Journal of Electroanalytical Chemistry 786 (2017) 28–34

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Waste to wealth: A sustainable and flexible supercapacitor based on office waste paper electrodes

Haibo Su [a,b], Pengli Zhu [a,*], Leicong Zhang [a], Fengrui Zhou [a], Gang Li [a], Tingxi Li [b,*], Qing Wang [b], Rong Sun [a,*], Chingping Wong [c,d]

[a] School of Materials Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, P.R. China
[b] Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, P.R. China
[c] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, USA
[d] Department of Electronics Engineering, The Chinese University of Hong Kong, Hong Kong.

ARTICLE INFO

Article history:
Received 24 October 2016
Received in revised form 4 December 2016
Accepted 1 January 2017
Available online 04 January 2017

Keywords:
Sustainable supercapacitor
Office waste paper
Graphene oxide sheets
MnO_2-nanowires

ABSTRACT

In order to develop a low cost, sustainable, and eco-friendly energy storage device, we demonstrated an all solid state symmetric flexible supercapacitor based on the office waste paper fibers-reduced graphene oxide-manganese dioxide (PF-RGO-MnO_2) which acts as both the positive and negative electrodes. With the assistance of facile solution phase assembly and vacuum filtration method, the flexible PF-RGO-MnO_2 electrodes with high physical flexibility and excellent mechanical strength were fabricated directly without any binder agents. Furthermore, owing to the advantages of the lager surface area and microfibers of the each single paper fiber, the PF-based hybrid flexible electrodes show high specific capacitance of 410 F g^{-1} at 0.8 A g^{-1} and retain 93% capacitance over 5000 cycles, indicating outstanding electrochemical performance. In addition, the assembled solid-state symmetric supercapacitors exhibit high energy density (19.6 Wh kg^{-1} at 400 W kg^{-1}) and excellent cycling stability of 85.3% retention even after 2000 folding and bending cycles. These results propose a renewable way to turn "waste" into wealth, and provide a new method to fabricate the sustainable and freestanding paper-based supercapacitor for application in the flexible energy storage devices.

1. Introduction

Efficient energy storage in a sustainable and eco-friendly way has become a great challenge for traditional energy storage systems, especially for the flexible and wearable energy storage devices, owing to the rapidly increasing market in wearable electronic and active artificial skins, such as roll-up displays, smart textiles and implantable sensors [1,2]. Moreover, energy storage devices with low cost, light-weight, environmental friendliness, high power and energy densities and long cycle-lifetime are some indispensable requirements for the new generation energy storage systems [3–5]. Supercapacitors (SCs), as the most promising power source devices, have attracted considerable attentions because of their high power densities, long cycle lives, wide working voltage range, and so forth [6,7]. During the last years, a large amount of effort has been widely explored to investigate the supercapacitors with outstanding flexibility, thinness, and compressibility as well as lightweight. However, there is still a long way to go for the development of supercapacitors based on low cost, sustainable, environmental friendliness, as well as affordable materials.

At present, several kinds of substrates have been reported to be served as the flexible electrode for supercapacitors, for instance, nickel foam [8], polyethylene glycol terephthalate [9], and textile [10]. However, some of them are non-renewable materials, and cause lots of environmental problems. By contrast, paper, a ubiquitous material in our daily life, can be utilized for the next generation of flexible electronics in which it can be exploited as the substrate to fabricate flexible supercapacitors, display screens, sensors or other electronic devices [11,12]. The advantages of using paper as substrate mainly reflected in the following ways: (a) Paper usually consists of cellulose fiber and cellulose is an important structural component of the primary cell wall of green plants, which are the most abundant renewable organic materials on Earth [13]. (b) Paper is stemmed from cellulose fiber with superior hydrophilicity, excellent mechanical properties and flexibility, and is an ideal substrate for the flexible energy storage devices [14]. (c) Paper-based energy storage systems could make it possible to realize all-paper electronics [15,16]. In addition, commercial cellulose paper, such as office paper, is a renewable and cheap production. However, tens of thousands of tons of office paper are produced and used every day, which means that there is an abundant of waste paper will be discarded and pollute the environment. Therefore, how to make these papers from waste to wealth and used them in the flexible devices,

* Corresponding authors.
E-mail address: pl.zhu@siat.ac.cn (P. Zhu).

http://dx.doi.org/10.1016/j.jelechem.2017.01.002
1572-6657/

such as, flexible supercapacitors and sensors, has become a very meaningful and challenging work.

