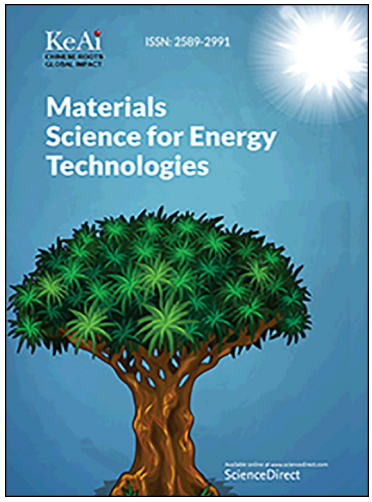


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PII: S2589-2991(18)30022-3
DOI: https://doi.org/10.1016/j.mset.2018.06.001
Reference: MSET 11

To appear in: *Materials Science for Energy Technologies*

Received Date: 28 April 2018
Revised Date: 3 June 2018
Accepted Date: 3 June 2018

Please cite this article as: P. Li, Y. Li, Z. Zhang, J. Chen, Y. Li, Y. Ma, Capillarity-Driven Assembly of Single-Walled Carbon Nanotubes onto Nickel Wires for Flexible Wire-Shaped Supercapacitors, *Materials Science for Energy Technologies* (2018), doi: https://doi.org/10.1016/j.mset.2018.06.001

# Capillarity-Driven Assembly of Single-Walled Carbon Nanotubes onto Nickel Wires for Flexible Wire-Shaped Supercapacitors

*Pan Li, Yiming Li, Ziqiang Zhang, Jun Chen, Yi Li*, Yanwen Ma**

Key Laboratory for Organic Electronics & Information Displays and Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, Nanjing 210023, China.

*Corresponding Author

Email: iamyli@njupt.edu.cn , iamywma@njupt.edu.cn.

**Abstract:** The carbon nanomaterials have been incorporated into composite electrode for wire-shaped supercapacitors (WSSs) to promote development of wearable electronics. Coating of carbon nanomaterials directly onto functional fiber is a facile strategy to prepare wire-shaped electrodes. However, it is still a critical challenge to maximize the adhesion of the nanomaterials onto aimed substrate fiber, while still maintaining the high specific area of the nanomaterials. Herein, both carbon nanotubes (CNTs) and graphene were coated onto the surface of nickel wires via capillary effect driven process. It was discovered that the one dimensional morphology of the CNTs not only benefited the adhesion of CNTs on the relatively smooth surface of the nickel metal wire, but also strengthened the infiltration of the electrolyte among the CNTs. On the contrast, the restacking of graphene oxide (GO)

sheets retarded the infiltration of the electrolyte, resulting in inferior capacitive performance. The prepared Ni-CNT electrodes showed excellent electrochemical double layer capacitive performance along with the mechanical robustness and high flexibility. The constructed all-solid flexible wire-shaped supercapacitors maintained a high specific capacitance of approximately 30 F/g after 3000 cycles when bent by 45 degree.

**Keywords**: nickel wires; carbon nanotubes; graphene oxide; capillary effect; wire-shaped supercapacitors.

## 1. Introduction

Flexible energy storage devices such as wire-shaped supercapacitors (WSSs) have been widely studied to accelerate development of the wearable electronics.[1-6] Consequently, as major part of the supercapacitors, the electrodes are required to be made into a wire or fiber configuration, instead of the conventional planar format. Carbon nanotubes (CNTs)[7-11] and graphene[12-14] are among the most promising electrode materials due to their prominent electrical, mechanical, and thermal properties, low weight and large specific surface areas.[15-18] Our group fabricated a WSS by spinning CNT and reduced graphene oxide (RGO) into fibers and reported a high specific capacitance of 38.8 F/cm$^3$.[5] However, the relatively low shear stress and complex preparation process of these fibers has hindered their application in industrially weaving and knitting process.[19]

Recently, CNTs and graphene were wrapped onto metal wire to fabricate WSS electrodes with good mechanical strength and electrochemical performance.[20-22] For example, the core-shell yarn electrodes prepared by coating the carbon nanotubes on the stainless steel provided a high volumetric capacitance of 263.31 F/cm$^3$ and energy density of 0.067 Wh/cm$^3$.[23] In these systems, the immobilization of carbon nanomaterials on the substrate surface need to be enhanced before the performance could be further improved. Specifically, the key issue is how to engineer the assembly process according to the characteristics of both the substrate yarn and the coated nanomaterials. Commercial yarns such as elastic and cotton fibers have also been selected as substrate for nanomaterial coating because of the flexibility offered in the resulting supercapacitors. The WSS made by using a coaxial structure of aligned CNT sheets on elastic fibers as electrodes achieved good stretchability and high specific capacitance simultaneously. For example, the wire-shaped supercapacitor constructed on RGO/Ni electrode delivered an energy density of 6.1 mWh/cm$^3$ and a power density of 1400 mW/cm$^3$.[24] The specific capacitance of CNT/elastic fiber based capacitor is maintained by more than 95% after multi-cycle stretching at a strain of 75% with no obvious structural damages observed.[1] The facilitated contact between the electrode and electrolyte enabled by the aligned geometry CNTs was considered crucial to yield the excellent performance. Nonetheless, these normally insulating substrates usually depend strongly on the coating of the conductive layer or active material to guarantee the conductivity, making the preparation process complicate. The WSS electrode built through growing CuCo2O4 nanostructures on Ni wires was

considered having strong interaction between active material and the substrate. However, the morphology of the gown nanostructure is usually hard to control, decreasing the device performance.[25] Moreover, the nitrogen - doped core - sheath carbon nanotube array was also used as an elastic electrode for WSS, utilizing the excellent contact between the materials.[26] It is noteworthy that the above mentioned wire-shaped substrates face a common challenge to achieve good adhesion between different components of the electrodes, while still offering good conductivity and porous structure for easy electrolyte wetting.[27]

