

Preparation of graphene nanoscroll / polyaniline composites and their use in high performance supercapacitors

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Abstract: The graphene nanoscroll is a kind of tubular graphene with an open end and a helical nanostructure. Different amounts of polyaniline were formed on the surface of the nanoscroll by the in-situ polymerization of aniline. SEM observation shows that the polyaniline nanoparticles are evenly distributed on the nanoscrolls and the number of free polyaniline clusters increases with the amount of monomer used. The electrochemical performance of three composites with different polyaniline/graphene nanoscroll ratios was evaluated. The best specific capacitance of the composites reaches 320 F/g at 1 A/g and a 92.1% retention capacitance rate is obtained at 100 A/g, indicating that the composite has a rate performance as good as graphene nanoscrolls and a higher specific capacitance.

Key Words: Graphene nanoscrolls; Polyaniline; Supercapacitors

1 Introduction

Graphene nanoscrolls (GNSs) are new topological structures of graphene materials with the unique one-dimensional tubular morphology and open inner cavity^[1–5]. The specialty of the structure provides GNSs with a good ion-transfer capability and high electrochemical performances^[5–9]. Electric double-layer capacitances (EDLC) of GNS-based supercapacitors are usually limited in the range of 100–200 F/g due to the intrinsic nature of carbon. Incorporating materials that have *pseudo*-capacitances like metal oxide and conducting polymer is an efficient way to improve specific capacitance of carbon-based supercapacitors. Attempts that combining metal oxide such as MnO₂ and Co₃O₄ have already been made^[8,10]. Mai's group reported the nanowire templated semi-hollow bicontinuous GNSs and the MnO₂ templated GNSs exhibited 317 F/g at 1 A/g^[10]. Unfortunately, the electrochemical performance of other aspects was not satisfying and conducting polymer hybrid GNSs have never been reported. Moreover, the rate capability of GNS-based composite materials has scarcely been reported^[9].

Polyaniline (PANI) is a famous conducting polymer that has been extensively studied and used in electrochemical devices. The facile synthesis, good environmental stability, electroactivity, simple doping/dedoping chemistry and light weight make PANI an ideal material for energy conversion/storage applications^[11–14]. In this paper, we report a novel method for preparing

PANI coated GNS (PANI@GNS) by *in-situ* polymerization. Mat-like PANI@GNSs was produced via filtration of the mixture. By adjusting the feed ratios, three kinds of PANI@GNSs were obtained. The electrochemical performance of GNS and PANI@GNSs samples were systematically tested and compared. The synergistic effect of PANI and GNS endows PANI@GNS2 much higher specific capacitance (320 F/g at 1 A/g) and excellent rate capability (92.1% retention rate at 100 A/g). This method can be applied to other conducting polymers to improve the performance of GNS-modified conducting polymers for use in high performance supercapacitors.

2 Experimental

2.1 Materials

Giant graphene oxide (GGO, Average sheet size: ~71 μm; Thickness: 0.8–1.0 nm; Dispersion ratio: 0.45) was purchased from C6G6 (www.c6g6.com). 85% N₂H₄·H₂O solution, ethanol, ammonium persulfate, sulfuric acid and perchloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. Aniline (>98%) was purchased from Shanghai Wulian Chemicals and used as received.

2.2 Preparation of GNSs

N₂H₄·H₂O solution was added dropwise into GGO dispersions (0.2 mg/mL) and the weight ratio of 85% N₂H₄·H₂O solution to GGO was about 15:1. After 5 min

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magnetic stirring, the above GGO dispersions were transformed into chemical reduced graphene (CRG) at 60 °C for 30 min with stirring in an oil bath. CRG dispersions were sprayed into liquid nitrogen bath and freeze dried in a lyophilizer with an optimized temperature profile. The as received samples were kept in a sealed container with N_2H_4 at 90 °C for 12 h to obtain GNSs.

