In-situ growth of high-performance all-solid-state electrode for flexible supercapacitors based on carbon woven fabric/ polyaniline/ graphene composite

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HIGHLIGHTS

- An flexible electrode is prepared through an in-situ growth and wrapping method.
- The covered graphene provides conductive networks enhancing the cycling stability.
- The supercapacitor delivers a high areal capacity and excellent mechanical property.

ARTICLE INFO

ABSTRACT

For the development of wearable electronic devices, it is crucial to develop energy storage components combining high-capacity and flexibility. Herein, an all-solid-state supercapacitor is prepared through an in-situ "growth and wrapping" method. The electrode contains polyaniline deposited on a carbon woven fabric and wrapped with a graphene-based envelop. The hybrid electrode exhibits excellent mechanical and electrochemical performance. The optimized few layer graphene wrapping layer provides for a conductive network, which effectively enhances the cycling stability as 88.9% of the starting capacitance is maintained after 5000 charge/discharge cycles. Furthermore, the assembled device delivers a high areal capacity (of 790 F cm^{-2}) at the current density of 1 A cm^{-2}, a high areal energy (28.21 uWh cm^{-2}) at the power densities of 0.12 mW cm^{-2} and shows no significant decrease in the performance with a bending angle of 180°. This unique flexible supercapacitor thus exhibits great potential for wearable electronics.

1. Introduction

The occurrence of wearable electronics will possibly bring a revolution in our lives, allowing for more health and comfort. To meet the requirement of this tendency, it is needed to not only miniaturize of the size of electronic devices, but also to combine them with cloths and accessories (watches, glasses, etc.) [1–3]. The requirements are thus to ensure low-weight, low-cost, deformability, safety (human-friendly) and a good electrochemical performance. Traditional button storage components, such as button supercapacitors and batteries, can hardly satisfy the application needs especially in flexible smart electronics due to their rigidity. Therefore, investigations on wearable energy storage and conversion, such as flexible supercapacitors and batteries, have become a hot topic in recent decades. There are many excellent works aiming at high-performance flexible devices [2,4]. To enable flexibility, flexible substrates must be considered. Herein, the key component, is a

new kind of flexible substrate, carbon woven fabric, which has recently attracted an enormous attention thanks to the properties respect to conventional materials based on a metal mesh, polymers, etc. Furthermore, carbon woven fabric features low-cost, high-conductivity, very high mechanical strength, excellent structural stability and good corrosion resistance. These features allow it to be used as a platform for building flexible supercapacitors with improved properties and functionalities. The active materials were selected to ensure a high capacitance performance of the device. So far, extensive research has been carried out on developing new materials and electrode architectures, mainly based on composites combining several metal oxides [5–7] and conductive polymers [8–10]. However, such inorganic pseudocapacitive materials usually display a poor mechanical performance and human-toxicity. In contrary, conductive polymers, such as polyaniline (PANI) and polypyrrole (PPy) are stable highly flexible and non-toxic, making them suitable for flexible applications. Among conductive

polymers, PANI has been frequently applied in electrochemical devices [11–13], however, its large interface resistance and volume fluctuation during the charge/discharge process leads to a poor electrochemical performance and limited long-term stability, as testified by the sharp decline of the capacitance [14].

To address this problem, many efforts have been focused on improving the cycling life. In-situ electrodeposition of PANI could effectively reduce the problems of interfacial resistance without the need of using a binder. In addition, it was recently found that the combination of PANI with graphene could reduce its volume change upon charging, thus enhancing the cycling property. For instance, Yan et al. incorporated PANI with graphene and carbon nanotubes, and improved the capacitance retention upon 1000 cycles from 56% to 85% [15]. Wang et al. deposited the PANI directly on the graphene surface resulting in a 87% retention after 1000 cycles [16]. Wu et al. prepared a graphene/PANI film via vacuum filtration showing a retention of 79% after 800 cycles [17]. Though the graphene has excellent intrinsic physical properties, its tendency to form aggregates has a negative influence on the device performance; namely, the stacking hinder ions to access to the entire surface and lowers the efficiency versus electrochemical reactions [18,19]. It is believed that suitably covered graphene sheets would benefit for long-term stability without experiencing such dramatic performance decline. In addition, thanks to the high specific area and abundant reaction sites graphene could sensibly improve the performance of electrodes.

Here we report on the development of an electrochemically-deposited PANI layer with a controllable wrapping graphene coating obtained by a facile impregnation method and we explore the electrochemical performance of this hybrid electrode. The highly conductive substrate, carbon woven fabric (CWF), ensures the flexibility and mechanical resistance of the prepared flexible supercapacitor (FSCs). Poly (allylamine hydrochloride) (PAH) which is rich of amine groups is introduced into the reaction system. Due to of strong chemical and electrostatic interaction force, few-layer reduced graphene oxide (rGO) nanosheets effectively envelop polyaniline particles deposited at the CWF surface. Such nanostructure not only act as an ion buffer space due to the mesopores created by the crumpling of graphene, but also limits the volume inflation of active materials. The obtained PANI/rGO composite textile electrode possesses good rate capability as well as excellent cycling performance compared to the bare PANI particles. Furthermore, the assembled FSC exhibits excellent deformation properties, meaning that its electrochemical properties are not influenced under deformation.