In this work, through facile capillary action, single-walled CNTs (SWNTs) and GO were assembled directly and tightly onto nickel wire to compose the electrodes for WWS (Fig.1). The capillary effect was generated inside the narrow space between Ni wires in the bundle. The adsorption of CNTs on the Ni surface with parallel grooves was facilitated by their nanowire geometry. Furthermore, the coating of dense mat of SWNTs on Ni wire significantly enhanced the conductivity and promoted the infiltration of the electrolyte. Additionally, in our system, the GO coating fabricated by the same process only provided a moderate performance due to the restacking of the GO sheets. Symmetrical all-solid WSSs were assembled from the as prepared composite Ni-SWNT fibers, and showed excellent electrochemical double layer capacitive performance along with the mechanical robustness and high flexibility. The WSS reached a high specific capacitance of 34.7 F/g and maintained at 83% of the initial value for 3000 cycles after bent by 45 degree.

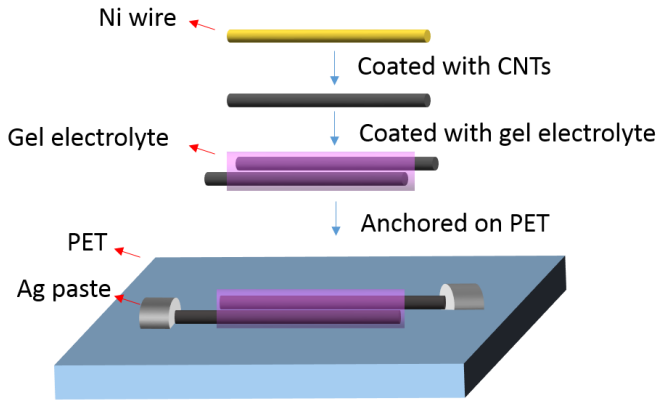


Figure 1. Illustration to the structure and schematics of the fabrication procedures of the flexible fiber-shaped supercapacitor.

## 2. Material and methods

### 2.1 Preparation of carbon nanomaterials-coated Ni wire

The Ni wires were firstly bound into a bundle, and used for the following coating of carbon nanomaterials without any further treatment. The SWNTs were pretreated by acidizing in concentrated $H_2SO_4$ and $H_2O_2$ at 100$^{o}$C for 12 h. Then the SWNT powder was collected after vacuum filtration and dried at 60$^{o}$C overnight in vacuum environment. The 0.2 g of SWNTs were dissolved in 500 mL ethanol to form a homogeneous SWNTs dispersion. Then the Ni wire bundle was dipped into the solution, stayed for 5 min (Fig. S1). Driven by the capillary effect, the CNTs were evenly coated upon the whole surface of Ni wire. The bundle of Ni wires with SWNTs coating was subsequently dried at 60$^{o}$C for 10 min. The coating process was repeated for 30 times, and then the Ni-SWNT hybrid fibrous electrodes were dried at 60$^{o}$C overnight in vacuum environment.

GO was synthesized through a modified Hummers method with concentrated

$H_2SO_4$ and $KMnO_4$ as oxidants.[28] The GO sol (2.0 g) was dispersed in 120 mL ethanol, stirred for 30 min. The solution was then subjected to a coating process following the same procedure with that of the CNTs. The reduction of GO was realized by dipping the Ni -GO wires in 10 mL of hydrazine hydrate solution, which was stored in a 100 mL beaker. The beaker was then sealed and kept in an 80$^{o}$C oil bath for 4 h. The as-prepared RGO fibers were washed with ethanol and deionized water sequentially and finally dried at 100$^{o}$C for 12 h in vacuum condition.

**2.2 Preparation of Ni-CNT wire based all-solid-state WSSs.**

Two Ni-CNT wires were immersed in LiCl/PVA gel electrolyte (1 g of LiCl and 1 g of PVA dissolved in 10 mL of deionized water) for 12 h. Then the wires were stuck together with an effective overlapping length of 2 cm after drying in air for 1 h. The reserved electrode heads were connected to metal foils by Ag paste, and anchored on polyethylene terephthalate (PET) substrate for the following electrochemical test under bending deformation.

**2.3 Materials characterization**

The structure and morphology of the composite wires were characterized by scanning electron microscopy (SEM, Hitachi S-4800). Raman spectroscopy of the carbon nanomaterials were collected on Raman Microscope, Renishaw, with the 514 nm laser as the excitation laser. The dispersion of the carbon nanomaterial was drop-coated onto 1 cm*1 cm $Si/SiO_2$ substrate to form a thin layer, and dried in air before the Raman characterization. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on PHI 5000 Versa Probe using 200 W monochromated Al Kα

radiation. The 500 μm X-ray spot was used for XPS analysis. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing.

**2.4 Electrochemical characterizations**

Electrochemical measurements were carried out on an Autolab workstation. The cyclic voltammetry (CV) curve, galvanostatic charge/discharge curve and electrical impedance spectroscopy (EIS) for each electrode were taken with a three electrode configuration in 0.5 M $Na_2SO_4$ electrolyte. A saturated calomel electrode (SCE) and a platinum wire served as reference and counter electrodes, respectively. The specific capacitances were derived from the CV curves and were calculated by taking into account the weight of all the active carbon nanomaterials.

