





SUBJECT AREAS:

ELECTRONIC MATERIALS

NANOCOMPOSITES

ELECTRONIC PROPERTIES AND

MATERIALS

Received 28 November 2012

ORGANIC-INORGANIC NANOSTRUCTURES

Accepted
11 February 2013

Published 27 February 2013

Correspondence and requests for materials should be addressed to H.S.P. (penghs@ fudan.edu.cn)

# Conducting polymer composite film incorporated with aligned carbon nanotubes for transparent, flexible and efficient supercapacitor

Huijuan Lin<sup>1</sup>, Li Li<sup>1,2</sup>, Jing Ren<sup>1</sup>, Zhenbo Cai<sup>1</sup>, Longbin Qiu<sup>1</sup>, Zhibin Yang<sup>1</sup> & Huisheng Peng<sup>1</sup>

<sup>1</sup> State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, and Laboratory of Advanced Materials, Fudan University, Shanghai 200438, China, <sup>2</sup>College of Food Science and Technology, Shanghai Ocean University, Shanghai 201306, China.

Polyaniline composite films incorporated with aligned multi-walled carbon nanotubes (MWCNTs) are synthesized through an easy electrodeposition process. These robust and electrically conductive films are found to function as effective electrodes to fabricate transparent and flexible supercapacitors with a maximum specific capacitance of 233 F/g at a current density of 1 A/g. It is 36 times of bare MWCNT sheet, 23 times of pure polyaniline and 3 times of randomly dispersed MWCNT/polyaniline film under the same conditions. The novel supercapacitors also show a high cyclic stability.

onducting polymers such as polyaniline, polypyrrole, and poly(3,4-ethylene-dioxythiophene) have been widely studied for electrode materials in electrochemical supercapacitors due to the high electrical conductivity, high pseudo capacitance, and low cost<sup>1-7</sup>. However, the considerable volume change during the repeated intercalation and depletion of ions in the charge and discharge process has largely decreased their mechanical stability in the use<sup>8</sup>. To this end, carbon nanotubes (CNTs) which show a high surface area and high mechanical strength, electrical conductivity and chemical stability are widely incorporated to improve the performance of supercapacitors<sup>9,10</sup>. However, the improvements are far from expected as CNTs are randomly aggregated in the composite electrode by a typical solution process, and the produced charges have to cross a lot of boundaries in random CNT networks<sup>11</sup>. Therefore, the alignment of CNTs in the composite electrode may provide an effective solution to achieve the desired high capacitance and stability. For instance, the aligned CNT arrays were found to facilitate ionic motions compared with the CNT network<sup>11</sup>. However, the use of aligned CNT composite materials for supercapacitors is rare. On the other hand, transparent and flexible supercapacitors had been recently proposed for unique and promising applications in various portable and integrated equipments<sup>12-14</sup>, but they have not been realized with high performances yet.

Herein, we have developed a general method to synthesize continuous conducting polymer composite films incorporated with highly aligned multi-walled carbon nanotubes (MWCNTs) at large scale through an electrodeposition process. The composite films are robust and electrically conductive with a high optical transmittance, which makes them very promising as new and effective electrode materials. The resulting supercapacitors were shown to be transparent and flexible with a high specific capacitance.

### Results

MWCNT sheets were drawn from spinnable MWCNT arrays which had been synthesized by chemical vapor deposition and reported elsewhere  $^{15-20}$ . Here the spinnable arrays showed a height of about 250  $\mu$ m, and the used MWCNTs were uniform with a diameter of about 10 nm. The widths of MWCNT sheets were controlled from several millimeters to centimeters by varying the widths of spinnable arrays, and the average thickness of a layer of sheet was about 25 nm. Layers of MWCNT sheets could be further stacked along the same direction to produce thicker films. The length of MWCNT sheets had generally achieved tens of to hundreds of meters. Figure 1a shows a typical scanning electron microscopy (SEM) image of MWCNT sheet. MWCNTs had been highly aligned along the drawing direction to provide the sheets with high electrical conductivities of  $(10^2-10^3)$  S/cm. Therefore, these MWCNT sheets could function as effective electrodes for electrodeposition of conducting polymers. Polyaniline