2.3 Preparation of PANI@GNS

Different amounts of aniline were dissolved in 10 mL ethanol/ H_2O mixed solutions and added to GNS/ethanol suspension (10 mg GNS was immersed in 3 mL ethanol), resulting in GNS/aniline mixture solutions. After magnetic stirring for 1 h at room temperature, the solutions were transferred to ice-water bath. Ammonium persulfate was dissolved in 1 M perchloric acid and added dropwise to the GNS/aniline mixture solutions (mass ratio of aniline to ammonium persulfate is 1:1.5). The polymerization lasts for 18 h at -10 °C. The PANI@GNS samples were separated from the suspensions by vacuum filtration and repeatedly washed by 1 M perchloric acid to get rid of excess monomers. 1 M H_2SO_4 was used to displace the perchloric acid for the following electrochemical tests. According to the mass ratios of GNS/aniline (1:1.8, 1:3.6 and 1:7.7), PANI@GNSs samples were named as PANI@GNS1, PANI@GNS2 and PANI@GNS3, respectively.

2.4 Assembly of supercapacitor

Two pieces of testing samples were sealed into a detachable stainless steel cell (custom-made from Institute of Physics, CAS) as two electrodes with a mixed cellulose acetate ester membrane as a separator (Yaxing Purification Materials Factory, $\Phi=0.45\ \mu m$) and 1 M H_2SO_4 as an electrolyte.

2.5 Characterization

SEM images were taken on a Hitachi S4800 field-emission SEM system. TGA was conducted on a PerkinElmer Prisma 1 system in nitrogen flow at a heating rate of 10 °C/min. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements were performed using an electrochemical workstation (CHI 660e, CH Instruments, Inc.). All electrochemical tests of supercapacitors are based on two-electrode system.

3 Results and discussion

The composition and structure of GNS and PANI@GNSs were studied by thermogravimetric analysis (TGA) as shown in Fig. 1. The peaks of GNS are attributed to the removal of absorbed water (~200 °C), removal of residual oxygenate groups (~350 °C) and further carbon sketch loss (~600 °C) [15, 16]. The total weight loss of GNS at

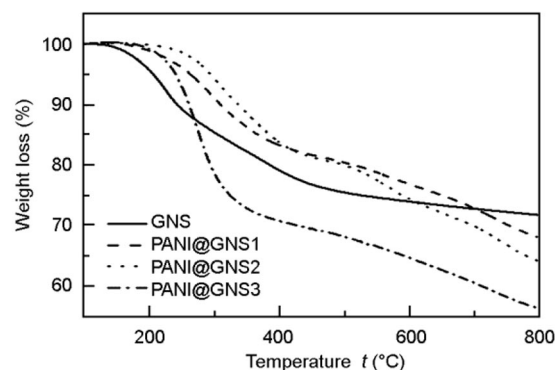


Fig. 1 TGA curves of GNS and different PANI@GNS samples.

800 °C is 28%. For PANI@GNS samples, the peaks at around 300-350 °C attributed to the removal of residual oxygenate groups. The stages at around 500 °C correspond to the carbonization of PANI. The final peaks at 600 °C indicate the subsequent loss of carbon sketches. With the increase of monomer amount, the final weight losses of PANI@GNS1 to PANI@GNS3 are 32%, 36% and 44%, respectively.

Fig. 2a is the characteristic morphology of GNS without compression. The length of one GNS is tens of micron and the diameter is about 100-500 nm. There are many entanglements and junctions between GNSs, which result in the aerogel at macro scale. Due to the weak interactions, compression and solvent infiltration will lead to the transformation from 3D aerogel to 2D film. The 1D GNS can be clearly observed on the surface of the film (Fig. 2b), which is like a GNS mat. At the break cross-section, GNSs were pulled out from the film (Fig. 2c).

