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Hydrophilic carbon fiber paper based electrode coated with graphene for high performance supercapacitors

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ABSTRACT

In this paper, we report a facile and cost-effective approach to synthesis carbon fiber paper (CFP) based electrode coated with reduced graphene oxide (RGO) by vacuum filtration and carbonization. The SEM image showed that graphene was deposited on each individual carbon fiber and the hybrid electrode paper retained its three dimensional structure which provided efficient percolation path ways for electrons. The specific capacitance of the hybrid paper reached 1076 mF cm^{-2} at 5 mV s^{-1} according to cyclic voltammetry measurement. Further, the assembled symmetric supercapacitor delivered a high capacitance of 344 mF cm^{-2} at 0.5 mA cm^{-2}. In a word, this feasible method should be appropriate for the fabrication of carbon fiber paper based electrodes.

1. Introduction

Supercapacitor has become one kind of promising energy storage device in recent years due to its large capacitance, high energy density and long cycle life [1]. Carbon fiber paper, with high porosity, satisfactory conductivity and high chemical stability, has been commonly used in the field of energy storage [2]. The single carbon fiber in CFP provides an efficient percolation path for electrons, and its appropriate pore channels formed between the microfibers may beneficial for fast mass transport of electrolytes to all the electrochemically active materials [3]. Therefore, CFP is a promising collector/support for the deposition of other active materials.

Graphene, as a kind of 2-D carbon nanomaterial, has been extensively studied in the field of energy storage due to its large capacitance, high conductivity and large surface area [4]. Thus, introducing graphene into other active materials (such as polypyrrole or MnO_2) has been a common way to enhance the electrochemical performance of the supercapacitor [5]. Recently, a spray coating technique was applied to coat graphene on the surface of carbon fiber paper [6]. However, the experimental device was expensive and the experimental process was tedious.

Herein, for the first time, we report a hybrid electrode based on hydrophilic carbon fiber paper decorated with graphene prepared by an easy and cost-effective vacuum-filtration method followed by high temperature carbonization. Due to the hydrophobicity of CFP, liquid cannot penetrate to the inner space of CFP and instead, will remain on the surface of CFP. In our design, H_2SO_4 was used to etch carbon fiber paper by introducing more oxygen-containing groups so that hydrophilic graphene oxide solution (GO) could make fully contact with cross-linked carbon fibers by vacuum filtration. Further, the carbonization process ensured not only the high level reduction of graphene oxide but also the activation of carbon fiber paper [3,7]. The characterization results showed that graphene was filled in the vacancy of criss-cross carbon fibers. Moreover, the CFP/RGO paper used as a binder-free electrode delivered a high area capacitance of 1076 mF cm^{-2} at a current density of 5 mV s^{-1}. This work provides a facile strategy for the fabrication of carbon fiber paper based electrodes.

2. Experimental

2.1. Preparation of CFP/RGO electrode paper

Carbon fiber paper (from Shanghai Hesen Electric. Co. Ltd.) was first etched by pure H_2SO_4 at 60 °C for 2 h to raise its hydrophilicity [8]. Then, dispersed graphene oxide solution (obtained from Tanfeng Tech. Inc.) with a low concentration of 0.2 mg ml^{-1} was coated on the surface and inner space of the carbon fiber paper through a vacuum filtration device. The obtained CFP/GO paper was cut into small pieces with geometric area of 2 × 1 cm^2 and then transferred into a tube furnace and calcined at 550 °C for 3 h to achieve CFP/RGO electrode paper.

2.2. Assemble of the symmetric supercapacitor (ASSC)

5 g polyvinyl alcohol and 5 ml H_2SO_4 was dissolved in 50 ml deionized water and mechanically stirred for 1 h until the solution

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became clear to obtain the PVA/H_2SO_4 gel. Two pieces of CFP/RGO paper were soaked into the mixed gel and then dried in air to evaporate the excess water for 4 h. A piece of cellulose paper with porous structure was inserted into the two electrodes and the final product was compressed at 0.2 MPa for 30 min to achieve the symmetric supercapacitor.