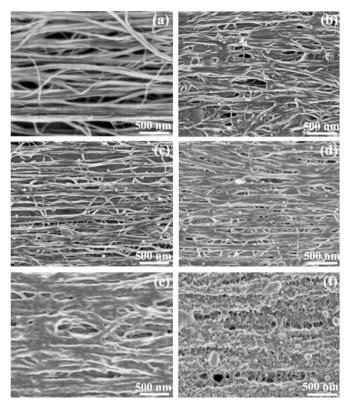


Figure 1 | Scanning electron microscopy (SEM) images of MWCNT sheets before and after incorporation of PANI with different weight percentages. (a) Bare AMWCNT sheet. (b) 12%. (c) 23%. (d) 50%. (e) 70%. (f) 86%.

(PANI) had been firstly investigated as a model. The sizes of voids among MWCNTs were mainly varied from several to tens of nanometers, and PANI was mainly attached onto the outer surfaces (Figure S1) and infiltrated into the voids. Figures 1b–1f show typical SEM images of the resulting MWCNT/PANI composite films with increasing PANI weight percentages of 12, 23, 50, 70 and 86%. The sizes of voids among aligned MWCNTs were decreased with the increasing PANI percentage as more PANI was infiltrated into the voids. At a weight percentage of about 70%, almost all voids were filled with the PANI. With the further increase of electrodeposition time, the additional PANI was mainly coated at the top of the sheet. For instance, almost no MWCNTs could be observed by SEM at 86% as they were totally covered by the PANI layer.

Raman spectroscopy was further used to characterize the MWCNT/PANI composite film. Figure S2 has compared Raman spectra of PANI, MWCNT sheet and MWCNT/PANI composite films with increasing PANI weight percentages of 12%, 23%, 50%, 70%, 86%. The C-H bending of the quinoid ring at 1165 cm<sup>-1</sup>, C-H bending of the benzenoid ring at 1255 cm<sup>-1</sup>, C-N<sup>+</sup> stretching at 1333 cm<sup>-1</sup>, and C-C stretching of the benzene ring at 1485 and 1623 cm<sup>-1</sup> were observed in the aligned MWCNT/PANI composite film. The peaks at 1643 cm<sup>-1</sup> and 1165 cm<sup>-1</sup> in the bare PANI shifted to 1623 and 1167 cm<sup>-1</sup> in the composite film, respectively, which indicated the  $\pi$ - $\pi$  interaction between MWCNT and PANI<sup>21-23</sup>. As both D and G bands in MWCNTs are overlapped with the peaks of PANI, it is difficult to compare them before and after formation of composite films.

The aligned MWCNT/PANI composite films were transparent (Figure S3). According to the UV-vis spectrometer characterization, the transmittance values for the composite films were higher than 84, 72, 70, 70 and 60 at PANI weight percentages of 12, 23, 50, 70, and 86% in a wavelength range of 300–900 nm, respectively. A typical