**3. Results and discussions**

Ni wires were used to offer the flexibility and serve as a robust conducting substrate, and the carbon nanomaterials, CNTs and graphene, were studied as active materials for the electrodes of the supercapacitors. Here SWNTs were applied because of their remarkable electric conductivity resulted from the near perfect graphitization structures. Besides, the surface grooves of the Ni wire are believed to provide ideal adsorption sites for the CNTs, which have typical nanowire morphology. Meanwhile, the GO sheets are chosen because they are easy to disperse and compatible with the wet-coating process to make a uniform coating. Using the two typical active nanomaterials for WSS electrode, investigation was carried out on how the structure, morphology and assembly characteristics of the coating material influence the

electrochemical performance of the wire.

The SEM images in Fig. 2 showed the wrapping state of SWNTs and RGO. As the substrate, the Ni surface was full of nearly parallel grooves, which certainly benefits the capillary force driven coating process. It was obviously seen in Fig.2e and Fig.2f that, the wrinkled RGO covered the wire uniformly, which actually made the Ni surface smoother after the coating. The CNTs was deposited as continuous high-density network, as seen from the SEM images under both lower and higher magnification. Unlike the RGO sheet with large area, the CNT layer followed the surface undulation of the Ni wire quite closely, and thus the original surface morphology of the Ni wire could still be told (Fig.2g and Fig.2h).

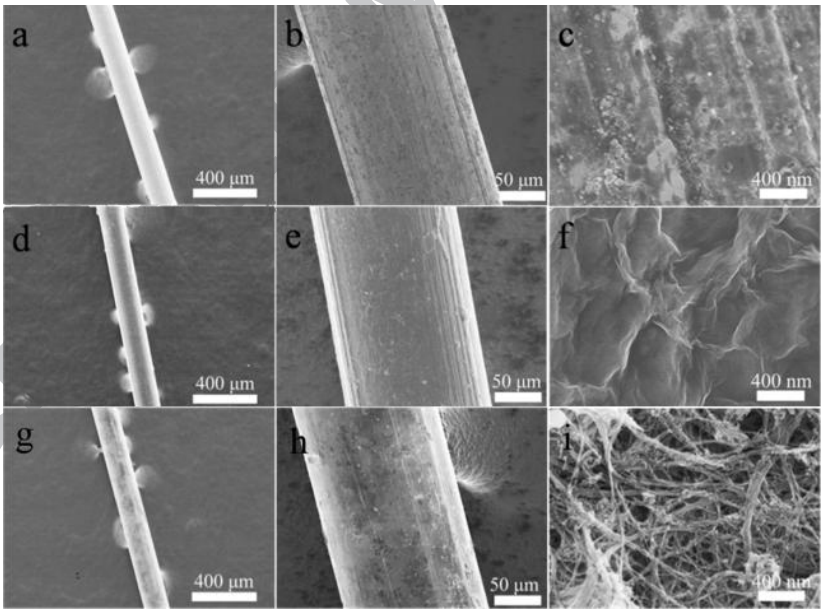


Figure 2. SEM images of the composite fibers with Ni wires coated by carbon nanomaterials. (a-c) pristine Ni wire; (d-f) Ni-RGO wire; (g-i) Ni-SWNT wire.

The electrochemical performance of the two composite wires were compared. Fig. 3a and 3b showed typical CV curves measured by the three-electrode system, with increasing scan rates from 10 to 200 mV/s. At lower scan rates, such like 10 mV/s and

20 mV/s, both the Ni-RGO and Ni-SWNT supercapacitor had CV curves in near-rectangular shape. The current of the Ni-RGO electrode was larger than that of the Ni-SWNT under the same scan rates, which corresponds to a higher specific capacitance. At scan rates higher than 50 mV/s, the CV curves of the Ni-RGO deviated from the rectangular shape to spindle shape. This observation indicates that the device possesses large internal resistance.[29] As for the Ni-SWNT wire, the CV curves maintained their rectangular shape well even at scan rate as high as 200 mV/s, which reflects a high electrochemical stability in the double-layer capacitor.[30]

Fig.3c and Fig. 3d depicted the galvanostatic charge/discharge curves of the Ni-RGO and Ni-SWNT supercapacitor, respectively. Both sets of curves were in symmetric triangular shapes, indicating high reversible charge/discharge process. It is noteworthy that, the curves of the Ni-SWNT electrode assumed longer charging and discharging time than the Ni-RGO at the same current densities. The capacitance obtained through charge-discharge cycling confirmed a better capacitive performance of the Ni-SWNT electrode. For example, at the current density of 0.2 A/g, the capacitance of Ni-SWNT electrode was 58.2 F/g, much higher than that of the Ni-RGO electrode, which was 28.8 F/g.

Then the rate performance was evaluated through analyzing the specific capacitance under different scan rate, as shown in Fig. 3e. The specific capacitance of the Ni-SWNT electrode was maintained at 90% when the scan rate increased by a factor of 20 from 10 to 200 mV/s. However, the Ni-RGO possessed an inferior rate performance, with a high specific capacitance of 46 F/g under 10 mV/s decreased

rapidly to 21 F/g at 200 mV/s. Remarkably, under scan rate lower than 50 mV/s, specific performance of the Ni-RGO was much higher than that of the Ni-SWNT electrode, and the superiority reversed as the scan rate further increased. This was due to the fact that slower scan rate offered enough time for the electron movement and ion diffusion to the most surface area of the electrode, yielding high specific capacitance. When the scan rate increased, the rapid formation of the electrochemical double-layer requires good conductivity and convenient infiltration of ions, which was provided most efficiently by the highly conductive Ni-SWNT electrode.