After polymerization, the surface of PANI@GNS1 film (Fig. 2d) shows the similar mat-like morphology as GNS film. As a matter of long time stirring, reaction and filtration, GNSs are swollen in solvents and a small part of scrolls is unfold to sheet morphology, which is inevitable. The nano-cones of PANI are evenly distributed on the surface of GNSs as observed in a high magnification. PANI nanoparticles are successfully grown onto GNSs (Fig. 2e-f).

With the increase of monomer amounts, PANI clusters are gradually formed. As shown in Fig. 3, although PANI distributes uniformly on GNSs, PANI clusters exist in both PANI@GNS2 and PANI@GNS3.

The capacitive performance of symmetric supercapacitors composed of GNSs and PANI@GNSs were evaluated by using cycle voltammetry (CV) and galvanostatic charge/discharge tests. Fig. 4a shows the CV curves of GNSs and PANI@GNS samples at a scan rate of 10 mV/s. The curve of GNSs is rectangular shape, showing the EDLC property. The integral areas of PANI@GNSs are all larger than that of GNSs due to the contribution of *pseudo*-capacitance. The two pairs of redox peaks are attributed to the redox of PANI, corresponding to the leucoemeraldine/emeraldine and emeraldine/pernigraniline

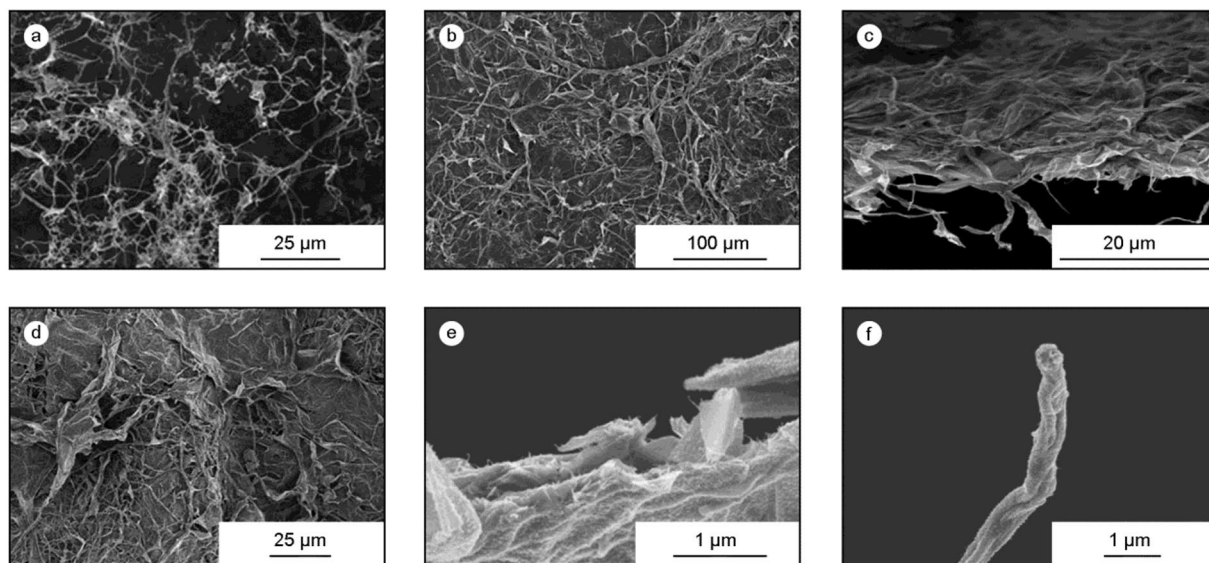


Fig. 2 Morphologies of (a) GNS foam, (b) surface of GNS film and (c) cross-section of GNS film; (d) surface morphology of PANI@GNS1 film, (e) cross-section of PANI@GNS1 and single fiber of PANI@GNS1 pulled from PANI@GNS1 film.