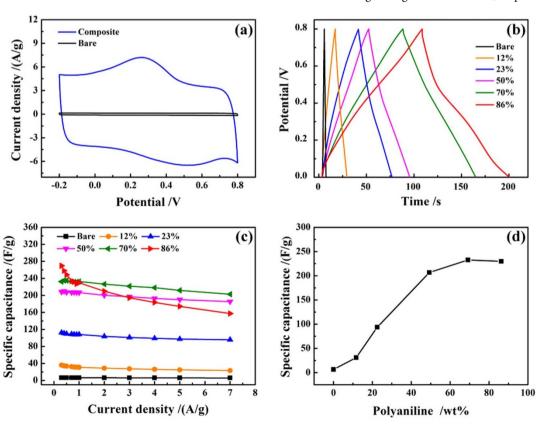


Figure 2 | (a) CV curves of the bare MWCNT sheet and composite film (weight percentage of 70% for PANI) as electrodes in a potential range of -0.2 to 0.8 V at a scan rate of 50 mV s<sup>-1</sup> in H<sub>3</sub>PO<sub>4</sub>-PVA gel electrolyte. (b) Galvanostatic charge-discharge curves of bare MWCNT sheet and composite films with different PANI weight percentages of 12, 23, 50, 70 and 86% at a current density of 1 A/g. (c) Dependence of specific capacitance on current density. (d) Dependence of specific capacitance on weight percentage of PANI.



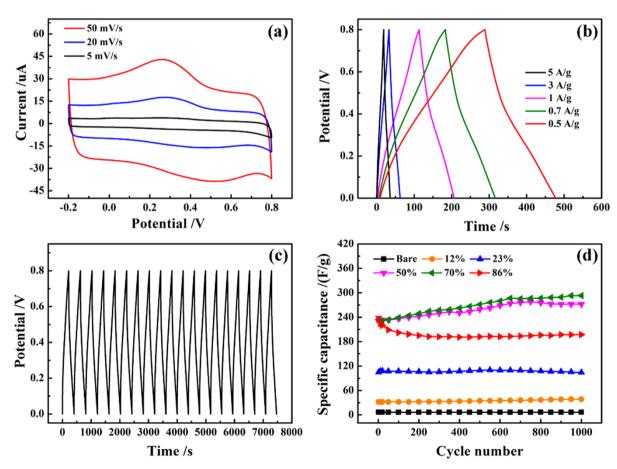
UV-vis spectrum in Figure S4 further shows a desorption peak at around 350 nm, indicating that PANI mainly existed in an emeraldine structure. The composite films were flexible and could be easily bent into different morphologies (Figure S3). In addition, the electrical conductivities remained almost unchanged during the bending process. Therefore, such composite films may be stably used as a new family of flexible electrode materials.

Cyclic voltammetry was first used to characterize the electrochemical property of aligned MWCNT sheet and MWCNT/PANI composite film. Figure 2a has compared cyclic voltammograms (CVs) of an MWCNT sheet and MWCNT/PANI composite film with PANI weight percentage of 70% measured in a two-electrode system at a scan rate of 50 mV/s in H<sub>3</sub>PO<sub>4</sub>-PVA gel electrolyte. Obviously, a typical rectangular shape which corresponded to an electrochemical double layer capacitor was obtained for the MWCNT sheet, while redox peaks which indicated a pseudo-capacitance derived from different oxidation states of PANI were observed for the MWCNT/ PANI film<sup>6,7,24–26</sup>. As expected, the current density for the composite film was much higher than that of the bare MWCNT sheet. Figure 2b has compared the typical galvanostatic charge-discharge curves of MWCNT sheet and MWCNT/PANI composite film electrodes between 0 and 0.8 V at a current density of 1 A/g. The charge curves were nearly symmetric to their corresponding discharge curves in the potential range, which indicated a high reversibility between charge and discharge processes.

The specific capacitances were firstly increased with the increasing PANI weight percentage and then reached a platform (Figures 2c and

2d). Specifically, they were increased from 6.38, 31.0, 93.8, 207 to 233 F/g with the increasing PANI weight percentage from 0, 12, 23, 50, to 70% at a current density of 1 A/g, respectively. With the further increase of PANI, the specific capacitance was maintained, e.g., 230 F/g at 86%. The increasing specific capacitance at PANI weight percentages of less than 70% was mainly derived from the higher pseudocapacitance of PANI. PANI was mainly incorporated among aligned MWCNTs, where the excellent electrical properties of MWCNTs such as high conductivity had been effectively used. At higher percentages, the additional PANI was covered at the top of composite films, and could not efficiently interact with aligned MWCNTs. Therefore, besides the introduction of higher pseudocapacitance of PANI, a synergetic interaction between aligned MWCNT and PANI plays a critical role for the high capacitance of composite films. The dependence of specific capacitance on PANI weight percentage had been also confirmed by the alternate current impedance spectra of supercapacitors (Figure S5).

