Sulfonated polyaniline decorated graphene nanocomposites as supercapacitor electrodes

Bo Song [a], Chia-Chi Tuan [a], Xiaogu Huang [a,b], Liyi Li [a], Kyoung-Sik Moon [a,**], Ching-Ping Wong [a,c,*]

[a] School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, GA 30332, United States
[b] School of Physics and Optoelectronic Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China
[c] Department of Electronic Engineering, The Chinese University of Hong Kong, Shanti, Hong Kong

ARTICLE INFO

ABSTRACT

A sulfonated polyaniline (SPANI)/graphene nanocomposite has been fabricated as the electrode material for supercapacitors. The SPANI nanostructure that was uniformly embedded within the graphene network can effectively facilitate the charge transfer between graphene layers and improve the overall electrochemical performance. The as-synthesized nanocomposite has delivered high specific capacitance up to 262 F/g, excellent rate performance, and cycling stability with over 87% of capacitance retained after 10000 charge/discharge cycles.

© 2015 Published by Elsevier B.V.

1. Introduction

Energy storage and conversion have attracted tremendous attention due to the increasing demand for electronic devices [1,2]. Recently, supercapacitors have been developed as attractive power sources with high charge/discharge rates and long cycle life [3]. Among different supercapacitor materials, graphene has been regarded as a promising candidate with superior electrical conductivity, high mechanical strength and large surface area[4,5]. However, graphene materials produced via chemical reduction of graphene oxide (GO), hydrothermally treated GO, and activation of carbon precursors, have delivered limited charge storage capability compared to the theoretical capacitance of 550 F/g for pristine grapheme [6–8]. Therefore, graphene has been decorated with other electrochemically active materials to form hybrid nanostructures [9]. Particularly, polyaniline (PANI), with high intrinsic pseudocapacitance, has been incorporated within porous graphene network to enhance the overall capacitance of the composite materials [10–12]. The unique mechanical strength and flexibility of graphene sheets serves as a robust support to anchor PANI chains or particles, thus improving the structural stability

and charge transfer behavior of the conducting polymer [13].

Herein, we report a water-dispersible sulfonated polyaniline (SPANI) decorated reduced graphene oxide (rGO) nanocomposite as a high capacitive electrode material. With high water solubility, SPANI can be well dispersed with aqueous GO solution and achieve uniform coatings within rGO sheets after reduction. Furthermore, SPANI embedded within graphene can also enlarge the graphene interlayer spacing and contribute to the pseudocapacitive charge storage. The as-prepared rGO/SPANI composite with optimized SPANI loading exhibits a high specific capacitance of 262 F/g with unique rate performance and electrochemical stability.

2. Experimental

The detailed materials preparation and characterizations are available in ESI.
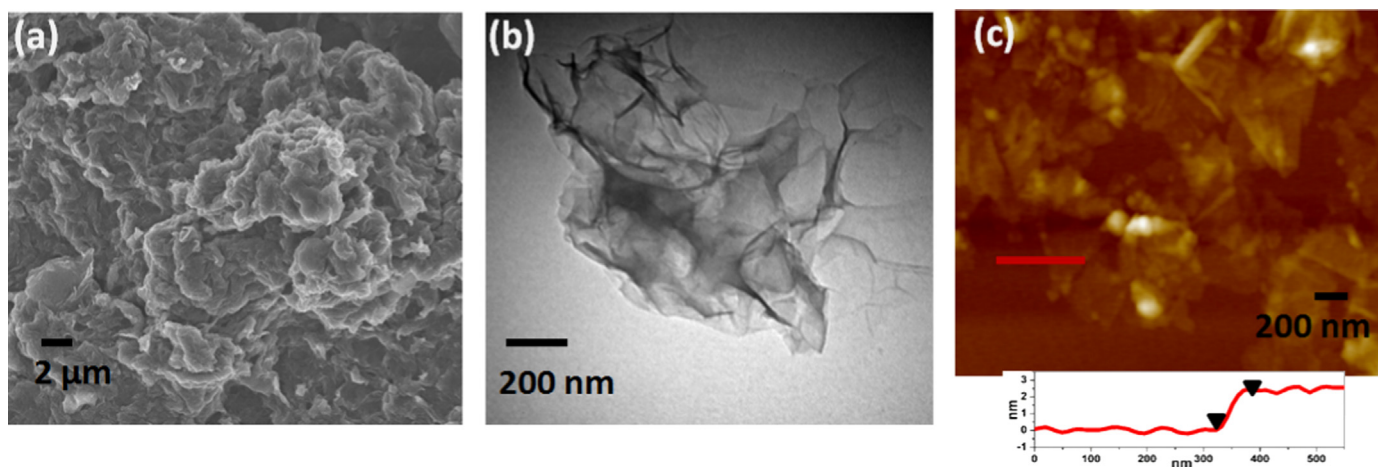
3. Results and discussion

The SEM image of the rGO/SPANI composite is shown in Fig. 1 (a), which shows a typical layer-by-layer stacking graphene structure with wrinkled surface texture. As shown in Fig. 1(b), the darker areas show the uniform coating of SPANI on graphene sheets under the electron beam of TEM, while the brighter region

Fig. 1. (a) SEM and (b) TEM images of the rGO/SPANI composite; (c) AFM image of few-layer rGO/SPANI coated on Si substrate with the height profile.

indicates the good exfoliation of graphene flakes upon SPANI modification. As a reference, the AFM image of rGO control sample is shown in Fig. S1(a), which presents a sheets-like morphology with an average layer thickness around 0. 65 nm. Upon SPANI decoration (Fig. 1(c)), the surface roughness greatly increases and some particle-shaped spots are observed, which can be attributed to the SPANI nanostructure embedded between graphene na-nosheets or adsorbed on graphene surface. Based on the height profile, the rGO/SPANI sheets has an average depth around 2.4 nm (1–3 layers). This graphene/SPANI interconnected network can be stabilized through the π–π interactions between aromatic rings of SPANI and conjugated graphene basal planes. The aqueous-dis-persible nature of the SPANI can further enable the uniform dis-tribution of polymer within rGO sheets.