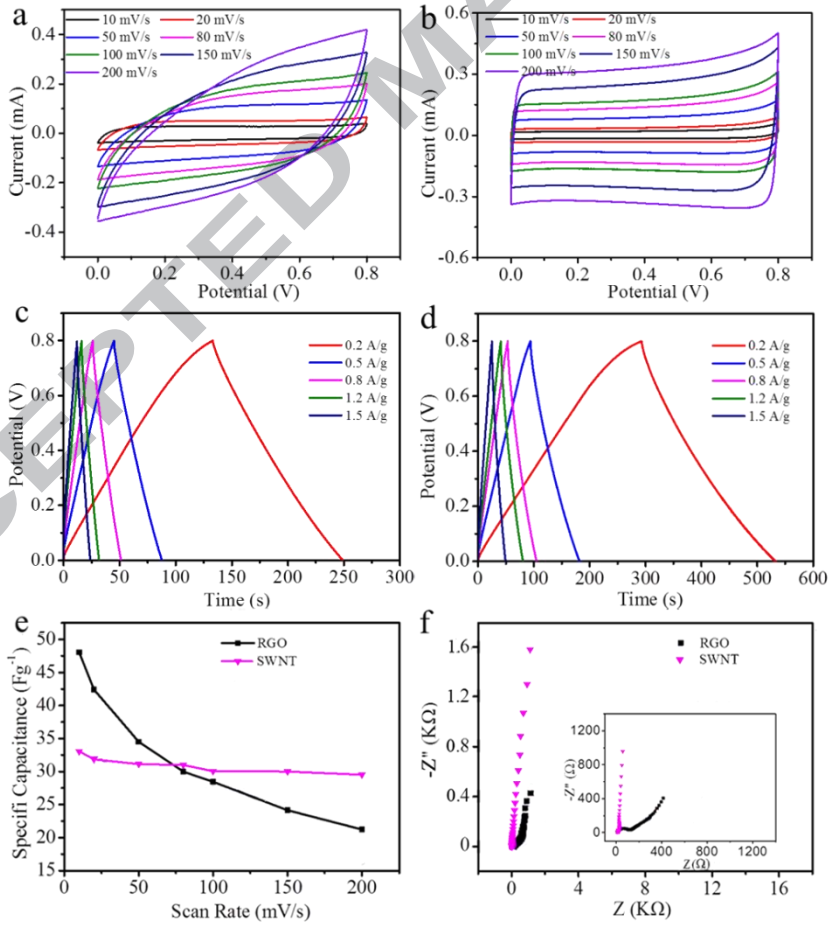


Figure 3. Electrochemical performance of the composite electrodes. (a-b) CV curves under series of scan rates for Ni-RGO (a) and Ni-SWNT (b), respectively;

(c-d) Galvanostatic charge–discharge curves of Ni-RGO (c) and Ni-SWNT (d), respectively. (e) Dependence of specific capacitance on the scan rates. (f) EIS of different wire based supercapacitors, the inset displays the expanded view of the high frequency range. The CV and Galvanostatic charge–discharge measurements were performed in 0.5 M $Na_2SO_4$ electrolyte with a three electrode configuration. The specific capacitance was calculated from corresponding CV curves.

It is known that, the internal resistance largely determines the capacitive performance of each device. Every component of the supercapacitor contributes to the internal resistance, including the intrinsic resistance of the active materials and the electrolyte, and the interface resistance between active materials and the current collector. [31] The internal resistance of different electrodes were directly compared from the Nyquist plot in Fig. 3f. As obviously seen, the internal resistance of Ni-SWNT based WSS was much lower than that of a Ni-RGO based supercapacitor. The larger resistance for a Ni-RGO based supercapacitor was supposed to be determined by the following two factors: first, since the charging and discharging processes were realized through the movement of electrons toward or away from the electrode, the abundance of surface oxygen groups of the GO sheets gave rise to the increased resistance to electrical current flowing across GO layers. Second, in the present electrode configuration, the carbon nanomaterials not only served as the active materials, but also occupied the whole surface of the metal foil as part of the current collectors. The inferior conductivity of GO layer compared to that of SWNT network could also contribute to higher internal resistance.

The dependence of electrochemical properties on the structure can be understood comprehensively in terms of the following aspects. First, the fact that the enhanced performance by SWNT coating can be attributed to excellent electrical conductivity of the CNT and large surface area provided by the network structure. [32-33] The three dimensional multi-layer network structure improves the wettability of the electrode, as well as benefits the infiltration of gel electrolyte through the CNT sheet. Second, the inferior electrochemical performance of the Ni-RGO electrode is believed to be caused by the low conductivity of GO sheet and the restacking when wrapping onto the Ni wire surface. [34-35] The capillary effect driven adsorption of GO sheets via a layer-by-layer manner actually reinforced the restacking. The quite limited space between different layers of GO hinders the penetration of the electrolyte ions.

To evaluate the potential of applying the composite electrode in practical system, we examined the electrochemical performance using two-electrode configuration. Considering the relatively low fluidity and high viscosity of the LiCl/PVA gel electrolyte, an easily accessible electrode structure is necessary. Thus, the supercapacitor was fabricated based on the Ni-SWNT wires, following the procedure depicted in Fig. 1. The CV curves of the fiber supercapacitor at scan rates of 10 to 200 mV/s possessed a rectangular shape within 0–0.8 V (Fig. 4a), corresponding to an ideal double-layer capacitive behavior. Additionally, the charge/discharge curves illustrated in Fig. 4b had symmetrical triangle shapes with no obvious IR drop at the initial portion of the discharge curve. These were believed to arise from the good electrical conductivity of CNT networks and effective charge propagation into the

CNT layers. The inherent high conductivity of the Ni-SWNT electrode was also confirmed by the EIS result in Fig. 4c.