The composite film-based supercapacitors were stable during the use. Figure 3a compares CV curves of the supercapactior prepared from the MWCNT/PANI composite film with PANI weight percentage of 70%. The covered area of the CV curve was enhanced with the increasing scan rate. Figure 3b compares charge-discharge curves of the supercapactior under different current densities. The charge-discharge curves are similar in shape between 0 and 0.8 V, indicating that the supercapacitor can be stably performed in a wide range of current densities<sup>27</sup>. The supercapacitor stability was also confirmed by the cyclic measurement. Figure 3c shows typical charge-discharge



**Figure 3** | (a) CV curves for a supercapacitor based on the PANI weight percentage of 70% at different scan rates. (b) Galvanostatic charge/discharge curves for a supercapacitor based on the PANI weight percentage of 70% at different current densities. (c) Galvanostatic charge/discharge curves for a supercapacitor based on the PANI weight percentage of 70% with the time at a current density of 1 A/g. (d) Dependence of specific capacitance on cycle number for supercapacitors fabricated from bare and composite films with different PANI weight percentages. The specific capacitance was calculated from the charge–discharge curves at the current density of 1 A/g in H<sub>3</sub>PO<sub>4</sub>-PVA gel electrolyte.



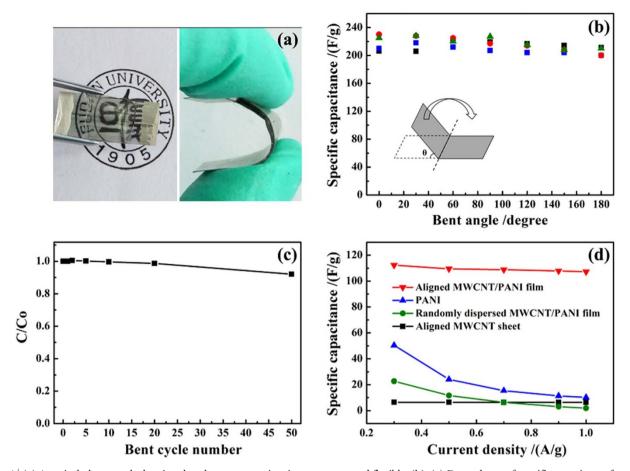


Figure 4 | (a) A typical photograph showing that the supercapacitor is transparent and flexible. (b), (c) Dependence of specific capacitance for a supercapacitor based on the PANI weight percentage of 70% on bent angle and cycle number, respectively.  $\theta$  is the bent angle, and  $C_0$  and C correspond to the specific capacitance before and after bending for different cycles, respectively. (d) Comparison of specific capacitances for supercapacitors fabricated from bare MWCNT sheet on PET, PANI on flexible ITO, randomly dispersed MWCNT/PANI film on PET and aligned MWCNT/PANI film on PET.

curves in a continuous operation for 19 cycles. Obviously, these curves are the same in shape. The cyclic performances of supercapacitors derived from MWCNT sheet and aligned MWCNT/PANI composite films were further compared and extended to 1000 cycles at a discharge current density of 1 A/g (Figure 3d). The specific capacitances remain almost unchanged for both MWCNT sheet and composite films with the PANI weight percentage of 12 and 23%. Interestingly, the specific capacitances are slightly increased at 50% and 70%. The Coulomb efficiency was also slightly increased to almost 100% after 1000 cycles (Figure S6). It remains unclear about the mechanism yet. In the case of a higher weight percentage of 86%, the specific capacitances are obviously decreased in the first 250 cycles and then maintained almost the same in the following cycles.