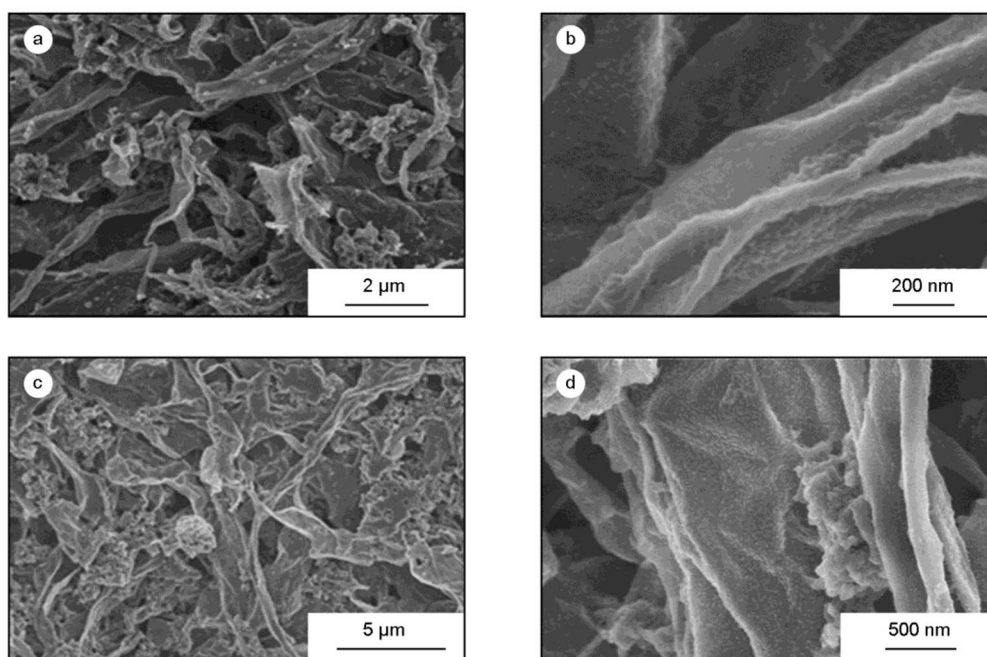


Fig. 3 Morphologies of (a, b) PANI@GNS2 and (c, d) PANI@GNS3.

structural conversions. The specific capacitances of GNSs, PANI@GNS1, PANI@GNS2 and PANI@GNS3 are 91, 301, 347, 352 F/g, respectively.

Fig. 4b demonstrates the galvanostatic charge/discharge curves of the supercapacitors tested at a current density of 1 A/g. GNSs exhibit a triangular-shape curve, implying EDLC is the main contribution to capacitance. The discharging curve of PANI@GNSs show two voltage ranges. The range of 0.8–0.45 V relates to the EDLC and the range of 0.45–0 V is ascribed to a combination of EDLC and faradic capacitance of PANI. The specific capacitances of GNSs,

PANI@GNS1, PANI@GNS2 and PANI@GNS3 are 87, 253, 320, 326 F/g, respectively.

According to the tests, electrochemical performance of PANI@GNSs is all superior to that of pure GNSs. Moreover, the specific capacitance increase with the monomer amounts. Nevertheless, the rate capabilities of GNSs and PANI@GNSs show different tendencies. As mentioned by our former report, GNSs have a good rate capability as a matter of the special 1D spiral open structure. GNSs have reversible swelling behavior in solvents and electrolytes, which is beneficial to the fast transformation of ions. From