The rate performance was showed in Fig.4d. When the scan rate increased from 10 to 200 mV/s, the specific capacitance decreased from 34.5 F/g to 21.7 F/g, maintaining 63% of the initial value. Specifically, at a scan rate of 50 mV/s, the specific capacitance was 24 F/g, which is comparable to previously reported CNT based fiber shaped supercapacitors.[1] The degraded rate performance compared with that measured in three-electrode system were attributed to the slow charge-discharge kinetics of Ni-SWNT wire in the gel electrolyte. In other words, when the scan rate is high, it is difficult for the ion to diffuse and access the surface of the CNTs and Ni wire in such a short time.[36-37]

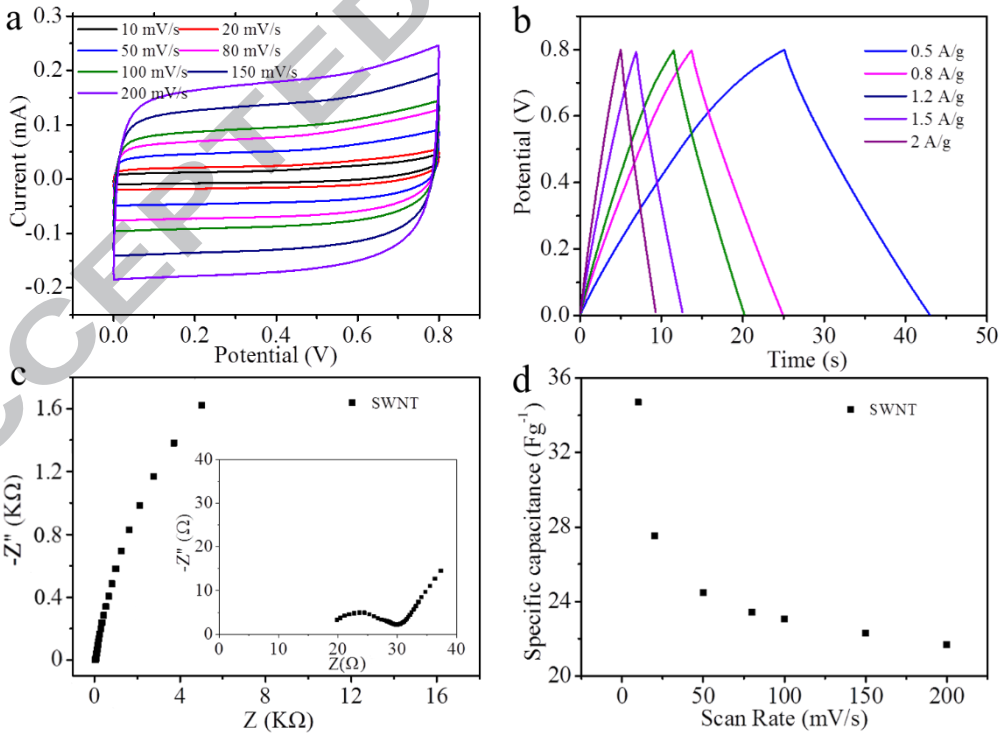


Figure 4. Electrochemical performance of two-ply Ni-SWNT based WSS. (a) CV curves; (b) Galvanostatic charge/discharge curves; (c) EIS of Ni-SWNT based

WSS, the inset gives the expanded view of Nyquist plot at the high frequency range; (d) Dependence of specific capacitance on the scan rates. The specific capacitance was calculated from CV curves in (a).

The electrochemical properties of the Ni-SWNT based WSS under mechanical deformation, were also studied and compared with the undeformed capacitor, to evaluate the device flexibility (Fig.5). A bending of $45^{o}$ angle was applied to the wire-shaped capacitor. Both the unbent and bent WSSs showed a capacitance retention of above 93% over 1000 cycles, revealing the good flexibility and electrochemical stability of the electrode. Furthermore, after 3000 charge-discharge cycles, the specific capacitance of the bent WSS was maintained at 83%, comparable to 86% of the unbent one. It was supposed that the multi-layer CNT network structure could buffer the damage to the coating layer under strain. Hence, when the CNT layer was combined with the ductile Ni wire, the composite electrode was capable of withstanding large deformation without sacrificing electrical conductivity. In addition , the gel electrolyte, which had high viscosity, bound different parts of the WSS together, guaranteeing the structural integrity under bending condition.

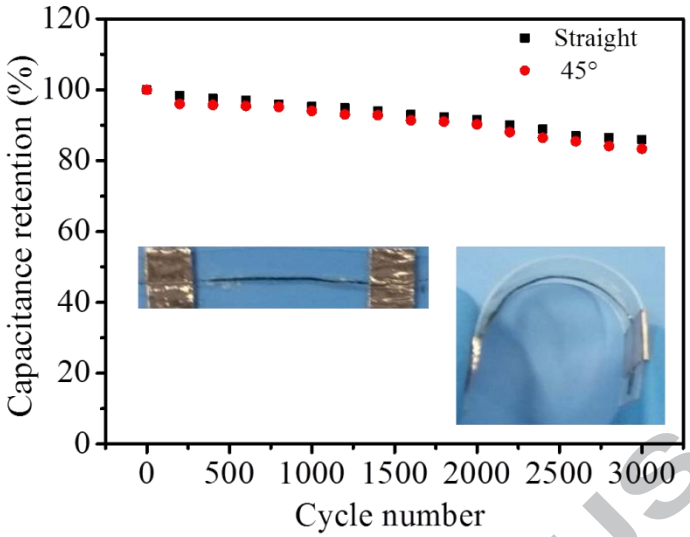


Figure 5. Cycling stability of the fiber supercapacitor before and after bent at 45 degree upon charging/discharging at a current density of 0.8 A/g. The insets depict the WSSs at the original (left) and bent states (right).