## **Discussion**

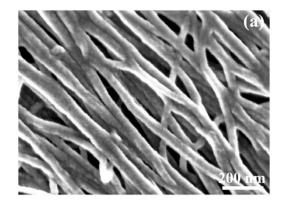
The supercapacitors based on aligned MWCNT/PANI composite films were transparent (Figure 4a). In addition, they were flexible and could be bent for over a hundred times without an obvious decrease in structure stability traced by SEM. The flexibility and stability were further characterized by measuring the galvanostatic charge-discharge curves under different bent angles and cycles. Figure 4b shows dependence of specific capacitance of a supercapacitor fabricated from an aligned MWCNT/PANI composite film (PANI weight percentage of 70%) with the increasing bent angle from 0 to  $180^{\circ}$ . The values of specific capacitances remain almost unchanged with the increasing bent angle. In addition, the  $C/C_0$  values are only slightly decreased by less than 8% after bending for

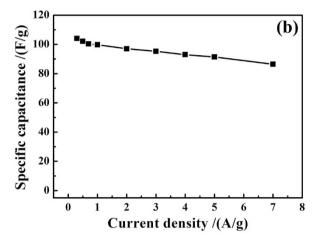
50 cycles (Figure 4c). Here  $C_0$  and C correspond to the specific capacitances before and after bending for different cycles.

As a comparison, we had further studied the supercapaciors by electrodeposing PANI on the randomly dispersed MWCNT film under the same condition. Figure 4d shows the dependence of the specific discharge capacitance in the supercapacior on the basis of randomly dispersed MWCNT/PANI composite films on the current density (Figure S7). The specific capacitances are seriously decreased for the randomly dispersed MWCNT/PANI composite films with different PANI weight percentages at a current density range of 0.3-1.0 A/g. As previously discussed in Figure 2c, the capacitances for the aligned MWCNT/PANI composite films were well maintained during this current density range. In addition, the specific capacitances for the randomly dispersed MWCNT/PANI composite films were much lower than the aligned MWCNT/PANI films. As another comparison, the specific capacitance based on the aligned MWCNT/PANI film was also much higher than 10.2 F/g for pure PANI deposited on a flexible indium tin oxide (ITO) substrate (Figure 4d). It should be noted that the supercapacitor derived from the pure PANI on generally used rigid fluorine-doped tin oxide achieved a specific capacitance of 416 F/g at 1 A/g. The very low specific capacitance of flexible PANI/ITO electrode was possibly derived from much lower electrical properties.

The other conducting polymers such as poly(pyrrole) (PPy) were also incorporated into aligned MWCNT to produce composite films (Figure 5a). The aligned MWCNT/PPy composite films had been used to fabricate novel supercapacitors. For instance, for a composite film with PPy weight percentage of 70%, the specific capacitance of







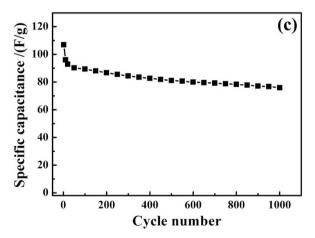


Figure 5 | Characterization of the aligned MWCNT/PPy composite film with PPy weight percentage of 70% and the resulting supercapacitor.
(a) SEM image. (b) Dependence of specific capacitance on current density.
(c) Dependence of specific capacitance on cycle number at a current density of 1 A/g.

resulting supercapacitor was slightly decreased with the increasing current density of 0.3–7.0 A/g (Figure 5b). The cyclic performances were also studied in 1000 cycles at a discharge current density of 1 A/g (Figure 5c), and the specific capacitance was about 76.0 F/g after 1000 cycles.