In order to improve the performance of the paper-based sustainable hybrid supercapacitors, suitable active materials with high electrical conductivity and good electrochemical performance should be carefully selected. Recently, numerous studies have fabricated the paper-based flexible electrodes via introducing the high energy storage materials, such as graphene [17], conducting polymers [18] and some transition metal oxides [19]. For instance, Weng et al. [20] constructed graphene-cellulose paper as the flexible electrode on filter paper via a facile vacuum filtration way, and Feng et al. [21] developed the multi-layered graphite/Ni/Co_2NiO_4-cellulose paper electrodes on cellulose paper by a simple drawing-electrodeposition-anodic oxide combined method; In this point of view, paper has shown great potential application in the flexible energy storage systems. In our previous study, we also successfully prepared the flexible PF-Ni-MnO_2 electrode with MnO_2 layer directly grown on the filter paper via the electroless plating together with following electrochemical deposition process, and the electrode exhibits great flexibility and high specific capacitance [22]. Nevertheless, in the above researches, the active materials were only coated on the surface of the insulation of paper substrate, and the as-prepared electrode shown low rate capability, which limit the practical applications to a great extent. Thus, in order to take full advantage of the lager surface area and microfibers of the each single paper fibers, further investigations are needed to be developed.

In this study, we developed a sustainable and flexible electrode by using the office waste paper fibers-reduced graphene oxide-manganese dioxide (PF-RGO-MnO_2) film. The mono-dispersed of PFs are obtained from the office waste paper with ultra-sonication, wash, and activation procedure. Due to the abundant functional groups on the surface of the GO sheets, it could be easily anchored on the PFs. After a simple reduction and vacuum filtration process, the PF-RGO-MnO_2 hybrid film was obtained in which the RGO sheets were strongly anchored on each single PF and the MnO_2-nanowires were uniformly attached on the surface of the RGO sheets. As a result, owing to the excellent mechanical flexibility of PFs, great electrical conductivity of RGO sheets, and high electro-activity of MnO_2-nanowires, the as-prepared hybrid PF-RGO-MnO_2 electrode exhibits excellent rate capability and high specific capacitance of 410 F g^{-1} at 0.8 A g^{-1}. Moreover, the PF-RGO-MnO_2 electrode owns superior mechanical strength and can withstand different deformation without significant influence on the electrochemical performance. In addition, the assembled solid-state symmetric supercapacitors exhibit high energy density (19.6 Wh kg^{-1} at 400 W kg^{-1}) and excellent cycling stability of 85.3% retention even after 2000 folding and bending cycles. This study demonstrates a renewable way to turn “waste” into wealth, and provides a sustainable method to build the paper-based supercapacitor for application in the wearable and flexible energy storage devices.

2. Experimental

2.1. Materials

Graphite flakes (325 mesh), Potassium permanganate ($KMnO_4$, 99%), Glutaraldehyde (GA, 50%) and Sodium nitrate ($NaNO_3$, 99%) were acquired from Aladdin, China. Manganese sulfate ($MnSO_4$), Ammonium persulfate ($(NH_4)_2S_2O_8$), Hydroiodic acid (HI) and other regents were analytical grade and used as received without further purification.

2.2. Preparation of PFs

Firstly, 2 g office waste paper was cut into small pieces and added into 150 mL deionized (DI) water with continuous vigorous stirring for 12 h, and the obtained slurries of paper fibers were washed with abundant deionized water and ethanol for several times. Then, the paper fibers were ultrasonicated and immersed in 2 M NaOH solution for another 3 h. Finally, the paper fibers were cleaned with abundant DI water for several times by filtration and freeze dry for later experiment.

