



Flexible Graphene-Based Composite Films for Supercapacitors with Tunable Areal Capacitance



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ABSTRACT

Flexible supercapacitors based on paper-like electrodes have attracted significant interest because of the increasing demands in the energy storage, and they are recently claimed to be minimized and portable for meeting practical applications. As promising binder-free electrode materials in the supercapacitors, graphene-based films have been developed for enhancing their performance in energy storage by inserting “spacers” in-between nanosheets to prevent inevitable aggregations. In this study, a facile and versatile strategy is presented for fabricating graphene-based composite films by introducing activated carbonized cotton fibers to regulate the chemical composition, surface area and pore size distribution. The obtained composite films permit to present substantially increased energy storage capability (capacitance of 310 F g⁻¹ and 150 F g⁻¹ at 0.1 A g⁻¹ and 10 A g⁻¹ in 6 mol L⁻¹ KOH electrolyte, respectively). Furthermore, tunable areal capacitance is realized by altering the stacked film layers without loss of mass specific capacitance. The devices based on composite films with excellent power density (up to 156.5 mW cm⁻²) and energy density (240 μWh cm⁻²) highlight a controllable, mini-sized and high-efficiency stage for energy storage. Such unique strategy suggests great potential in the commercialization of portable electronic devices, which require greater capacitance in a limited area.

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1. Introduction

Because of tremendous expansion in the energy and environmental issues along with the increasing energy consumption, sustainable development of renewable energy sources has become one of the most important topics that the society faces in this century. The energy markets urgently required electrochemical energy storage devices with the ability of high efficient energy storage and conversion, such as portable electronic devices and electronic vehicles [1–5]. In the tide of “new energy fever”, supercapacitors have attracted significant interest for their high power density, long life-cycles, short charge time, light weight, and good operational safety [6,7].

Graphene is considered as a promising candidate electrode material for supercapacitors due to its outstanding theoretical capacitance, high specific surface area, excellent electrical conductivity and remarkable mechanical properties [8–12], which makes it possible to fit in the approaching era of micro-scale

supercapacitors that are required to power the next generation of wearable- and micro-electronic devices [13]. Furthermore, free-standing graphene films of flexibility and foldability are more suitable for the promising requirement in the energy storage devices [14–19], thus being mainly taken as the potential objects for achieving the goal. However, due to the strong van der Waals attraction and π - π interactions between isolated graphene sheets, the irreversible agglomeration and restacking into graphite greatly hindered the effective transport of ions and further suppressed the accessible specific surface area, actual specific capacitance and intrinsically conductivity [11,20–22]. Recent advances in inserting “spacers” in-between graphene sheets [9], such as carbon nanotubes [23–25], carbon fibers [26], activated carbon [27], start new ways to address this challenge. For example, the “spacers” of carboxylated multi-walled carbon nanotube were trapped in the reduced graphene oxide (rGO) film to avoid excessive accumulation between sheets, which presented increasing gravimetric capacitance 200 Fg⁻¹ at 1 A g⁻¹, compared to the neat rGO film with 150 Fg⁻¹ [26].

Many researches have focused on the specific capacitance based on the mass value of active materials. However, when all the materials, such as conducting carbon black and binder are included, the specific capacitance is actually very low for the

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whole electrode due to the large amount of inactive materials. In addition to gravimetric capacitance, the areal capacitance is a crucial factor determining the design and practical application of wearable- and micro-electronic devices. Combined with the flexibility and foldability of graphene films, the areal capacitance is a crucial factor determining the design and practical application of wearable- and micro-electronic devices. Although areal capacitance of film materials has been reported in previous studies [28–40], the final value is generally lack of being controlled. Multi-layer graphene/porous carbon woven fabric films were prepared for fiber supercapacitor electrodes by the process of chemical vapor deposition, which performed areal capacitance of 44.7 mF cm^{-2} , representing a much more room for improvement for energy-related applications [28]. Therefore, there is still a great challenge to achieve controllable and enhanced areal capacitance for practical devices, whose application is required in a certain area.

For settling such above mentioned problems, we here demonstrate a facile and versatile strategy for tuning areal capacitance in the graphene-based composite films by altering the stacked film layers. The free-standing composite films (ACC-rGO) without using any conducting materials and binder are prepared by embedding activated carbonized cotton (ACC) fibers in the sheets of rGO film to prevent the agglomeration. The ACC-rGO composite films of flexibility and foldability could be stacked into different layers to tune the areal capacitance according to practical requirements. ACC-rGO composite films are allowed to present substantially increased energy storage capability (capacitance of 310 F g^{-1} and 150 F g^{-1} at 0.1 A g^{-1} and 10 A g^{-1} in 6 mol L^{-1} KOH electrolyte, respectively) in the binder-free system, compared to the neat rGO film (100 F g^{-1} at 0.1 A g^{-1}) under the same conditions. The solid-state devices of three layers of ACC-rGO composite films with high power density (up to 156.5 mW cm^{-2}) and energy density ($240 \mu\text{Wh cm}^{-2}$) are well competitive to those reported carbon-based supercapacitors. This design suggests great potential in the realization of portable electronic devices, which require greater capacitance in a limited area.