MWCNT/PPy and MWCNT/PANI composite films were further compared in conductivity in Figure S8. The conductivities of MWCNT sheet, PPy, and PANI are 570, 0.1, and 0.05 S/cm, respectively. The aligned MWCNT/PPy composite film showed a higher conductivity of 424, compared with 331 S/cm in the MWCNT/PANI

composite film under the same weight percentage of 70% for the polymer content. However, PANI was observed to form a rough surface while PPy produced a smooth surface in the composite film. Therefore, the higher specific capacitance based on the aligned MWCNT/PANI film may be derived from the rougher surface<sup>30</sup>.

In summary, aligned MWCNT/conducting polymer composite films with high optical transmittance and good flexibility have been synthesized by an electrochemical polymerization. These composite films have been further used as electrodes to fabricate transparent and flexible supercapacitors. The synergetic interaction between aligned MWCNT and polymer provides the supercapacitor with much improved performance compared with bare MWCNT sheet, pure polymer, and randomly dispersed MWCNT/polymer film. For instance, the specific capacitances in the resulting supercapacitors based on aligned MWCNT/PANI composite films are 36 times of bare MWCNT sheet, 23 times of pure PANI film, and 3 times of the randomly dispersed MWCNT/PANI film. In addition, the supercapacitors based on aligned MWCNT composite films also showed a high cyclic stability.

### Methods

Synthesis of MWCNT/PANI and MWCNT/PPy composite film electrodes. The synthesis of spinnable MWCNT arrays had been reported elsewhere 15-20, and aligned MWCNT sheets were continuously prepared from the arrays through a dry-drawing process. The randomly dispersed MWCNT films were prepared by coating an MWCNT/N-cyclohexyl-2-pyrrolidone dispersion with concentration of 1 mg/mL onto poly(ethylene terephthalate) (PET). Electrochemical deposition of PANI and PPy was made on MWCNT sheets or randomly dispersed MWCNT films through an electrochemical analyzer system (CHI 660D) using platinum wire and saturated calomel electrode (SCE) as counter and reference electrodes, respectively. Prior to electrochemical deposition, the aligned MWCNT sheet or randomly dispersed MWCNT film on PET were dipped in the electrolyte for 10 min. Electropolymerization of aniline had been performed at a potential of 0.75 V vs. SCE in a solution containing 0.1 M aniline and 1.0 M H<sub>2</sub>SO<sub>4</sub>. After polymerization, the as-prepared MWCNT/PANI composite films were washed with de-ionized water and then dried at 80°C for over 2 hr. As a comparison, pure PANI was also electro-deposited on flexible ITO at a potential of 0.75 V vs. SCE. Electropolymerization of pyrrole was made at a potential of 0.70 V vs. SCE in a solution containing 0.1 M pyrrole and 0.1 M KNO<sub>3</sub> at a pH of about 3. The formation of composite films had been confirmed by Fourier transform infrared spectra (Figures S8 and S9)28,25

Fabrication of supercapacitors based on composite films. The MWCNT/PANI composite films were used as electrodes to fabricate flexible supercapacitors. The supercapacitor was typically composed of two composite film electrodes separated by  $\rm H_3PO_4$ -poly (vinyl acetate) gel electrolyte. The density of aligned MWCNT sheets was  $1.41~\mu g/cm^2$ , and the mass of PANI and PPy in the composite film had been calculated from the total Faradic charge consumed in the electropolymerization reaction by assuming an average of 2.5 and 2 electrons per monomer, respectively  $^{14}$ .

Characterization and electrical measurements. The structures of MWCNT/PANI composite films were characterized by transmission electron microscopy (TEM, JEOL JEM-2100F operated at 200 kV), scanning electron microscopy (SEM, Hitachi FE-SEM S-4800 operated at 1 kV), Raman spectroscopy (Renishaw in Via Reflex with an excitation wavelength of 633 nm and laser power of 20 mW) and Fourier transform infrared spectroscopy (Thermofisher Nicolet 6700). The electrical conductivities were generally measured by a four-probe method on Resistivity Measurement System (RTS-8). Galvanostatic charge/discharge measurements of supercapacitors were made at a current density of 1 A/g. The specific resistances were measured by an alternating current complex impedance method. The average specific capacitance of the electrode derived from the galvanostatic discharge curve was calculated according to the following equation:  $C = 2i_0/[m(\Delta V/\Delta t)]$ , where  $i_0$ , m and  $\Delta V/\Delta t$  correspond to the discharge current, mass of the active material in the electrode and average slope of the discharge curve, respectively.