2.3. Preparation of the MnO_2-nanowires

To prepare the MnO_2-nanowires, 0.01 mol of $MnSO_4$ and 0.02 mol of KOH were added into 60 mL DI water, and the suspension was stirred for 10 min using magnetic stirrer. Thereafter, 0.02 mol of $(NH_4)_2S_2O_8$ was added into the suspension, and the resulting solution was stirred for another 20 min. Finally, the solution was transferred into a Teflon-lined autoclave and maintained at 140 °C for 5 h. The precipitate was washed repeatedly with DI water and then freeze-drying for later experiment. Additionally, the synthesis of the MnO_2-nanowires is based on the redox reaction between $MnSO_4$ and $(NH_4)_2S_2O_8$, as shown in Eq. (1):

$$MnSO_4 + (NH_4)_2S_2O_8 + 4KOH \rightarrow MnO_2 + (NH_4)_2SO_4 + 2K_2SO_4 + 2H_2O \quad (1)$$

2.4. Preparation of PF-RGO-MnO_2 electrode

Conventional GO was obtained from graphite flakes by modified Hummer's Method [23]. Briefly, 2.0 g graphite powder and 1 $NaNO_3$ were added to 90 mL H_2SO_4 with the magnetic stirring at 300 rpm in an ice bath for 30 min. Then 6 g $KMnO_4$ was slowly added into the suspension at 35 °C for another 120 min. After that 90 mL DI water was added into the mixture in an oil bath for 15 min at 98 °C, and other 20 mL H_2O_2 was slowly added to the mixture. Finally, the GO suspension was obtained by purification process with abundant of DI water and diluted HCl solution. For PF-RGO-MnO_2 electrode, 24 mL 1 mg mL^{-1} GO suspension containing 56 mg PFs were added into beaker and ultrasonicated for 60 min under ambient temperature. And the resulting mixture was reduced by 55% HI with the magnetic stir at 100 °C for 120 min. Subsequently, the reaction mixture were filtered and washed with DI water for several times until the pH value was neutral. After that, the dispersion of PF-RGO was added with 20 mg MnO_2 nanowires and stirring for another 30 min, then the PF-RGO-MnO_2 film was obtained by vacuum filtration through Polyvinylidene Fluorideanodic (PVDF) membrane (0.22 μm pore size, 50 mm in diameter) and dried in an oven at a temperature of 60 °C for 6 h. For comparison, the compared PF-RGO electrode was fabricated in the same process without adding MnO_2.

2.5. Assembly of PF-RGO-MnO_2//PF-RGO-MnO_2 symmetric supercapacitors

For electrolytes, briefly, 1 g PVA were added into 10 mL 1.0 M Na_2SO_4 solution, and the mixture were heated to 85 °C with vigorous stirring until the solution become clear. The PVA-Na_2SO_4-GA hydrogel was prepared via mixing the PVA-Na_2SO_4 solution with diluting glutaraldehyde under vigorous stirring to react for 10 s before used. And the PVA-Na_2SO_4-GA Hydrogel was used as the separator, electrolyte and packaging materials, simultaneously, and the choice of PVA-Na_2SO_4-GA hydrogel not only to simplify the assembled and packaging technology and the whole process would be finished in 1 min, but also to enhance the mechanical strength of the devices. The symmetric supercapacitor was assembled by building the PF-RGO-MnO_2, PVA-Na_2SO_4-GA, and PF-RGO-MnO_2 layer-by-layer. And the whole process was completed as soon as possible (about 60 s) before the PVA-Na_2SO_4-GA lost fluidity.

2.6. Characterization and measurement

The morphological features of MnO_2, PF, PF-RGO, and PF-RGO-MnO_2 were studied by field-emission scanning electron microscope (FE-SEM, FEI Nova Nano SEM 450). The oxidation status and chemical