All-carbon composite paper as a flexible conducting substrate for the direct growth of polyaniline particles and its applications in supercapacitors

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Polyaniline (PANI) has been recognized as an ideal candidate for electrode materials in supercapacitors. However, its relatively low electrical conductivity and poor cyclic stability greatly limit its potential applications in supercapacitors. In this study, nano-sized PANI particles have been immobilized onto a conducting paper-like substrate which utilizes graphene (G) sheets and pristine carbon nanotubes (CNTs) as building blocks, thus obtaining flexible G–CNT–PANI ternary hybrid papers with hierarchical nanostructures. The ternary hybrid paper exhibits a reversible capacity of up to 432 F g⁻¹ at a discharge rate of 0.5 A g⁻¹, which is much larger than that of bare G–CNT composite paper (172.4 F g⁻¹); and, its cyclic performance is dramatically enhanced sustaining greater than 96% of its original capacitance after 600 charge–discharge cycles. The dimensional confinement of PANI particles on the surface of the all-carbon planar substrate prohibits volume expansion and shrinkage upon electrolyte soakage, and meanwhile, the immobilized PANI particles can endow the all-carbon composite paper with pseudocapacitive behavior and an improved electrode–electrolyte interfacial structure. Besides, the good electrical conductivity of the G–CNT composite paper provides improved conductive pathways for charge transfer at the electrodes thus resulting in superior capacitance during charge–discharge processes. Therefore, the method reported here provides a simple and efficient approach to fabricating G–CNT–PANI ternary hybrid papers with designed hierarchical nanostructures, and may be easily extended to the design of next generation high performance flexible supercapacitors.

Introduction

Flexible papers, which utilize graphene (G) sheets as building blocks in vacuum-assisted self-assembly, have already been developed as binder-free flexible electrodes for supercapacitors due to their excellent mechanical flexibilities and electrical conductivities. ¹–⁶ Nevertheless, in most cases, the large specific surface area of the closely-packed and oriented G sheets throughout the G papers is inevitably lost which significantly reduces their potential application as supercapacitor electrodes. ⁷–¹² Thus, it is still a great challenge to develop a feasible and effective way to fabricate G-based hybrid papers as flexible electrodes with relatively high capacitances and without the sacrifice of their good cyclic stabilities. ¹³–¹⁴

At the present time, two kinds of electroactive materials have been developed, based on two different energy storage mechanisms for supercapacitors. ¹⁵,¹⁶ One is electric double layer (EDL) capacitance in which energy storage is achieved by utilizing EDLs formed at the interface between the electrode and electrolyte. Generally, carbon materials with high surface area and good electrical conductivity show excellent EDL capacitance. ¹⁴ Unfortunately, the relatively low capacitance achieved precludes their practical application. ¹⁸ The other mechanism is pseudocapacitance, also called redox supercapacitance, which is based on fast and reversible reduction–oxidation reactions in electroactive materials. A pseudocapacitor normally shows a much larger capacitance than an EDL capacitor; however, it also exhibits poor cyclic stability over long periods of charge–discharge processing. ¹⁹ Polyaniline (PANI), is one of the most promising electrode materials for pseudocapacitors, possessing high capacitance, low cost, ease of synthesis and environmental friendliness. ¹⁵,¹⁶,¹⁷–¹⁹ However, PANI normally exhibits mechanical shrinkage during long charge–discharge cycling periods and relatively low electrical conductivity, which greatly limits its further application as an electrode material for supercapacitors. ²⁰,²¹ Therefore, in order to achieve a higher energy density while maintaining a good cyclic stability, more efficient methods for preparing hybrid electrode materials that possess both EDL capacitance and pseudocapacitance should be developed for the fabrication of high-performance supercapacitors.

To date, much attention has been devoted to the preparation of supercapacitor electrodes by combining PANI with carbon
nanomaterials. Coupling carbon-based nanomaterials with PANI, such as in G–PANI,11 porous carbon–PANI12 and carbon nanotube (CNT)–PANI hybrids,22 has been considered to be an effective approach to combine their respective advantages. Among these, it should be noted that the record capacitance value of carbon–PANI supercapacitors is 1270 F g\(^{-1}\) even at a large current density, which is achieved by the potentiostatic deposition of aniline on a hierarchically porous carbon monolith.22 In addition, flexible electrodes for supercapacitors based on PANI and carbon nanomaterials have been intensely studied, which greatly expands the potential uses of carbon–PANI supercapacitors. Wei et al. reported a one-step template-free approach for synthesizing large arrays of vertically aligned PANI nanowires on various conducting substrates, and the highest specific capacitance of the PANI nanowire arrays was measured to be 950 F g\(^{-1}\) and remained as high as 780 F g\(^{-1}\) at a large charge–discharge current density (40 A g\(^{-1}\)).24 Li et al. prepared G–PANI hybrid films via the chemical oxidative polymerization of aniline within G hydrogels with laterally oriented microstructures, which show excellent rate and cycling stabilities combined with a good capacitance of 530 F g\(^{-1}\) at a current density of 10 A g\(^{-1}\).25