- Burke, A. R&D considerations for the performance and application of electrochemical capacitors. *Electrochim. Acta* 53, 1083–1091 (2007).
- Frackowiak, E., Khomenko, V., Jurewicz, K., Lota, K. & Béguin, F. Supercapacitors based on conducting polymers/nanotubes composites. *J. Power Sources* 153, 413–418 (2006).
- Girija, T. C. & Sangaranarayanan, M. V. Analysis of polyaniline-based nickel electrodes for electrochemical supercapacitors. *J. Power Sources* 156, 705–711 (2006).
- 4. Kim, J.-Y., Kim, K. H. & Kim, K. B. Fabrication and electrochemical properties of carbon nanotube/polypyrrole composite film electrodes with controlled pore size. *J. Power Sources* **176**, 396–402 (2008).
- Wang, G., Zhang, L. & Zhang, J. A review of electrode materials for electrochemical supercapacitors. Chem. Soc. Rev. 41, 797–828 (2012).

Q

- Zhang, H. et al. Influence of microstructure on the capacitive performance of polyaniline/carbon nanotube array composite electrodes. *Electrochim. Acta* 54, 1153–1159 (2009).
- Zhang, H. et al. Tube-covering-tube nanostructured polyaniline/carbon nanotube array composite electrode with high capacitance and superior rate performance as well as good cycling stability. Electrochem. Commun. 10, 1056–1059 (2008).
- 8. Peng, C., Zhang, S., Jewell, D. & Chen, G. Z. Carbon nanotube and conducting polymer composites for supercapacitors. *Prog. Nat Sci.* **18**, 777–788 (2008).
- Issi, J.-P., Langer, L., Heremans, J. & Olk, C. H. Eectronic properties of carbon nanotubes:experimental results. *Carbon* 33, 941–948 (1995).
- 10. Ma, R. Z. *et al.* Study of electrochemical capacitors utilizing carbon nanotube electrodes. *J. Power Sources* **84**, 126–129 (1999).
- Huang, F., Vanhaecke, E. & Chen, D. In situ polymerization and characterizations of polyaniline on MWCNT powders and aligned MWCNT films. *Catal. Today* 150, 71–76 (2010).
- Chen, P.-C., Shen, G., Sukcharoenchoke, S. & Zhou, C. Flexible and transparent supercapacitor based on In<sub>2</sub>O<sub>3</sub> nanowire/carbon nanotube heterogeneous films. *Appl. Phys. Lett.* 94, 043113 (2009).
- 13. Wei, D. et al. Transparent, flexible and solid-state supercapacitors based on room temperature ionic liquid gel. Electrochem. Commun. 11, 2285–2287 (2009).
- Yu, A., Roes, I., Davies, A. & Chen, Z. Ultrathin, transparent, and flexible graphene films for supercapacitor aplication. Appl. Phys. Lett. 96, 253105 (2010).
- Peng, H. Aligned carbon nanotube/polymer composite films with robust flexibility, high transparency, and excellent conductivity. J. Am. Chem. Soc. 130, 42–43 (2008).
- Peng, H. et al. Electrochromatic carbon nanotube/polydiacetylene nanocomposite fibres. Nature Nanotechnol. 4, 738–741 (2009).
- Chen, T. et al. Flexible, light-weight, ultrastrong, and semiconductive carbon nanotube fiber for highly efficient novel solar cell. Angew. Chem. Int. Ed. 50, 1815–1819 (2011).
- Chen, T. et al. Nitrogen-doped carbon nanotube composite fiber with a coresheath structure for novel electrode. Adv. Mater. 23, 4620–4625 (2011).
- Yang, Z. et al. Aligned carbon nanotube sheet for electrode of organic solar cell. Adv. Mater. 23, 5636–5639 (2011).
- 20. Sun, X. et al. Unusual reversible photomechanical actuation in polymer/nanotube composites. Angew. Chem. Int. Ed. 51, 8520–8524 (2012).
- Li, L. et al. Facile fbrication of uiform core-shell structured carbon nanotubepolyaniline nanocomposites. J. Phys. Chem. C 113, 5502–5507 (2009).
- Fan, H., Wang, H., Zhao, N., Zhang, X. & Xu, J. Hierarchical nanocomposite of polyaniline nanorods grown on the surface of carbon nanotubes for high-performance supercapacitor electrode. *J. Mater. Chem.* 22, 2774–2780 (2012).
- Wu, T.-M., Lin, Y.-W. & Liao, C.-S. Preparation and characterization of polyaniline/multi-walled carbon nanotube composites. *Carbon* 43, 734–740 (2005).
- Hu, C.-C. & Lin, J.-Y. Effects of the loading and polymerization temperature on the capacitive performance of polyaniline in NaNO<sub>3</sub>. *Electrochim. Acta* 47, 4055–4067 (2002).

