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Silver Fiber Fabric as the Current Collector for Preparation of Graphene-Based Supercapacitors

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ABSTRACT

During the past few years, a considerable attention has been devoted to the development of textile- based energy storage devices and wearable electronics applications. In this paper, for the first time, we report a flexible high performance graphene-based supercapacitor using silver fiber fabric as the current collector. The silver fiber fabric offers remarkable advantages such as light weight, mechanical flexibility and ease of integration with electronic textiles, which well-suited for wearable energy storage devices. A new hybrid material of graphene-silver fiber fabric (rGO/SFF) was prepared through a facile electrophoretic deposition of graphene and being used as a binder-free flexible supercapacitor electrode. In order to obtain the optimum condition, the effect of deposition time was investigated and a duration time of 10 minute was selected as an optimum condition. The as-prepared binder-free electrode based on rGO/SFF-10 showed excellent electrochemical performance in the three-electrode configuration using KOH (3 M) as the supporting electrolyte, with the highest capacity of 172 mF/cm^2 at 4 mA/cm^2 and a capacitance retention of 97% after 5000 charge–discharge cycles. The high performance of rGO/SFF electrode is associated to the superior conductivity, high mechanical flexibility as well as good electrochemical stability of the silver fiber fabrics. The results suggest that the prepared electrode is a promising candidate for wearable energy storage applications due to its advantageous properties and the ease of preparation.

1. Introduction

Electrochemical capacitors (ECs), also known as supercapacitors, have attracted considerable attention over the last decade due to their higher power density and longer life cycle than rechargeable batteries as well as their higher energy density compared to traditional dielectric capacitor [1]. Based on energy storage/delivery mechanism, supercapacitors can be divided into two categories; electrochemical double layer capacitors (EDLCs) and pseudo-capacitors [2,3]. For EDLCs, energy is stored by electrostatic accumulation of charges at the interface between the surface of an electrode and an electrolytic solution. While, pseudo-capacitors store electrical energy via reversible and faradaic redox reactions [4,5]. Although pseudocapacitors display high capacitance, their performance decays after a prolonged cycling application. On the contrary, EDLC can be charged and discharged up to one million cycles without loss of power efficiency [6]. Moreover, charge transfer in EDLCs is faster than redox reaction, resulting in a high charge-discharge rate and power density [6]. Superior electrical conductivity, porous structure and specific surface area are three important parameters that affect the electrochemical performances of EDLC electrodes. In this regard, large electrode specific surface area is an essential parameter for achieving high specific capacitance due to the enhanced electrode/electrolyte interface [36]. Carbon-based materials including activated carbon, carbon nanotubes, carbon fibers, and graphene sheets are commonly used in EDLCs [7]. Among carbon-based materials, graphene has received considerable attention as building blocks for electrodes of EDLCs because of its unique properties such as high theoretical surface area (2630 m^2/g) [8], electrical conductivity of 2×10^3 S/cm [9], and specific capacitance of 550 F/g [5]. Despite the aforementioned advantages, the aggregation or restacking of graphene nanosheets which occurred due to the strong π-π interactions leads to the loss of effective electrode surface area and in turns degrade the capacitance performance of the electrode. Moreover, the intrinsic contact

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resistance between graphene and current collector increases as a result of agglomeration between individual graphene sheets [10,11]. To overcome the first challenge, graphene sheets are prepared as three-dimensional (3D) architectures that would hinder the re-stacking of graphene sheets effectively and preserve their high specific surface area, resulting in good electrode performances [12]. In this regard, developing 3D graphene structures by a facile and simple method is an important necessity. Several methods have been reported for fabricating 3D graphene networks. One of the most general strategies for preparing 3D graphene materials is self-assembly. As a typical example through which various 3D graphene structures including aerogels, foams, and sponges, can be produced is the gelation process of GO dispersion followed by reduction to convert GO to rGO [13–15]. For this purpose, reducing agents like hydrazine monohydrate, hydroxylamine, sodium borohydride, hydroquinone, hydroiodic acid (HI) and L-ascorbic acid can be used [16–18]. On the other hand, to reduce the contact resistance of 3D graphene materials, some specially engineered binder-free 3D structures have been developed to contact graphene sheets onto the current collector directly without the help of any binders or conductive agents [19–23]. In this respect, several insightful methods, such as electrophoretic deposition (EPD) [24], chemical vapor deposition [25] and vacuum filtration deposition [26] have been applied to prepare binder-free electrodes. As already mentioned, in the process of depositing graphene-based materials, choosing the current collectors and methods of deposition are the most critical key factors that affect the performance of supercapacitor. However, the procedures that can concurrently solve two mentioned technical problems have been rarely reported. Among various methods of film deposition and coatings, electrophoretic deposition (EPD) can be considered as one of the most interesting approaches to deposit the films on the surface of conductive substrates since it is a green, low cost and facile method to form an electroactive layer [27,28]. It also provides several advantages including high deposition rate, uniformity, controlled thickness, large scale, and binder-free contact [29]. Regarding to graphene, EPD technique has been applied as a convenient method to produce graphene-based films [30] in which by changing the EPD parameters such as deposition time and/or applied voltage, the thickness of graphene film can be controlled [31]. Moreover, EPD can be applied to flexible substrates and complex structures. In recent years, substantial attentions have been paid to flexible energy storage devices. The most important component for fabricating flexible supercapacitors is acquirement of appropriate flexible electrodes with high capacitance and high electrical conductivity to ensure fast charge-discharge process. Up to now, various kinds of current collectors are used in design and fabrication of supercapacitors including metal foils [32,33] and synthetic polymer films [34] with conductive coatings. The most widely used flexible current collector, which is pointed in the literature, is carbon cloths (CCs) [35]. However, apart from CCs the current collectors available for flexible supercapacitors are still very limited and to the best of our knowledge, there is no report on the use of silver cloth as flexible current collector. Herein, a silver fiber fabric (SFF) was used for the first time as the current collector for the fabrication of a high performance graphene-based supercapacitor. SFF was coated with partially reduced graphene oxide layer via an electrophoretic deposition (EPD) process (denoted as rGO/SFF electrode) which was further used as a flexible binder-free electrode. Furthermore, ascorbic acid (AA) was choose as a mild reducing agent, which is considered as a non-toxic and environmentally friendly reducing reagent in comparison to the conventional reductants such as hydrazine and hydrazine hydrate used in GO reduction. SFF showed excellent properties such as high conductivity, good flexibility, and high electrochemical stability. Using such substrate with high-performance and mechanical flexibility can open up inspiring opportunities for wearable energy storage applications.