## 4. Conclusions

A capillary effect driven coating process was developed to prepare composite fibers of Ni wire and carbon nanomaterial, GO and SWNT. It is revealed that, although GO sheets often served as a good composition for the composite electrode, the assembly process should be carefully designed to avoid hindering the electrolyte infiltration by close packing of GO and improve the electrochemical performance. The combination of CNTs with Ni wire was found to yield excellent electrochemical performance and used to fabricate a flexible WSS. The incorporation of CNT coating effectively maintained the high conductivity of the electrode, ensured high contact area between the electrode and electrolyte, and thus endowed the assembled WSS with high specific capacity, desirable flexibility and cycling stability. The specific capacitance

still maintained at 30 F/g after 3000 cycles under a 45$^{o}$ bending.

**Acknowledgements**

This work is jointly supported by NSFC (51772157, 61504062), Jiangsu Provincial NSF (BK20150863, BK20160890), Priority Academic Program Development of Jiangsu Higher Education Institutions (YX03001), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Synergistic Innovation Center for Organic Electronics and Information Displays, Jiangsu Province "Six Talent Peak" (2014-XCL-014), Qing Lan Project of Jiangsu Province, Jiangsu Higher Education Institutions NSF (17KJB430026), and Scientific Research Foundation of NUPT (NY217012).

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**Supporting Information**

I. Capillary effect driven coating of carbon nanomaterials onto the surface of nickel wire.

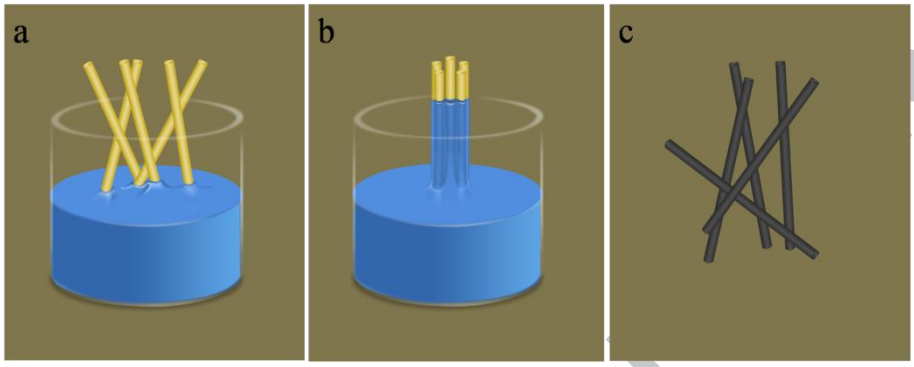


Figure S1.Schematics for the capillary effect driven assembly. (a) The metal wires dipped randomly in the dispersion of coating nanomaterials, with no coating on the wire above the liquid surface; (b) Capillary effect occurred when the bundle of the meatal wires were dipped into the dispersion solution, with even coating of carbon nanomaterials along the wire; (c) The composite electrode of Ni wire coated with layer of carbon nanomaterials after drying.

II. Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) characterization of the reduced graphene oxide (RGO) and GO.

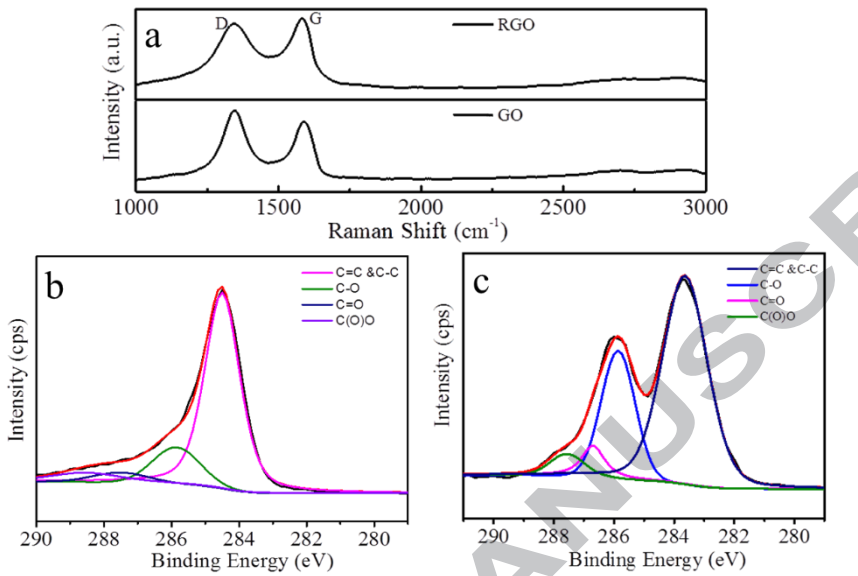


Figure S2. Raman spectroscopy and XPS results of the RGO and GO materials. (a) Raman spectra of GO sheets before and after the reduction; (b, c) XPS spectra of the RGO and GO sheets.

