germany) equipped with attenuated total reflectance (ATR) cell. Thermal gravimetric analysis (TGA) was carried out under nitrogen atmosphere with a TG209F1 thermogravimetric analyzer (NETZSCH, Germany) at a heating rate of 10 °C min^{-1}. The surface conductivity was measured by a digital four-point probe resistivity measurement system (RTS-9, 4Probes Tech. Co., China) with copper electrodes under a pressure of 5 N.

The electrochemical properties of the membrane electrodes were measured based on a symmetric two-electrode system with 2.0 M sodium chloride (NaCl) aqueous solution as electrolyte and a filter paper as separator. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were recorded with an Autolab PGSTAT302N electrochemical workstation (Metrohm AG, Switzerland). The CV measurements were carried out from −0.9 V