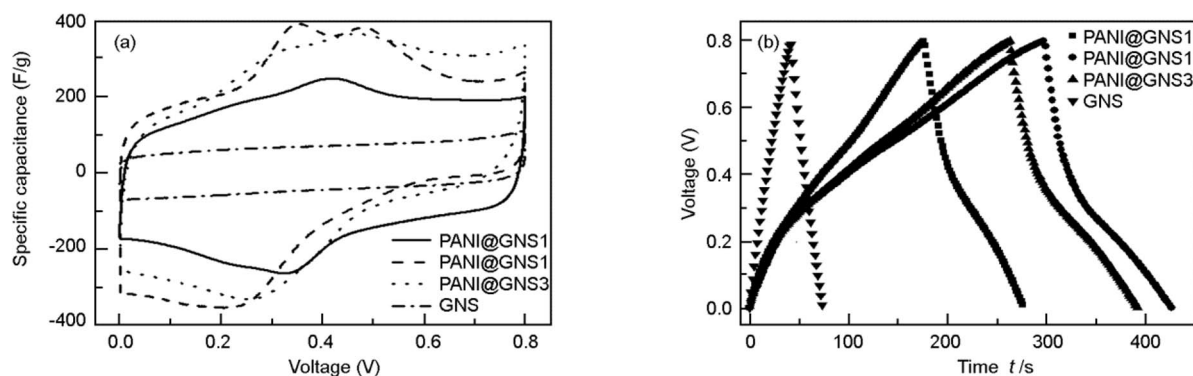


Fig. 4 (a) CV curves of GNS and PANI@GNS samples at 10 mV/s and (b) galvanostatic charge/discharge curves of GNS and PANI@GNS samples at 1 A/g.