In this study we report a new strategy for the synthesis of PANI nanostructures on a flexible G–CNT composite paper substrate, which can be directly used as flexible electrodes possessing both EDL capacitance and pseudocapacitance. This method has at least three advantages over traditional methods reported in the literature: (1) compared with bare G paper, G–CNT composite papers exhibit much improved electrical conductivities and interconnected networks of all-carbon structures, which are promising as flexible substrates for hybridization with PANI; (2) this study develops a simple and efficient method for preparing flexible hybrid electrode materials with unique hierarchical nanostructures possessing both EDL capacitance and pseudocapacitance; (3) the immobilization of PANI particles on the all-carbon paper substrate limits the volume expansion and shrinkage upon electrolyte soaking; and meanwhile, the PANI particles on the paper surface can endow the all-carbon composite papers with pseudocapacitive behavior and an improved electrode–electrolyte interfacial structure.

**Experimental section**

**Materials and methods**

Multi-walled carbon nanotubes (CNTs, an outer diameter of 10–20 nm) were supplied by Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, China. Graphite oxide was prepared according to a modified Hummers method.26–28 Aniline, ammonium persulfate (APS), and hydroiodic acid (HI, 55 wt% in aqueous solution) were purchased from Alading Reagent Co., Shanghai, China. All the other reagents were supplied by Sinopharm Chemical Reagent Co. Ltd and used as received.

**Preparation of homogeneous dispersions of graphene oxide–CNT (GO–CNT) composites**

Graphite oxide powder was suspended in water by sonication for 1 h at a power of 135 W, thus giving a homogeneous dispersion of graphene oxide (GO) (2.0 mg mL\(^{-1}\)). The above suspension was directly used to disperse CNTs throughout the experiments. Typically, a designed quantity of CNTs was added into the suspension of GO. After being sonicated for 1 h at a power of 145 W, the mixed suspension was centrifuged at 4000 rpm for 10 min to remove insoluble CNTs, thus giving a homogeneous suspension of GO–CNT composites with weight ratios of 6/1, 4/1, 2/1, and 1/1, respectively.

**Preparation and chemical reduction of GO paper and GO–CNT composite papers**

Designed volumes of suspensions containing GO–CNT composites were vacuum filtered through a nylon-6 filter membrane (pore size: 220 nm, Shanghai Xinya Purification Material Factory). The weight ratios of GO to CNTs were varied while the total weight was kept constant at 20 mg. After filtration, the pre-dried paper sample on the filter membrane was wetted with ethanol, and then carefully peeled away from the filter membrane. For comparison, neat GO paper was also fabricated using the same method. The chemical reduction of the GO paper and GO–CNT composite papers was realized as follows: the paper samples were soaked in a HI solution at 100 °C for 2 h, washed with DI water and ethanol, respectively, and then dried at 40 °C overnight, thus obtaining G paper and G–CNT composite papers for subsequent use.

**Immobilization of PANI particles on G paper and G–CNT composite papers**

Hierarchical G–CNT–PANI ternary hybrid papers were synthesized by in situ polymerization of aniline monomer in the presence of G–CNT composite paper. Typically, a designed amount of aniline and APS (molar ratio: 4/1) was added into 1 M \(\text{H}_2\text{SO}_4\) solution. Then the G–CNT composite paper was immersed into the above solution, and allowed to react at 0 °C for 6 h without stirring. The as-obtained G–CNT–PANI ternary hybrid papers were then washed with water, and dried at room temperature. For comparison, PANI particles were immobilized on the G paper using the same method.