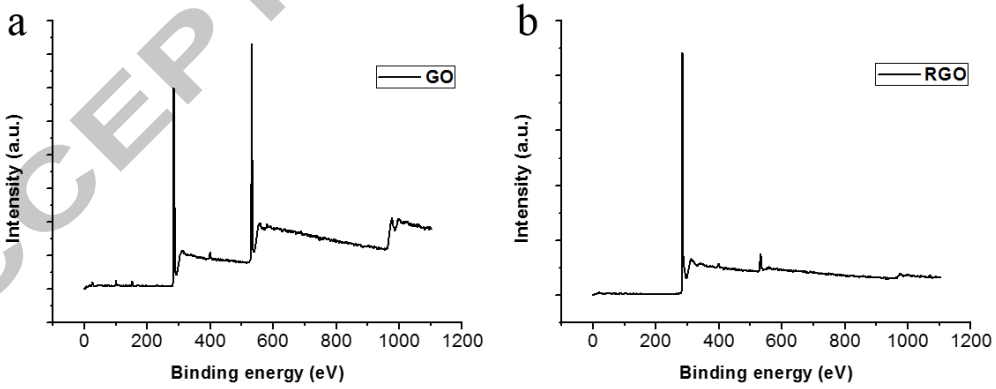


Figure S3. XPS spectra of the RGO and GO materials. (a) GO; (b) RGO.

III. Characterization of the carbon nanotubes used for coating.

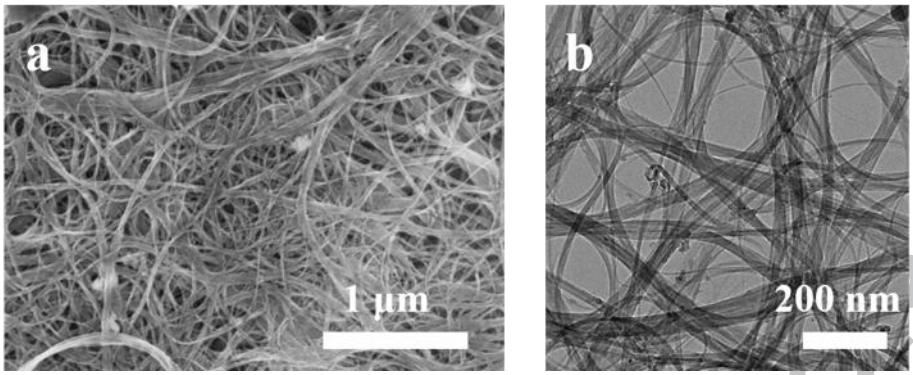


Figure S4. SEM image (a) and TEM image (b) of the SWNT sample.

IV. Characterization of the uniformity of the coating of the carbon nanomaterials on the Ni wire.

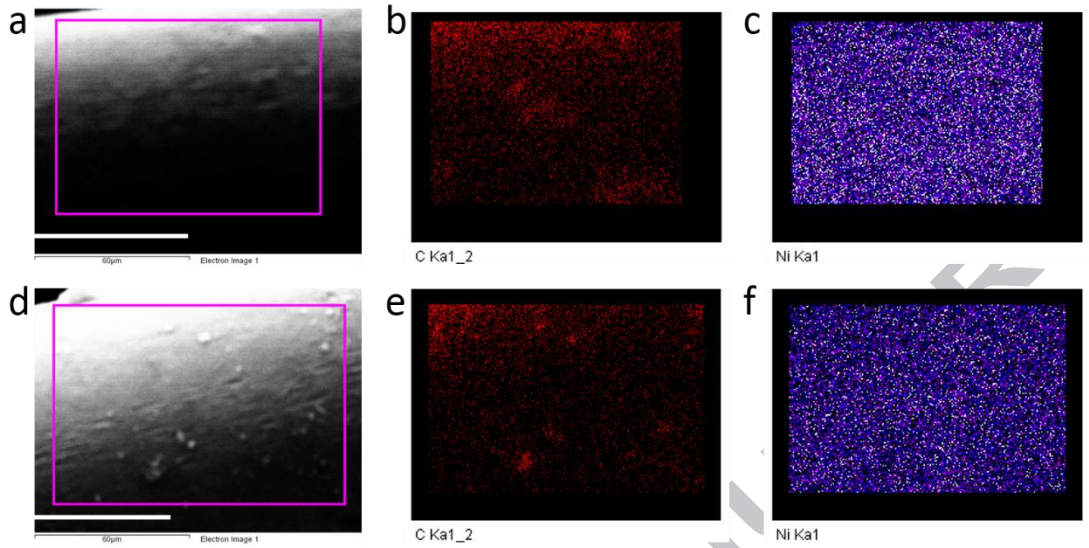


Figure S5. Investigation on the distribution of carbon nanomaterials on the Ni wire by EDX mapping. (a-c) The carbon elemental mappings of the Ni-RGO wire; (d-f) The nickel elemental mappings of the Ni-SWNT wire. The scale bars in (a) and (d) are both 60 um.