2. Experimental

2.1. Synthesis of GO

Graphite oxide (GO) was made by a modified Hummers method [41]. Nature graphite powders (2 g) and NaNO_3 (1 g) were added into H_2SO_4 (120 mL) in the ice bath and the mixture was kept at 0°C for 1 h, then KMnO_4 (6 g) was added gradually. After stirring for 2 h, the solution was heated up to and kept at 30°C for 0.5 h. Subsequently, deionized water (150 mL) was added dropwisely, followed by adding H_2O_2 (50 mL, 5%). Finally, the solution was washed with deionized water and HCl (5%) to obtain the GO aqueous solution.

2.2. Synthesis of ACC

The commercial cotton was directly used as the starting material without any further pre-treatment. Typically, a piece of cotton was cut into a certain shape (determined by the furnace size) and subjected to carbonization under N_2 atmosphere at 900°C for 2 h with a heating rate of 5°C min^{-1} . The carbonized cotton (CC) was further treated under ultrasonication for 1 h with the presence of mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$ ($v/v=1/3$) in order to improve the hydrophilicity. The resulted sample was then immersed in the aqueous solution of KOH in the mass ratio of CC: KOH = 1:2, and then dried at 90°C overnight to make water evaporation, thoroughly. The mixtures were then thermally annealed at 800°C for 1 h under N_2 atmosphere with a heating rate of 5°C min^{-1} . The resulted sample (ACC) was washed with

10 wt\% HCl aqueous solution and deionized water, and then dried at 90°C .

2.3. Synthesis ACC-rGO composite films

The as-prepared ACC was ground and mixed with GO aqueous solution (2 mg mL^{-1}) under vigorous stirring and ultrasonic treatment to form homogeneous suspension. Then ACC-GO composite films were obtained by vacuum filtration of the suspension, and then dried at 90°C for 24 h. The resulted films were immersed in hydroiodic acid for 24 h, and then washed with deionized water, and dried at 90°C . The as-prepared products were calcined at 300°C under Ar/H_2 mixed atmosphere (flow ratio, 100:15).

We denoted the products as ACC-rGO-1 ($m_{\text{ACC}}: m_{\text{GO}} = 1: 4$, mass ratio), ACC-rGO-2 ($m_{\text{ACC}}: m_{\text{GO}} = 1: 1$), and ACC-rGO-3 ($m_{\text{ACC}}: m_{\text{GO}} = 3: 1$), corresponding to the increasing amount of ACC fibers used. For comparison, neat rGO film was also obtained with the same preparation process, except that no ACC fibers were added. All the films have the same total mass of about 48 mg and mass density of about 3.2 mg cm^{-2} .

2.4. Characterizations

The structures of ACC-rGO composite films were explored by field-emission scanning electron microscopy (FESEM, ZEISS supra 55) and transmission electron microscopy (TEM, JEOL JEM-2010). The nitrogen absorption/desorption isotherms associated with specific surface area and pore diameter distribution data were tested with Autosorb-iQ2-MP (Quantachrome) analyzer at 77k. X-ray photoelectron spectroscopy (XPS) was acquired on PHI-5300.

2.5. Electrochemical measurements

The electrochemical performance of composite films was determined in a three-electrode cell with basic aqueous solutions. The ACC-rGO composite films were directly pressed onto nickel foam under the pressure of 10 MPa to act as working electrode without using any conductive agent and binder. A three-electrode system was fabricated in 6 mol L^{-1} KOH solution. Hg/HgO and Platinum foil electrodes were used as reference electrode and counter electrode, respectively.

The electrochemical performance of ACC-rGO-2 was further determined in a gel electrolyte by using a two-electrode device. In a typical preparation of the electrode, PVA powder (2 g) was dissolved in distilled water (20 mL) under vigorous stirring at 85°C . Until a stable PVA aqueous solution was formed, two working electrodes with PVA aqueous solution in between were stacked, followed by adding excessive 6 mol L^{-1} KOH aqueous solution. The PVA-based gel, which acted as the electrolyte and separator, was settled for 24 h, allowing them to form a robust flexible solid-state device.

The potential window was set $-1\sim 0 \text{ V}$ (vs. Hg/HgO) in three-electrode configuration and $0\sim 1 \text{ V}$ in two-electrode configuration, respectively. Galvanostatic charge/discharge was tested at various current densities using LAND-CT2001A (Wuhan Jinnuo Electronics, Ltd.). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out using a CHI660C electrochemical workstation (CH Instruments, Inc.).

3. Results and discussion

The schematic representation illustrates the fabrication of ACC-rGO composite films and corresponding optical photographs (Fig. 1). The commercial cotton (Fig. 1a) after carbonization and activation with porous structure was ground into short fibers.

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