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RESEARCH PAPER

High-performance flexible wire-shaped electrochemical capacitors based on gold wire@reduced graphene oxide

Yun-zhen Chang[1], Gao-yi Han[1,*], Yao-ming Xiao[1], Hai-han Zhou[1], Miao-yu Li[1], Dong-ying Fu[2], Wen Zhou[1]

[1]The Institute of Molecular Science, Key Laboratory of Materials for Energy Conversion and Storage of Shanxi Province, Taiyuan 030006, China;

[2]Institute of Crystalline Material, Shanxi University, Taiyuan 030006, China

Abstract: Flexible gold @reduced graphene oxide sheathed wires (WAu@rGO) were prepared by soaking a gold wire (100μm in diameter) in the center of glass capillaries with inner diameters of 1.0, 1.3 and 1.8 mm in a suspension of graphene oxide (GO) in a L-ascorbic acid aqueous solution at 30 °C for 48 h. The WAu@rGO wires were obtained after removal of the capillaries, and their microstructures were characterized by SEM and their electrochemical properties as flexible electrodes in electrochemical capacitors were investigated by electrochemical tests. Results show that the specific capacitance of the WAu@rGO wire with the smallest diameter is 5.47 mF cm^{-1} or 176.7 F g^{-1} at a scan rate of 1 mV s^{-1}. A symmetric all-solid-state flexible electrochemical capacitor based on the two smallest wires and a polyvinyl alcohol/H_3PO_4 gel electrolyte shows a maximum capacitance of 2.06 mF cm^{-1}, or 6.87 mF cm^{-2} or 411.9 mF cm^{-3}. The solid-state capacitor has energy and power densities of 9.48×10^{-4} mWh cm^{-2} and 0.017 mW cm^{-2}, respectively, based on the whole device. Three devices connected in series can light a light-emitting diode with a threshold voltage of 2.5 V. Moreover, the device also shows a long cyclic stability and a good bending ability.

Key Words: Flexible; Reduced graphene oxide; Network; Electrochemical capacitor; Fiber

1 Introduction

Electrochemical capacitors (ECs) are considered as a new kind of energy storage devices with the advantages of both the high specific power of dielectric capacitors and the high specific energy of rechargeable batteries. Their excellent cyclic life and low maintenance cost make them arouse great commercial and research interests for next generation portable electronics [1-4]. According to energy storage mechanisms, two types of ECs' can be classified. One is mainly based on electrical double layer capacitors and the storage of electric energy is achieved by accumulation of charges at the electrode/electrolyte interfaces. Another one is mainly based on a rapid and reversible faradic process and the corresponding materials are named as pseudocapacitor materials [5]. In most cases, these two mechanisms may exist simultaneously according to the nature of the materials.

Recently, the development of versatile flexible and deformable electronic devices requires energy storage devices with good flexibility, high energy and power densities. It is well known that the energy storage devices depend strongly on the materials of electrodes, current collectors and electrolytes. Up to date, various flexible electrode materials based on transition metal oxides or hydroxides and conducting polymers have been investigated [6-8]. It is proved that these types of materials have the disadvantages of the short cycling stability and low rate-capability, which limit their practical application although they exhibit relatively large specific capacitances (C_s) owing to a rapid and reversible faradic reaction [9]. Among various materials of electrodes, carbon-based materials have attracted a wide attention owing to their relatively low cost, fast charge-discharge rates and high chemical stability. For example, the materials such as carbon fibers, carbon nanotubes, graphene, activated carbon and carbide-derived carbons [10-14] have been intensively studied as electrode materials. As a new kind of two-dimensional (2D) material, graphene is considered as a promising flexible electrode material owing to its distinctive properties [15-17] such as high strength, high conductivity, large specific surface area and chemical stability.

Up to date, many methods have been developed to prepare graphene paper and wire for the fabrication of flexible graphene-based electrodes. For example, graphene paper can be prepared via assembling graphene oxide (GO) first and then reduced by reducers, or by filtrating the chemically reduced GO (rGO) [18, 19]. The graphene fibers can be prepared by wet-spinning, assembly, hydrothermal process and chemical vapor deposition [20-24]. The obtained graphene paper

Received date: 15 Jul 2017; **Revised date:** 10 Dec 2017
***Corresponding author.** E-mail: han_gaoyis@sxu.edu.cn

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and wire have fairly good mechanical flexibility, light weight and high strength, which are favorable to construct deformable and wearable energy storage devices. Recently, Zhao et al.[25] have designed a graphene-based single fiber EC by combining a wet-spinning technique with dip-coating process, which possesses a C_s of about 205 mF cm^{-2} (182 F g^{-1}). Hu et al.[26] have reported an all-in-one-fiber graphene EC by combining a spinning method with controllable reduction of GO under laser irradiation, the C_s can reach 2 mF cm^{-2} at a current density of 800 μA cm^{-2} when an acetonitrile solution of $NaClO_4$ (0.1 M) is used as electrolyte. Kou et al.[27] have prepared the rGO@sodium carboxymethyl cellulose yarn ECs by using a coaxial wet-spinning assembly approach, the C_s in areal can reach 127 mF cm^{-2} (114 F cm^{-3} in volume, 3.8 mF cm^{-1} in length). Furthermore, Meng et al.[28] have fabricated a flexible graphene fiber@3D porous network-like graphene framework (GF@3D-G) by combining a hydrothermal strategy with electrochemical process, the C_s in length is about 20 μF cm^{-1} (1.2-1.7 mF cm^{-2} in area).