V. The plots of potential vs time for bent and unbent WSSs.

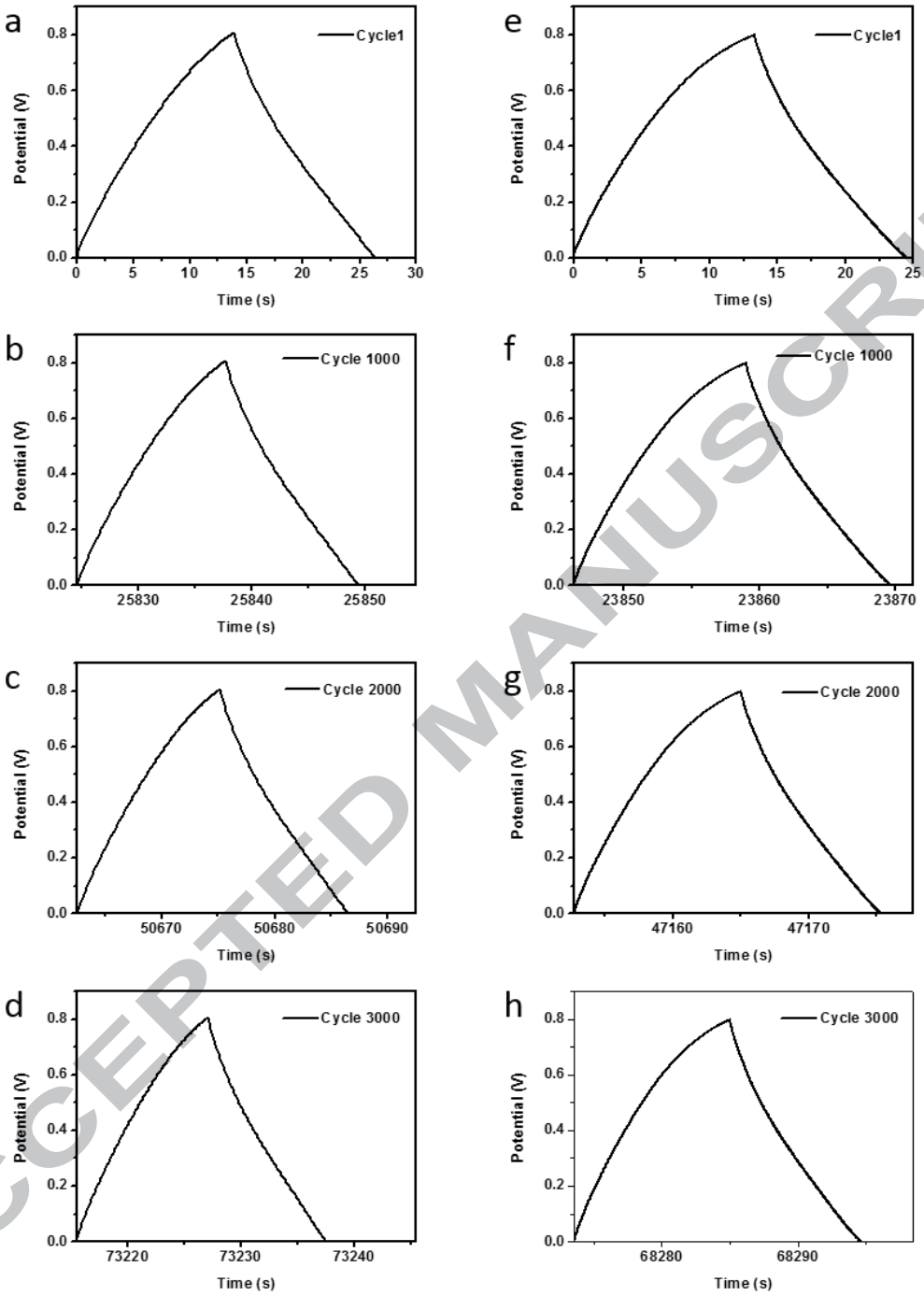


Figure S6. The galvanostatic charge/discharge curves of the Ni-CNT based WSSs at the original and bent states after 1, 1000, 2000 and 3000 cycles. (a-d) The charge/discharge curves of the WSSs at the original state; (e-h) The charge/discharge curves of the WSSs with a 45$^{o}$ bending. An interval of 30 s at X axis was set for the supercapacitors at the original state, and a 25 s interval for the

bent ones.

Table S1. The capacitance of the wire-shaped supercapacitors reported in this paper and in recent literatures.

| Electrode materials | $C_g$(F $g^{-1}$) | Ref |
|---|---|---|
| RGO on Ni wire | 28 at 0.1 V $s^{-1}$ | This work |
| CNT on Ni wire | 34.7 at 0.8 A $g^{-1}$ | This work |
| Gamma-Irradiated carbon nanotube | 9.2 at 0.1 A $g^{-1}$ | [S1] |
| Gamma-Irradiated carbon nanotube @PANI (polyaniline) | 82 at 0.1 A $g^{-1}$ | [S1] |
| Pt/CNT | 12 at 0.1 V $s^{-1}$ | [S2] |
| Pt/CNT@PANI | 72 at 0.1 V $s^{-1}$ | [S2] |
| CNT | 4.5 at 2 A $g^{-1}$ | [S3] |
| CNT@PANI | 274 at 2 A $g^{-1}$ | [S3] |
| nickel wire/pen ink | 25.8 at 2 A $g^{-1}$ | [S4] |
| Aligned CNT sheets on elastic fiber | 20 at 0.1 A $g^{-1}$ | [S5] |

Table S1 compares the Cg of the CNT/Ni and RGO/Ni wire-shaped supercapacitor in this paper and other wire-shaped supercapacitors reported in recent literature. The CNT/Ni has a much higher Cg than most of the CNT or CNT/metal wire based supercapacitor at similar scanning rates. It is noteworthy that improvement of the capacitive performance strongly depends on the involvement of the conductive polymer PANI. These facts indicate that the good performance has been achieved a by more convenient method and cheap metal wire substrate in our work.

**References**

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**Graphical abstract**