2. Experimental Section

2.1. Chemicals and reagents

All chemicals and reagents were of analytical grade and used as received without further purification. Expandable graphite powder (with a particle size more than 300 μm) was purchased from Asbury Carbons (3772, Asbury Graphite Mills USA). Analytical grade KOH, L-Ascorbic acid, $NaNO_3$, $KMnO_4$, N-N-dimethylformamide (DMF) H_2SO_4 (98%), H_2O_2 (30%), HCl (38%) were supplied by Chem-Lab Co.Ltd. Silver fiber fabric (Product No. SILVER30#, Weight: 33 g/m^2, Width: 150 cm) was obtained from Shaoxing Yunjia Textile Product Co. Ltd.

2.2. preparation of partially reduced graphene oxide

Firstly, Expandable graphite flakes were thermally treated at 1050 °C for 15 s [36]. Graphene oxide (GO) was synthesized by following the classical modified Hummer's method using dry expandable graphite flakes as the precursor [37]. The partial reduction of the GO was performed using ascorbic acid. In a typical procedure, 2 g L-ascorbic acid was added into a 100 mL of 4 mg/mL GO aqueous solution and stirred for 30 minutes. The mixture was transferred to a 125 mL Teflon-lined autoclave and kept at 100 °C for 5 h. The autoclave was naturally cooled to room temperature, and the obtained reduced graphene oxide hydrogel was taken out and redispersed in deionized water. Then, the suspension of rGO was filtered and washed with deionized water until the pH of the rGO dispersion reached about 7. Finally, the rGO was freeze-dried for 2 days.

2.3. preparation of rGO/SFF electrodes

For the electrophoretic deposition (EPD), 20 mg rGO was first dispersed in 20 mL N-N-dimethylformamide (DMF) and stirred for 24 h, then sonicated by a bath sonicator for about 3 h to completely disperse rGO suspension with a concentration of 1 mg/mL. A piece of silver fiber fabric, SFF ($1 \times 3cm^2$), was used as the positive electrode and stainless steel foil as the negative electrode in a two-electrode system cell that rGO suspension in DMF was used as electrolyte. The distance between electrodes in the cell was adjusted to be 1 cm. A constant voltage of 10 V was applied to two-sided electrodes for 5, 10, 15 and 20 min. After that, the deposits were washed and dried in air at room temperature. The prepared electrodes were denoted as rGO/SFF-t in which, t is the electrophoretic deposition time. rGO/SFF-t used as the supercapacitor electrode and before electrochemical tests, the rGO/SFF-t were hold in 3 M KOH electrolyte for 30 min.

2.4. Instruments and Characterizations

The deposited material was removed from the surface of silver fiber fabric (by sonication) and used to determine the chemical composition of rGO by Fourier transform infrared spectroscopy (FTIR) using ABB Bomem MB-100 FT-IR spectrophotometer. Field-emission scanning electron microscopy (Tescan Mira II) was applied to observe the surface morphologies of SFF and rGO/SFF. The graphene oxide (GO) and reduced graphene oxide (rGO) were characterized by UV–vis absorption spectroscopy in a double-beam spectrophotometer (Perkin Elmer, Lambda 950) over the wavelength range from 200 to 800 nm at ambient temperature. The suspension of GO and rGO in dionized water were prepared by