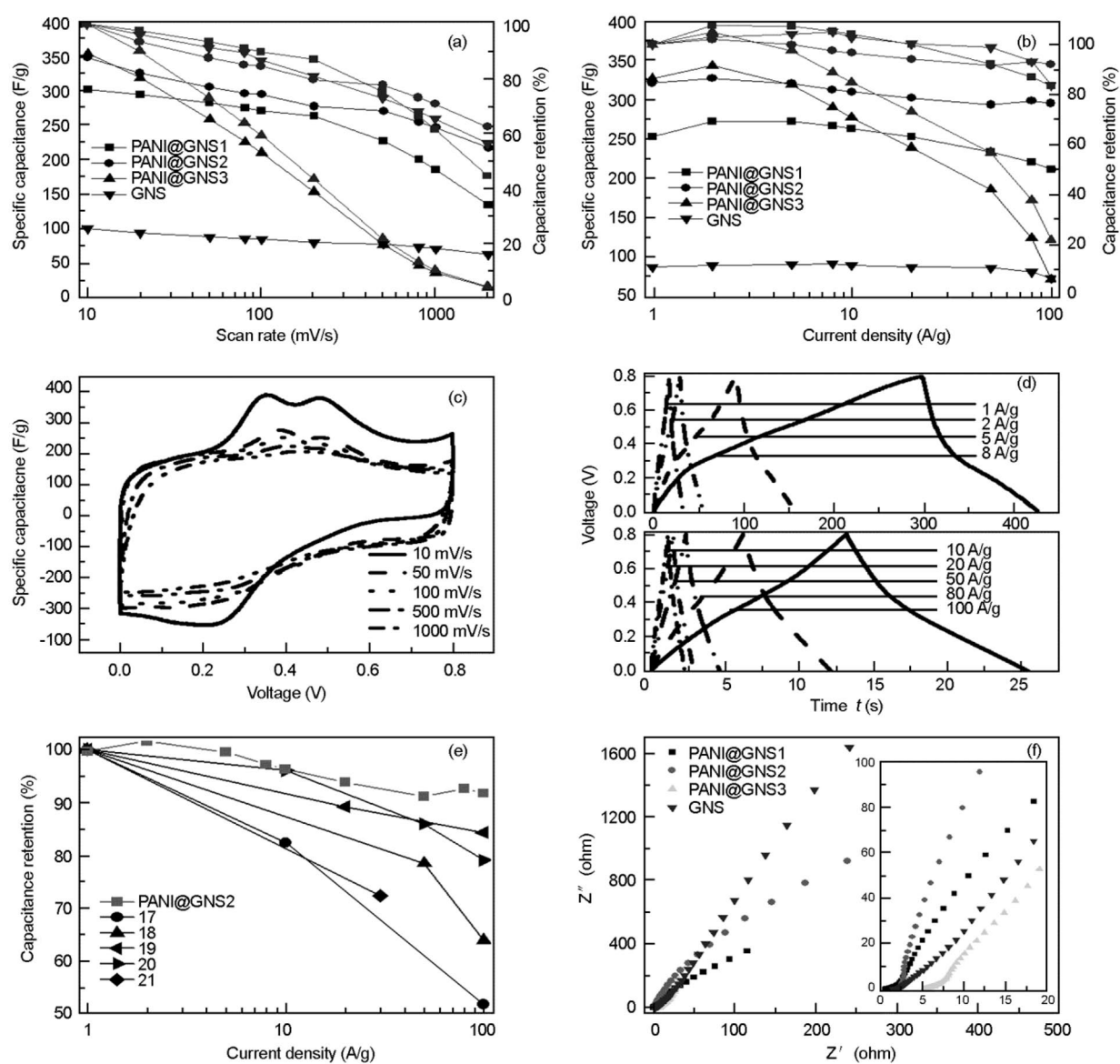


Fig. 5 Electrochemical performance comparisons of GNS and PANI@GNSs tested by (a) CV method and (b) galvanostatic charge/discharge method; (c) CV curves of PANI@GNS2 at different scan rates; (d) galvanostatic charge/discharge curves of PANI@GNS2 at different current densities; (e) Comparisons of PANI@GNS2 with data obtained from other literatures; (f) electrochemical impedance spectroscopy comparisons of GNS and PANI@GNSs.

10 mV/s to 2000 mV/s, GNSs show a 56% capacitance retention rate (Fig. 5a). And a 84% retention rate is observed by galvanostatic charge/discharge from 1 to 100 A/g (Fig. 5b) for PANI@GNSs. After the decoration of PANI, the flexibility and interaction of graphene sheets are changed. PANI@GNS1 and PANI@GNS2 inherit the good rate property of GNSs, showing similar capacitance retention rates with GNSs in both CV and galvanostatic charge/discharge tests (Fig. 5a and a). However, a further increase of PANI in PANI@GNS3 hinders the ion transporting routes and deteriorates the rate capability.

Normalized performances in CV tests of PANI@GNS2 are shown in Fig. 5c. From 10 mV/s to 1000 mV/s, the redox peaks become weak due to the hysteresis of redox reaction of PANI. However, the deterioration of integral area is little. Same tendencies are also observed in galvanostatic charge/discharge test (Fig. 5d). The excellent rate capability of PANI@GNS2 is also superior to that of other literature (Fig. 5e)^[17–21].

Electrochemical impedance spectroscopy was conducted from 0.01 Hz to 100 kHz and the Nyquist plots of all samples are shown in Fig. 5f. The Nyquist plot of GNSs is more vertical to the x axis than others, implying the ideal EDLC behavior. Compared with PANI@GNS1 and PANI@GNS2, the excess PANI in PANI@GNS3 hinders the effective entanglements of GNS, which lowers its electrical conductivity and leads to an increased equivalent series resistance. At the high frequency range, the semi-circle of PANI@GNS2 is smaller than others, proving the small charge-transport resistance.

4 Conclusions

Polyaniline has been successfully grown onto GNSs by *in-situ* polymerization. The nano-cone like PANI is evenly distributed on the surface of GNSs and the as-prepared PANI@GNS films seem like mats constructed by interconnected scrolls. PANI@GNS2 inherits the excellent rate capability of GNSs (92.1% retention rate from 1 A/g to 100 A/g) and has an obvious elevated specific capacitance (320 F/g at 1 A/g) compared with GNSs. This method can be applied to other conducting polymers and paves the way of high performance GNS-modified conducting polymer supercapacitors.

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