However, no matter how many advantages, the graphene-based materials have a poorer electric conductivity compared with metals, which will affect the capacitive performance of the devices due to the relatively larger inner resistance. Therefore, integrating graphene and metal into one flexible electrode is considered to be a good strategy. For example, Li et al.[29] have reported a fiber-shaped solid EC by electrodepositing rGO on gold fibers, the capacitor exhibits an excellent rate-capability and the C_s of the electrode in length is about 11.4 μF cm^{-1} (0.726 mF cm^{-2} in area) at a discharge current density of 2.5 μA cm^{-1}. Yet, the mass of rGO deposited on gold wires by electrodepositing is limited because the further deposited rGO will peel off the substrate, which will affect the property of the devices in the term of volume. Therefore, a key problem for high-performance graphene based wire-shaped ECs is to load more graphene on the metallic wires.

In the presence of L-ascorbic acid (L-AA), the GO can be reduced into rGO at room temperature and the rGO-gel will be formed. On the other hand, L-AA exhibits a mild reductive and nontoxic property and is naturally used as a reducing agent [30]. Based on this background, we demonstrate a facile and green approach to fabricate the flexible electrodes by coating rGO network on gold wires. With the help of capillary force, we make the gold wires stand in the mixture of GO and L-AA. After the system stands for 48 h at 30 °C, the wires of gold wrapped by rGO network (WAu@rGO) have been obtained after washing by water. The product of WAu@rGO has been characterized and the fiber-shaped solid ECs have been assembled by using WAu@rGO as electrodes and polyvinyl alcohol/H_3PO_4 (PVA/H_3PO_4) as electrolyte. The performances of the fiber-shaped devices have also been investigated in detail. It is believed that this methodology provides a simple, eco-friendly and convenient route to produce flexible graphene based on fiber-shaped ECs with high performance.

2 Experiments

2.1 Materials

Natural graphite powder (NGP, 325 mesh) was purchased from Tianjin Guangfu Research Institute. L-AA was obtained from Sinopharm Chemical Reagent Co., Ltd., and all other chemicals used in this study were of analytical grade. Deionized water was used in all of the experiments.

2.2 Preparation of WAu@rGO composites

GO was prepared by oxidation of NGP according to the method reported in the literature [31]. The procedure for preparation of WAu@rGO was as follows. Firstly, 80 mg L-AA was dissolved into 1.0 mL GO aqueous dispersion (8.0 mg mL^{-1}) under ultrasonication, the mixture was then poured into a small test tube. Subsequently, the capillaries (inner diameters of 1.0, 1.3, and 1.8mm) containing Au wires (Au diameter of 100 μm) were inserted into the small test tube and the Au wires were finely fixed and made as in the center of the capillaries far as possible. With the help of the capillary effect, the capillaries were filled fully with the mixture. Then，the reaction between GO and L-AA was carried out at 30 °C in a sealed container for 48 hours. Finally, the three wires of WAu@rGO with a diameter of about 460, 792 and 1305 μm were obtained from the capillaries with an inner diameter of 1.0, 1.3, and 1.8mm, respectively, which were released from the capillaries immersed into water to remove the impurities and used as electrodes for the fiber-shaped ECs. For characterization, the samples of WAu@rGO wires were freeze-dried after the impurities were removed. The simple illustration for preparation of WAu@rGO wires is shown in Fig. 1a. The WAu@rGO wire with a diameter of about 460 μm was used in the following experiment unless noted otherwise. For comparison, the fiber based on reduced graphene oxide without gold wire was also prepared using the capillary (inner diameter of 1.0 mm) under the same condition, and the obtained sample was named as rGO.

2.3 Characterization

The microstructure of WAu@rGO wires with different diameters was observed on a JEOL-JSM-6701 field emission scanning electron microscope (SEM) operating at an accelerating voltage of 10 kV. X-ray diffraction (XRD) patterns were recorded on a D8 Advance (Bruker) X-ray diffractometer with Cu $K\alpha$ radiation (λ=1.5406 Å) in the 2θ range of 5º-80º. X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCAl-ab220i-XL spectrometer (VG Scientific, England) using a monochromic Al $K\alpha$ source at 1486.6 eV.

2.4 Preparation of PVA/H3PO4 electrolyte

Water (10.0 mL) and phosphoric acid (1.0 g) were mixed adequately by magnetic stirring in a 25.0 mL glass bottle. PVA-124 (1.0 g) was added to the mixture slowly and soaked for 1 hour, and then the whole mixture was heated up steadily to 90 °C under vigorous stirring until the solution became clear.

2.5 Electrochemical characterization of individual WAu@rGO and rGO wires

In the three-electrode electrolytic cell, the electrochemical