**Characterization**

Atomic force microscopy (AFM) images were taken in tapping mode with a Scanning Probe Microscope (SPM) Nanoscope IV from Digital Instruments. Transmission electron microscopy (TEM) images were recorded on a Philips CM300 FEG TEM instrument operated under an acceleration voltage of 120 kV. A scanning electron microscope (SEM, VEGA TS 5136MM) was used to observe the top view morphology of the paper samples. A field-emission scanning electron microscope (FESEM, JEOL JSM-6700F) was used to observe the morphology of the fracture surface of the paper samples. The samples were coated with gold prior to FESEM observation. Raman spectra were measured using a LabRam-1B French Dilor Com (ex = 632.8 nm).
Electrochemical measurements

All the electrochemical properties were tested by cyclic voltammetry (CV) and galvanostatic charge–discharge measurements using a CHI 660D electrochemical workstation (Shanghai Chenhua Equipments, China). The electrochemical measurements were performed under three-electrode and two-electrode systems at room temperature. Before testing, the paper electrodes were soaked in the electrolytes overnight. For the three-electrode supercapacitor system, as shown in Fig. 1a, the as-made paper sample connected to a Pt wire were used as the working electrode. Pt foil (1 cm²) and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively, and 1 M H₂SO₄ aqueous solution was used as the electrolyte. For the two-electrode supercapacitor system, as shown in Fig. 1b, pieces of the paper sample with the same weight were used for both electrodes, and were separated by a filter paper soaked with electrolyte (1 M H₂SO₄). Two Pt wires were used as the current collectors. All of the components were assembled into a sandwiched structure between two pieces of flexible plastic sheet under a pressure of 10 MPa.

Results and discussion

Using the same procedures as in our previous studies on assisted dispersion of CNTs using GO sheets as versatile dispersants in aqueous media, we prepared homogeneous aqueous dispersions of GO–CNT composites with varied weight ratios. The aqueous dispersion of GO–CNT composites with different weight ratios was assessed by sedimentation experiments, as shown in Fig. 2. Due to the hydrophilic oxygen groups attached to the GO basal plane and edges, GO can easily form a dark brown aqueous colloidal suspension under sonication (Fig. 2a). From the AFM image and the corresponding height profile (Fig. 3), it can be seen that the thickness of the GO sheets ranges from 0.9 to 1.1 nm, indicating that large amounts of oxygen-containing groups are introduced onto the GO sheets during the Hummers oxidation process. Owing to strong van der Waals interactions and high conformational rigidity, the pristine CNTs show a very limited solubility (Fig. 2f). We then carried out experiments utilizing GO sheets as dispersants to stabilize the pristine CNTs in water. The proportions of GO to pristine CNTs were adjusted by producing GO sheet dispersions with a concentration of 2.0 mg mL⁻¹ and controlling the added amount of pristine CNTs. It was found that a stable black dispersion can be obtained when the weight ratio of GO to CNTs is larger than 2 (Fig. 2b–d). Adding a larger amount of pristine CNTs to the GO suspension will cause the co-precipitation of GO and CNTs (Fig. 2e). The formation of GO–CNT composites can be strongly supported by morphological observations. As shown in Fig. 4, hair-like CNTs were randomly adsorbed on the smooth surface of the GO sheets, and no individual GO sheets or CNTs were found in the view. This phenomenon clearly indicates strong interactions between the two kinds of nano-elements during the formation of GO–CNT composites.

Various techniques have been used to fabricate paper-like materials with lightweight, robust mechanical properties by utilizing two-dimensional nanosheets (e.g. G sheets, clay nanolamellates) as building blocks. Herein, the uniform dispersion of GO–CNT composites in water is beneficial to the subsequent filtration process, allowing GO–CNT composite papers with CNT-imbedded parallel GO frameworks to be fabricated and peeled away from the filter membrane for subsequent use. GO paper was also fabricated using the same method. To further increase the electrical conductivities of the GO paper and the GO–CNT composite papers, chemical reduction was carried out by soaking these free-standing papers in a HI solution. As shown in Fig. 5, the GO paper and GO–CNT composite papers are bendable and highly flexible before and after chemical reduction. After reduction, the G paper and G–CNT composite papers exhibit a shiny metallic luster. The electrical properties of these paper samples were investigated...
before and after chemical reduction, and the results are summarized in Table 1. The removal of large amounts of oxygen-containing groups and the further graphitization of these all-carbon composites during the chemical reduction step results in a remarkable enhancement of the electrical conductivities. The G–CNT (2/1) composite paper, possessing an electrical conductivity of 182 S m\(^{-1}\), can be considered to be an ideal candidate for a flexible conducting substrate. The superior conductivities of the G–CNT composites over the single component G or CNTs can be attributed to the removal of oxygen-containing groups and the further graphitization of these all-carbon composites during the chemical reduction step.

