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Remarkably enhanced performances of polyaniline/electrochemically surface-treated graphite electrodes with optimal charge transfer pathways for flexible supercapacitor application



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HIGHLIGHTS

- An electrochemical surface-treated method of GP is developed to obtain EST-GP.
- EST-GP provides optimized charge transfer pathways for PANI films relative to GP.
- PANI/EST-GP electrodes show high specific capacitance and good rate capability.
- A high performance flexible supercapacitor is fabricated by PANI/EST-GP electrodes.

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ABSTRACT

We propose a strategy to enhance the electrochemical performances of electrodes by optimizing charge transfer pathways at the current collector/electroactive material interface. A facile method is developed for electrochemical surface treatment of graphite, and the obtained electrochemical surface-treated graphite is utilized as substrate for electropolymerization of polyaniline, which facilitates the construction of high-quality electrical links at the interface of polyaniline and electrochemical surface-treated graphite. Effect of galvanostatic and potentiostatic polymerization on electrochemical properties of polyaniline electrodes is also examined. Electrochemical measurements indicate that the potentiostatically polymerized polyaniline electrode has superior supercapacitive performances. In particular, polyaniline/electrochemical surface-treated graphite electrode exhibits remarkably enhanced electrochemical properties in comparison with polyaniline/graphite electrode, which can be ascribed to the optimized charge transfer pathways at current collector/electroactive material interface for the former. Polyaniline/electrochemical surface-treated graphite electrochemical surface treated graphite electrochemical surface treated graphite electrochemical surface for the former. Polyaniline/electrochemical surface-treated graphite electrochemical surface treated graphite electrochemical surface-treated grap

1. Introduction

The development and utilization of high-efficiency energy storage devices have become increasingly important due to the challenging energy and environmental issues humankind faces [1,2]. As a kind of electrochemical energy storage device between batteries and traditional dielectric capacitors, supercapacitor has a broad range of applications from portable electronics, medical utilities, uninterrupted power supplies, to electric vehicles, because of its several advantages, including

short charging/discharging time, high power density, and long cycling life [3–5]. In recent years, great progress has been achieved for supercapacitor. However, current research activity is mainly focused on improving its energy density, while maintaining high power density [6–8].

It is well known that a supercapacitor consists of electroactive material, electrolyte, separator, and current collector. Commonly, electroactive materials are considered as the key component that affects the performances of supercapacitor, and they can be classified into two

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types depending on charge storage mechanism. One type is carbon materials used for electric double-layer capacitors, which store energy via reversible ion adsorption at the electrode-electrolyte interface. The other type is transition metal oxides and conducting polymers (CPs), which are utilized for pseudocapacitors and store charge by fast reversible faradic reactions at electrode surface, resulting in markedly enhanced charge storage ability as compared to electric double-layer based carbon materials [9–12].

Among pseudocapacitive electroactive materials, polyaniline (PANI) as one of CPs has attracted considerable attention because of its high pseudocapacitance, easy synthesis, low cost, and environmental stability [13–15]. In previous studies, PANI based electrodes have been prepared by a variety of approaches. These can be classified into chemical and electrochemical routes [16]. In order to prepare a paste, chemically polymerized PANI is usually required to mix evenly with polymer binders and additives, after which the obtained paste is pressed onto a current collector to construct an electrode. This type of fabrication procedure is time-consuming, and the participation of insulating polymeric binder decreases electrical conductivity of PANI. In contrast, electrochemically polymerized PANI is more attractive because it can directly grow on current collectors, which consequently lead to binder-free electrodes. Nevertheless, for either chemically or electrochemically polymerized PANI, high-quality electrical links between PANI active layers and current collectors are desirable in order to enhance supercapacitive properties of the electrodes.