Fig. 2(a) shows the thermogravimetric analysis (TGA) and de-rivative TG (DTG) curves of all the materials upon heating in air. It can be seen that rGO is relatively stable at low temperatures and the complete decomposition of the graphene occurs above 500 °C. However, the as-synthesized SPANI is thermally unstable, which exhibits initial weight loss at ∼100 °C due to the adsorbed water, sharp weight change between 200–350 °C due to the oxidative degradation of the polymer chain, and thorough structural de-composition above 400 °C [14]. Upon functionalization, SPANI wrapped by graphene sheets displays higher thermal stability with increased onset temperature from ∼200 °C to ∼280 °C for the oxidative decomposition. X-ray photoelectron spectroscopy (XPS) spectrum of the rGO/SPANI is presented in Fig. 2(b) to gain further insight into the elemental composition and chemical bonding. The amount of N was found to be ∼5.7%, which gives an estimated

∼42% mass loadings of SPANI nanostructure in the overall com-posite. The inset of C1s peak deconvolution indicates that there are 76.7% C=C (284.5 eV), 15.9% C=N and C–O (286.0 eV), and 7.4% C–N and C=O (287.4 eV). The large quantity of sp^2 hybridized carbon and the emeraldine form of SPANI ensures the high electrical conductivity of the composite (∼800 S/m) and the efficient charge transfer across the SPANI decorated graphene layers. The trace of S 2p peak (∼1.7%) also confirms the presence of sulfonate groups on polymer backbone and gives an approximately 30% degree of functionalization. As shown in Fig. 2(c), the S 2p spectra can be split into two spin-orbit components, S2p$_{3/2}$ and S2p$_{1/2}$, at binding energies of 167.8 and 168.8 eV respectively, which can be assigned to sulfur elements in sulfonate groups [15].

The electrochemical performance of the rGO/SPANI film was measured by a symmetric two-electrode configuration. The CV curves with scan rates ranging from 2 mV/s to 50 mV/s in 1 M H_2SO_4 electrolyte are shown in Fig. 3(a). The near rectangular-shaped CV profiles imply good charge propagation through the electrical double layer at the electrode/electrolyte. A pair of redox peaks are observed at ∼0.45 V and ∼0.35 V, which indicates the reversible Faradaic transitions between iminoquinine and amino-benzene forms of SPANI in acidic conditions. As presented in Fig. 3 (b), the specific capacitance values at different scan rates are de-termined to be 208 F/g at 50 mV/s, 242 F/g at 10 mV/s, and 262 F/g at 2 mV/s, which gives a significant increase in contrast to rGO (Fig. S2). The SPANI decorated rGO also shows comparable capa-citive performance with other PANI/graphene composite in lit-erature[14,16,17]. The loadings of the SPANI in the final composite varied with different initial precursor ratios. At the initial weight
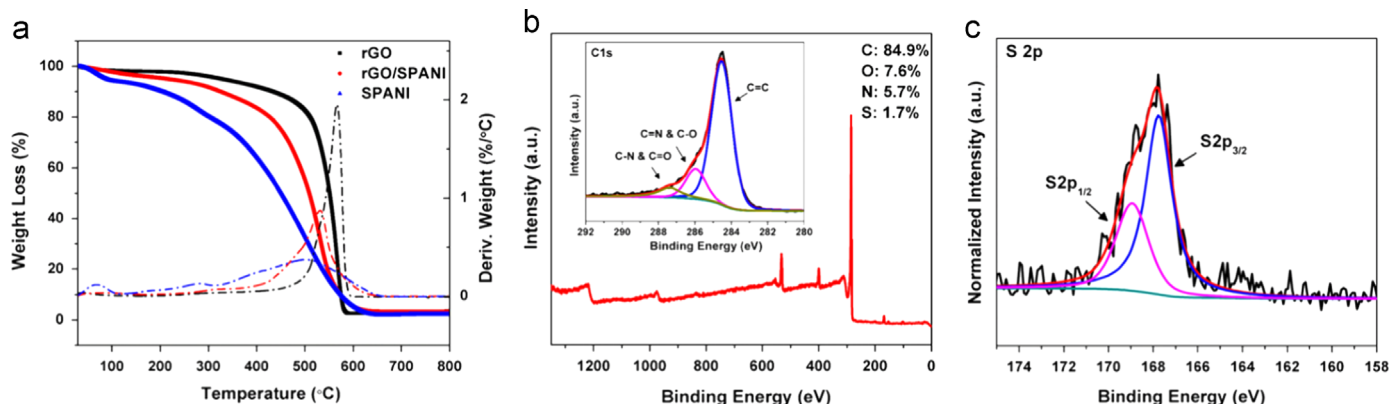
Fig.2. (a) TGA and DTG curves of the rGO, rGO/SPANI and SPANI at heating rate of 10 °C/min in air; (b) XPS survey spectrum with deconvoluated C1s spectrum in the inset and (c) S2p spectrum of the rGO/SPANI composite.