As we narrow down the study to the issue of fabricating flexible G-based hybrid papers decorated with PANI particles, we find that it is possible to achieve homogeneously distributed PANI particles adhered to the surface of neat G paper and G–CNT composite paper substrates \textit{via in situ} polymerization.\(^{37,38}\) The morphologies of the PANI particles grown on the G paper can be easily controlled by varying the initial aniline concentrations. After \textit{in situ} polymerization of aniline in the presence of G paper, the reaction solution gradually becomes dark green, and the surface color of the G paper changes from silver gray to dark green, indicating successful immobilization of PANI onto the G paper substrate. The top view SEM images of the G–PANI hybrid papers prepared using different aniline concentrations during the \textit{in situ} polymerization are shown in Fig. 6. The quite smooth surface of the G paper can be observed in Fig. 6a and b. In contrast, Fig. 6c and d indicate that a small number of PANI particles grow adhered to the surface of the G paper at a low aniline concentration. Homogeneously distributed PANI particles, in mono-layered structures on the G paper can be achieved at a higher concentration of aniline (0.03 mM), as shown in Fig. 6e and f. However, a further increase in the aniline concentration leads to G paper coated with disordered PANI particles (Fig. 6g and h), due to the rapid polymerization rate of aniline, the formation of dissociated PANI nuclei grown in the solution and the further adhering of these dissociated PANI particles onto the surface of the G paper. To further confirm the successful immobilization of PANI particles on the G paper, Raman spectra of the GO paper, G paper and G–PANI hybrid paper were collected and are shown in Fig. 7. For carbon materials such as GO and G, there are always two peaks appearing at 1300–1400 cm\(^{-1}\) and 1500–1600 cm\(^{-1}\) which are denoted as the D band and the G band, respectively. The Raman spectrum for the GO paper shows a lower D/G intensity ratio (~1.29) than that for the G paper (~1.50), implying a decreased sp\(^2\) domain size for the GO upon chemical reduction.\(^{39}\) The G–PANI hybrid paper shows two apparently new emerging peaks at approximately 1150 and 1440 cm\(^{-1}\), which can be ascribed to the C–H bending in the benzene- or quinine-type rings and the C=\(\text{N}\) stretching in emeraldine base (imines), respectively.\(^{38,40}\) These results clearly confirm that the PANI materials have been successfully decorated onto the G paper substrates.

Based on the above results, an initial aniline concentration of 0.03 mM was chosen as the optimum concentration for the immobilization of mono-layered PANI particles on the G paper and G–CNT composite papers. Top view SEM images of PANI particles immobilized on G paper and G–CNT composite papers are shown in Fig. 8. It can be observed that nano-sized PANI particles grew adhering to the surface of the G paper and G–CNT composite papers with a uniform distribution. More interestingly, as the CNT contents within the G–CNT composite papers increased, an urchin-like morphology becomes more obvious on the surface of the papers. This phenomenon can be ascribed to the exposed CNTs within the composite paper which serve as heterogeneous nucleation sites for the polymerization of PANI in solution. As shown in Fig. 9, cross-sectional SEM images of the G–CNT–PANI ternary hybrid paper show that PANI particles

### Table 1 Electrical conductivity properties of GO paper and GO–CNT composite papers before and after chemical reduction

<table>
<thead>
<tr>
<th>Samples</th>
<th>Electrical conductivities before reduction (S m(^{-1}))</th>
<th>Electrical conductivities after reduction (S m(^{-1}))</th>
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<tbody>
<tr>
<td>GO paper</td>
<td>4.3 \times 10(^{-5})</td>
<td>33</td>
</tr>
<tr>
<td>GO–CNT (6/1) paper</td>
<td>4.8 \times 10(^{-3})</td>
<td>36</td>
</tr>
<tr>
<td>GO–CNT (4/1) paper</td>
<td>0.86</td>
<td>127</td>
</tr>
<tr>
<td>GO–CNT (2/1) paper</td>
<td>1.6</td>
<td>182</td>
</tr>
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on the surface of the G–CNT composite paper are closely packed into thin films with a thickness of about 200–300 nm, as marked by the yellow lines in Fig. 9b.

In a three-electrode supercapacitor cell, CV measurements of neat G paper and G–CNT composite papers were performed at a scan rate of 10 mV s⁻¹ and shown in Fig. 10a. These electrodes are stable in acid electrolytes in the applied potential window, and all the CV curves show approximately rectangular shapes indicating EDL capacitor behavior. It can be clearly seen that the area surrounded by the CV curves increases with the increase in the CNT contents of the G–CNT composite papers, indicating that the addition of pristine CNTs to the G–CNT composite papers effectively improves the specific capacitance.
of the as-made papers due to the introduction of porous structures throughout the composite paper. Fig. 10b exhibits the CV curves of the G paper and G–CNT composite papers with the immobilized PANI particles. In contrast to the CV curves for the all-carbon materials above, the CV curves of the neat G paper and G–CNT composite papers with immobilized PANI particles clearly exhibit two pairs of redox peaks from $-0.2$ V to $0.8$ V, which are indicative of the typical pseudocapacitive characteristics of PANI. Furthermore, it can be clearly observed that the area surrounded by the CV curves of the paper samples with immobilized PANI particles is larger than those for the CV curves of the neat all-carbon papers, indicating a higher specific capacitance for these hybrid papers due to the introduction of pseudocapacitive PANI materials. Besides, the nano-sized PANI particles on the all-carbon papers not only serve as pseudocapacitive materials with high specific capacitances, but also improve the electrode–electrolyte interfacial structure, including an increased contact area and interfacial compatibility.