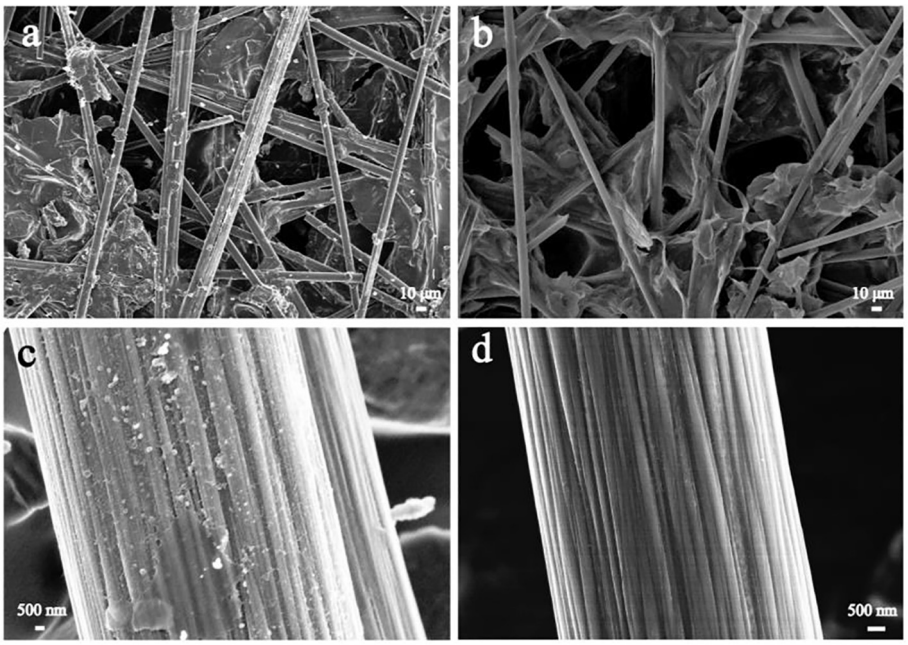

Fig. 1. SEM images of the original carbon fiber paper (a), CFP/RGO hybrid electrode (b), single carbon fiber before carbonization process (c), single carbon fiber after carbonization process (d).

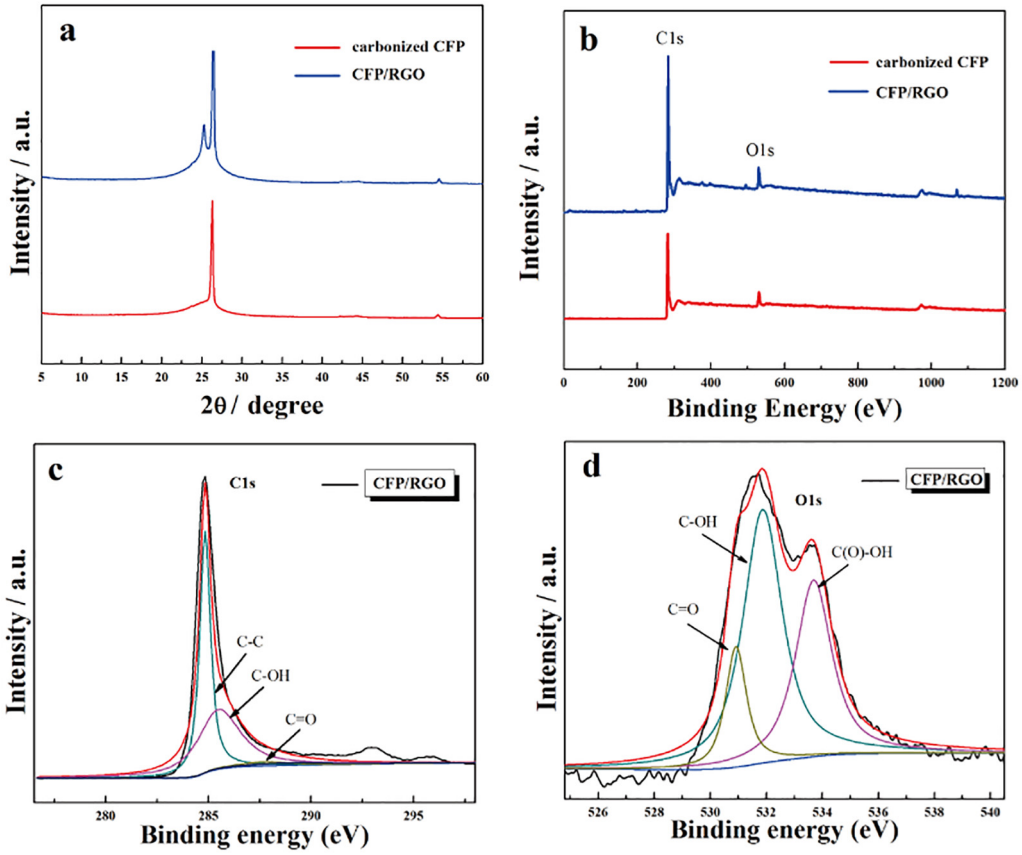

Fig. 2. XRD patterns of the carbonized CFP sample and the CFP/RGO electrode (a). XPS spectrum of pure carbonized carbon fiber paper and CFP/RGO hybrid electrode paper (b), deconvoluted C1s core level XPS spectra of the CFP/RGO electrode (c), deconvoluted O1s core level XPS spectra of the CFP/RGO electrode (d).