2. Experimental section

2.1. Reagents and materials

Aniline (ANI, AR > 99.5%), hydroiodic acid (HI, AR > 47%), and Poly (allylamine hydrochloride) (PAH) were purchased from the Aladdin Industrial Co. (Shanghai, China). Sulphuric acid and ethanol of analytical grade were supplied from Shanghai Chemical Reagent (Shanghai, China). All the reagents were used without further purification. Carbon woven fabric was purchased from Carbon Energy Industrial Co. (Taiwan, China), whose average weight and thickness are estimated to be 0.039 g and 0.26 mm, respectively.

2.2. Electrodeposition of PANI electrodes

The CWF is cut into the size $1 \times .5 \, cm^2$ and washed in a sonic bath in acetone, ethanol and deionized water, successively. A three electrode system is used to deposit PANI particles on the cleaned CWF working electrode with a Pt plate counter electrode and saturated calomel reference electrode (SCE). The electrolyte consists of $1 \, M \, H_2SO_4$ and 0.1 M aniline monomer, the electrodeposition is performed at a constant potential of 0.65 V at room temperature (before the

electrodeposition, the CWF is processed under ultrasonic bath to avoid the formation of bubbles at the interface). After that, a dark green electrode is obtained. The weight of PANI is controlled to be $2.2 \, mg \, cm^{-2}$ reaching the highest areal capacitance, for a higher loading would tend to flake off resulting in poor performance and long cycling instability.

2.3. Preparation of graphene enveloped PANI electrodes

Reduced graphene oxide (rGO) nanosheets are used to envelope the PANI particles electrode: rGO is anchored to the PANI electrode surface by dipping it sequentially into the PAH solution ($1 \, g \, L^{-1}$, for 1 h), then in the GO dispersion (0.5, 1, 3, $5 \, mg \, mL^{-1}$, for 5 h) and in the HI/ethanol solution (volume ratio, 3:1, for 12 h) at room temperature. The resulting five samples with different GO concentrations x ($x = 0$, 0.5, 1, 3, $5 \, mg \, mL^{-1}$, referred to as PANI, PANI-rGO-x) are investigated to derive the optimal conditions.

2.4. Characterizations

Transmission electron microscopy (TEM) images are recorded on a JEOL JEM-2010 microscope operated at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) is conducted on an S-3400N-II microscope. X-ray diffraction (XRD) is performed at a scan rate of $8° \, min^{-1}$ using a D/Max-IV with Cu Kα radiation. Raman spectroscopy is carried on a Jobin Yvon HR 800 micro-Raman spectrometer. Functional groups on the surfaces are identified via Fourier transform infrared spectroscopy (FTIR, Nicolet 6700 by Thermo Scientific). Finally, X-ray photoelectron spectroscopy (XPS; Amicus, Shimadzu, Japan) is performed to evaluate the surface chemical composition.

2.5. Electrochemical measurement

Electrochemical measurements including cyclic voltammetry (CV) curves and galvanostatic charge-discharge tests are conducted using an electrochemical workstation (CHI 660D) at room temperature. Electrochemical impedance spectroscopy (EIS) is recorded in the frequency range between 10000 and 0.01 Hz.

3. Results and discussion

Our approach to develop the flexible PANI@rGO electrode is schematically displayed in Fig. 1. The PANI particles are deposited on the CWF substrate in 20 min, successively, the composite is dipped into the PAH solution, which is easily grafted to the surface of PANI. PAH is a linear cationic polyelectrolyte with primary amine groups on the carbon chain. The hydrophobic long chain will tend to attach to the surface of CWF and PANI, providing to them abundant amine groups [20,21]. The subsequent immersion into GO dispersion lead to the surface covering with GO flakes through a ring-opening reaction occurring between the amine groups and the epoxy groups in the GO sheets [22,23]. In addition, the bonding is promoted by the electrostatic interaction between the positively charged PANI and the negatively charged GO platelets [24–26]. Both interactions resulted in strong connection between the electroactive materials and GO nanosheets, whose structure strengthen stability during charge/discharge processes. The obtained composites are then soaked in the HI/ethanol solution to reduce the GO into graphene [27,28]. In fact, such deposition-impregnation method used to prepare composite electrodes benefits from being simple, relatively low-cost and scaleble.

The successful deposition of PANI on the CWF skeleton is clearly observed on SEM images (Fig. S1). Figure S1a shows that the 3D network architecture of the CWF, which is based on overlapped and entangled carbon fibers. Carbon fibers display a smooth and defect-free surface morphology, providing for a high electron conductivity and