The scan rate dependent CV curves at different scan rates for the supercapacitor with the G–CNT–PANI symmetric electrode in a two-electrode system are shown in Fig. 10c. The two pairs of redox waves shown in all the CV curves of the G–CNT–PANI ternary hybrid papers are attributed to the redox characteristics of the immobilized PANI. The CV curves have large rectangular areas even at a high scan rate (100 mV s$^{-1}$), indicating the good rate stability of the assembled supercapacitor cell. More importantly, the CV curves in Fig. 10d show that the electrochemical performance of the symmetric supercapacitor cell does not significantly change under various bending conditions even at 180°.

Fig. 11a shows the galvanostatic charge–discharge curves of the G paper and the G–CNT (2/1) composite paper with and without immobilized PANI particles at a current density of 0.5 A g$^{-1}$. The voltage–time curves of the G paper and the G–CNT composite paper electrodes exhibit a linear and symmetric shape in the total potential range. However, for the curves of the G and G–CNT composite paper electrodes with immobilized PANI, a certain extent of deviation from the line at low potentials can be observed, indicating pseudocapacitive behavior due to the introduction of the pseudocapacitive PANI. Furthermore, across all the voltage–time curves, IR drops were hardly observed due to the significantly reduced internal resistance of the electrode. The specific capacitance ($C$) of the samples was calculated according to the following equation: $C = (I \times \Delta t)/(\Delta V \times m)$ where $I$ is the current loaded (A), $\Delta t$ is the discharge time (s), $\Delta V$ is the potential change during the discharge process and $m$ is the mass of active electrode material (g).

Fig. 11b shows the specific capacitances of the as-fabricated electrodes as a function of different discharge current densities. The specific capacitance of the G–CNT–PANI ternary hybrid paper is far superior to other paper electrodes at the same current density. In particular, it can be observed that the capacitance of the G–CNT–PANI ternary hybrid paper (432 F g$^{-1}$) at a current density of 0.5 A g$^{-1}$ is much higher than those of the G paper (131 F g$^{-1}$), G–CNT composite paper (172.4 F g$^{-1}$) and G–PANI hybrid paper (302.6 F g$^{-1}$). When the current density...
increases to 10 A g\(^{-1}\), the specific capacitance of the G–CNT–PANI ternary hybrid paper reaches 297.5 F g\(^{-1}\), which is 69% of the specific capacitance of the same sample at a current density of 0.5 A g\(^{-1}\). This high-rate capability is possibly due to the mechanically stable frameworks comprised of G and CNTs, combined with improved electrode–electrolyte interfacial structures.

Cyclic stability is one key factor in determining the electrochemical performance of electrode materials for supercapacitors. Cycling tests for the G–CNT–PANI ternary paper electrodes were carried out under a current density of 0.5 A g\(^{-1}\), as shown in Fig. 11c. It is shown that the specific capacitance of the as-made electrodes decreases by less than 4% after 600 charge–discharge cycles, demonstrating the good cyclic stability of the hybrid paper as a flexible electrode material.

Conclusions

In summary, flexible paper electrode G–CNT–PANI ternary hybrids for supercapacitors were fabricated by the in situ polymerization of PANI onto the surface of G–CNT composite papers which were prepared via vacuum-assisted self-assembly. The introduction of nano-sized PANI particles on the all-carbon papers greatly enhanced the electrochemical properties of the as-made G–CNT–PANI ternary hybrid papers, due to introduction of a typical pseudocapacitive characteristic to the all-carbon composite papers, combined with an improvement in the electrode–electrolyte interfacial structures including increased contact area and improved interfacial compatibility. The G–CNT–PANI ternary hybrid paper electrodes show a specific capacitance of 432 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\), retain almost 69% capacitance at a large current density of 10 A g\(^{-1}\) with excellent rate stability, and maintain 96% of the initial specific capacitance after 600 charge–discharge cycles with good electrochemical stability. Our study thus develops a simple and effective way to fabricate graphene-based hybrid papers with excellent properties in order to meet applications in many fields such as flexible electrodes for energy fields.

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Notes and references