- Hu, C.-C., Li, W.-Y. & Lin, J.-Y. The capacitive characteristics of supercapacitors consisting of activated carbon fabric–polyaniline composites in NaNO<sub>3</sub>. J. Power Sources 137, 152–157 (2004).
- 26. Sivakkumar, S. R. et al. Electrochemical performance of polyaniline nanofibres and polyaniline/multi-walled carbon nanotube composite as an electrode material for aqueous redox supercapacitors. J. Power Sources 171, 1062–1068 (2007)
- Yang, M., Cheng, B., Song, H. & Chen, X. Preparation and electrochemical performance of polyaniline-based carbon nanotubes as electrode material for supercapacitor. *Electrochim. Acta* 55, 7021–7027 (2010).
- 28. Feng, W. et al. Well-aligned polyaniline/carbon-nanotube composite films grown by in-situ aniline polymerization. *Carbon* 41,1551–1557 (2003).
- Zhang, X. T., Zhang, J. & Song, W. H. Controllable synthesis of conducting polypyrrole nanostructures. J. Phys. Chem. B 110, 1158–1165 (2006).
- Yang, Z. et al. Penetrated and aligned carbon nanotubes for counter electrodes of highly efficient dye-sensitized solar cells. Chem. Phys. Lett. 549, 82–85 (2012).

# **Acknowledgements**

This work was supported by NSFC (20904006, 91027025), MOST (2011CB932503, 2011DFA51330), MOE (NCET-09-0318), STCSM (11520701400, 12nm0503200), CPSF (2011M500724), Fok Ying Tong Education Foundation, The Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning and State Key Laboratory of Molecular Engineering of Polymers at Fudan University (K2011-10).

# **Author contributions**

H.L. and L.L. contribute equally to this work. They designed experiments and performed supercapacitor fabrications, characterizations and tests. J.R. and Z.C. participated in device fabrication and optimization. L.Q. and Z.Y. synthesized CNT films. H.P. wrote the paper. All authors contributed to discussion, analysis of results and preparation of manuscript.

# **Additional information**

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

License: This work is licensed under a Creative Commons Attribution-NonCommercial-ShareALike 3.0 Unported License. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-sa/3.0/

How to cite this article: Lin, H. *et al.* Conducting polymer composite film incorporated with aligned carbon nanotubes for transparent, flexible and efficient supercapacitor. *Sci. Rep.* 3, 1353; DOI:10.1038/srep01353 (2013).