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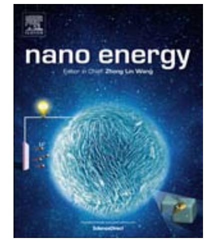

RAPID COMMUNICATION

Water-dispersible graphene/polyaniline composites for flexible micro-supercapacitors with high energy densities

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Abstract
Lightweight and mechanically compliant energy storage devices have attracted tremendous interest due to the increasing demand for flexible and miniaturized electronics. Recently, micro-supercapacitors (MSCs) have advanced rapidly as potential micro-sized power sources, but it is still challenging to build the micro-device using cost-effective technologies for large-scale manufacture. Here, we developed a simple solution-processible method to fabricate microelectrode patterns using a water-dispersible graphene/sulfonated polyaniline (rG/SP) as the active MSC material. The highly stabilized rG/SP dispersion in aqueous solution enables the direct thin-film deposition on flexible substrates and the formation of interdigital patterns by plasma etching. The as-fabricated solid-state MSC delivers an ultrahigh areal capacitance of 3.31 mF/cm^2 and volumetric stack capacitance of 16.55 F/cm^3 with excellent rate and cycling performance. Furthermore, the rG/SP based MSC demonstrates a superior energy density of 1.51 $mW\,h/cm^3$ while maintaining high power density. The micro-device also shows superior mechanical stability with 96.5% of capacitance retained under different bending and twisting conditions, which makes it suitable specifically for portable and wearable electronic applications.

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Introduction

Supercapacitors have drawn great interest recently due to their high power density and cycling stability [1,2]. As an energy storage device, supercapacitor has potential to supplement or replace batteries and electrolytic capacitors for wide range applications [3-6]. In an attempt to miniaturize the energy storage units for flexible and portable electronics, micro-supercapacitors (MSCs) have been recently developed with excellent electrical and mechanical compatibilities [7-10]. In contrast to traditional sandwich assembled supercapacitors, most of micro-supercapacitors are based on two-dimensional interdigital patterns. The unique design of microelectrode patterns in planar geometry has achieved significant size reduction and superior charge transfer characteristics, which enables the direct integration of MSCs into other electronic devices for high energy and power supplies.

Recently, several fabrication methods have been reported to make micro-supercapacitors using graphene-based materials. El-Gao and Katy et al. have developed a laser scribing approach to convert graphene oxide (GO) film into interdigital graphene patterns. [11,12] Lin et al. have used a combination of chemical vapor deposition (CVD) and lithographic techniques to fabricate graphene/CNT composite [13]. To make bendable and wearable energy storage devices, patterned graphene materials have also been made on a flexible polyethylene terephthalate (PET) substrate [14]. However, the substrate transfer process is complex and difficult to control. Moreover, for some of the aforementioned approaches, the high temperature requirement and photolithographic processing are not cost effective for large-scale production. Therefore, a facile solution-processible approach at low temperature is highly desirable for cost-effective and scalable micro-supercapacitor fabrication [15].

To achieve the desirable electrochemical properties of the MSCs, a variety of nanostructured materials have been studied. Different carbon structures including onion-like carbon, carbide-derived carbon, carbon nanotubes have been used for electrical double layer capacitors (EDLCs), while conductive polymers such as polyaniline (PANI) and polypyrrole have been used for pseudocapacitors [8,9,16-19]. Graphene, an sp^2 hybridized hexagonal carbon form, has been regarded as an excellent electrode material for EDLCs owing to its superior charge carrier mobility, mechanical strength and large surface area [20-22]. In addition, a pseudocapacitive material, particularly polyaniline (PANI), has been incorporated into graphene network to form composite materials with improved specific capacitance [23-26]. For example, it has been reported the covalent grafting of amino groups onto graphene oxide (GO) followed by an in-situ polymerization of PANI achieved a maximum specific capacitance of 500 F/g [27,28]. Non-covalent treatment has also been used to exfoliate graphene sheets via the strong π-π interactions and electrostatic forces between negatively conductive polymer and graphene [29]. Despite the unique structural and electrical properties of these graphene/PANI composites, the poor dispersion in aqueous solution poses limitations for its application in MSC fabrication through stencil printing and spin coating. The stable aqueous dispersion is the prerequisite to achieve thin-layer deposition with high uniformity. In this sense, a water-soluble graphene/polyaniline composite will be of great importance for the practical application of the electrode materials in MSC.

In this study, we report on newly developed flexible micro-supercapacitors with high energy density using a water-dispersible graphene/sulfonated polyaniline (SPANI) composite (rG/SP) as the electrode material through the combination of spin coating, shadow masking, and plasma etching approaches. To the best of our knowledge, this is the first time that the nanostructure of conductive polymer is applied in MSC to deliver enhanced capacitance. In particular, the hydrophilic nature of the rG/SP allows the direct thin-film deposition on a flexible substrate by spin coating without further chemical or thermal treatment, which provides the possibility for fast and large-scale fabrication. Moreover, we first demonstrate the use of pre-designed shadow mask for the formation of interdigital patterns, which presents obvious advantages over traditional multiple-step photolithography processes. The structural properties of the rG/SP electrodes and electrochemical behaviors of the corresponding MSC device are examined by various characterization techniques. The as-fabricated rG/SP-MSC delivers a superior volumetric capacitance of 16.55 F/cm^3 with excellent cycling performance. Remarkably, the flexible MSC device demonstrated here also performs exceptional electrochemical stability under multiple bending and twisting cycles, which presents tremendous suitability for flexible and portable energy storage.

Experimental section

Material preparation

GO was prepared using Hummers' method [30]. SPANI was synthesized by sulfonation of emeraldine salts as previously reported [31,32]. In a typical process, emeraldine salts were prepared by oxidizing aniline monomer in 1.2 M hydrochloric acid. The resulting emeraldine salts (3 g) were sulfonated by 7.27 g chlorosulfonic acid in 100 ml 1,2-dichloroethane at 80 °C for 5 h followed by hydrolysis in 150 ml water at 100 °C for 4 h. Finally, the concentrated precipitates were washed by acetone and water, and dried under at 55 °C overnight. For the rG/SP composite, 100 mg GO and 200 mg SPANI were dispersed in 100 ml DI water by sonication. Thereafter, 1 ml of hydrazine monohydrate (Alfa Aesar) was added to the water suspension of GO and SPANI and the suspension was stirred at 80 °C for 12 h. After cooling to room temperature, the rG/SP composite was obtained by vacuum filtration, washed repeatedly with water, and dried in oven at 55 °C overnight.

Fabrication of rG/SP interdigits

Kapton® FPC (flexible printed circuit) film (125 μm) was used as the flexible substrate, and treated in UV-Ozone (Novascan) chamber for 30 min before use. The rG/SP dispersion was sonicated for 1 h and spin coated (1000 rpm, 30 s; MTI Corp.) on the UV treated Kapton substrate. A stainless steel stencil with a 10-finger interdigital pattern (250 μm finger width, 350 μm interspacing, MiniMicroStencil Inc.) was used as a shadow mask. To fabricate the current collector, 10 nm Ti