Although current collectors play an important role by transporting electrons from/to electroactive PANI layers in the charging-discharging process, very few studies have been devoted to improving current collectors that can enhance supercapacitive properties of the electrodes. Sumboja et al. [17] prepared indium tin oxide (ITO) nanowire array as current collector via chemical vapor deposition (CVD), onto which PANI was electrodeposited to make PANI/ITO coaxial nanowire electrodes. Cheng et al. [18] fabricated cross-linked N-doped carbon nanofiber (CLCF) by electrospinning and carbonization process. Subsequently, CLCF was used as scaffold/current collector to support PANI and to obtain PANI/CLCF electrode. The above works improve electrochemical properties of PANI electrodes using newly developed current collectors, which facilitate the dispersion of PANI. Unfortunately, the fabrication of such current collectors requires sophisticated experimental setup and harsh conditions, thereby restricting their practical use in supercapacitors.

For traditionally used current collectors such as Pt sheet, stainless steel, carbon cloth, and graphite foil, they exhibit a planar surface and have a limited number of contact spots with active materials. According to contact resistance theory [19,20], small contact spot area inevitably results in a constriction and spreading resistance at the interface as current flow passes through it, thus reducing electrochemical performances of the electrodes. However, if the electrochemical properties of PANI electrodes can be remarkably enhanced by improving the charge transfer between PANI and traditionally used current collectors, such electrodes using conventional current collectors will be very promising for practical use in supercapacitors.

As one kind of conventional current collector, graphite (GP) has been extensively used in supercapacitors due to its commercialization, low price, high conductivity, and mechanical flexibility [21,22]. Therefore, this study is devoted to enhancing the supercapacitive performances of PANI electrodes by improving the charge transfer between PANI and GP current collector. For this purpose, we have developed a facile method of electrochemical surface treatment for GP, which allows construction of high-quality electrical links at the interface of PANI and electrochemical surface-treated GP (EST-GP) current collector. In addition, electrochemical performances of PANI electrodes are also optimized by comparing the galvanostatically and potentiostatically polymerized modes. To demonstrate the feasibility for flexible supercapacitor applications, a supercapacitor device based on PANI/ EST-GP electrodes is fabricated. The device shows a great promise for

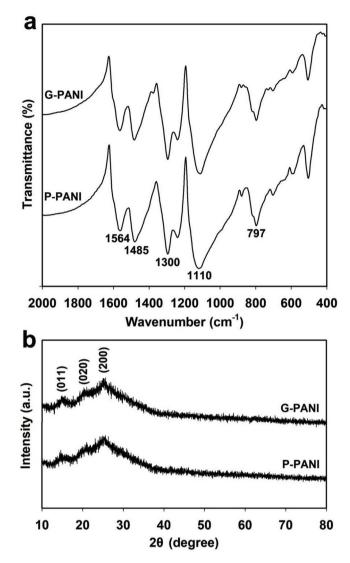


Fig. 1. (a) FT-IR spectra and (b) XRD patterns of G-PANI and P-PANI.

use in flexible electronics because of its high flexibility and superior supercapacitive performances.

2. Experimental

2.1. Electrode preparation and supercapacitor assembly

Electropolymerization of aniline was conducted on GP foils with conductive areas of $1 \times 1 \text{ cm}^2$ in a standard three-electrode cell, which contains a Pt sheet counter electrode and a saturated calomel electrode (SCE) as reference electrode. The aqueous deposition solution consisted of 0.2 M aniline and 0.5 M HCl. Two different electropolymerization modes (galvanostatic *vs.* potentiostatic) were compared. For galvanostatic polymerization, a current density of 1 mA cm^{-2} was performed for 1800 s. For potentiostatic polymerization, a polymerization potential of 0.8 V *vs.* SCE was used. The total charge density passed was set at 1.8 C cm^{-2} , same as galvanostatic mode. Here the galvanostatically and potentiostatically polymerized PANI on GP substrates were labelled as G-PANI/GP and P-PANI/GP electrodes, respectively.

Electrochemical surface treatment of GP was carried out in 1 mM poly (sodium 4-styrenesulfonate) (PSS) aqueous solution with a twoelectrode configuration, in which GP anode was placed in parallel to a Pt sheet cathode. A constant potential of 10 V was applied between them for 40 min to obtain EST-GP, which was further reduced in a Download English Version:

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