

# Fabricating CNT/ PEDOT:PSS Composite on Flexible Substrate Using Transfer Printing

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## ABSTRACT

In this paper, we propose a novel approach to fabricate CNT/ PEDOT:PSS composite with transfer printing, in which the highly oriented CNT could be obtained. The preparation of CNT/PEDOT:PSS composite started with the synthesis of the CNT films on Ni catalyst substrate using an ECR-CVD system at 500 °C. At the same time, PEDOT:PSS was spun coated on oxygen pretreated ITO substrate with a controllable thickness. Finally, CNT were applied in contact with PEDOT:PSS film. To enhance the adhesion of CNT with PEDOT:PSS, the samples were baked under atmosphere. SEM results show that the morphologies of CNT/PEDOT:PSS composites depend strongly on the thickness of PEDOT:PSS. The most dense CNTs with vertically aligned feature was obtained for PEDOT:PSS films with a thickness of around 120 nm in this study. By controlling the orientations of CNTs in composites, the composite could possibly be applied to various fields.

**Keywords:** carbon nanotubes, CNT/PEDOT:PSS composite, transfer printing, flexible electrode

## 1 INTRODUCTION

Carbon nanotubes (CNTs) have been considered to be a potential material for flexible electronic applications as a contact layer, due to their high conductivity, stability, optical transmittance and/or mechanical properties. Recently there are a lot of researches focusing on replacing conventional transparent conductive oxide (TCO) by either CNT or CNT/conductive polymer composites for organic light-emitting diodes or organic solar cells [1-2]. CNT and CNT composites have also been used in dye-sensitized solar cells (DSSCs) as the counter electrodes to catalyze the reactions of iodide/tri-iodide redox couple [3-4]. Depending on different applications, the morphologies of CNT or CNT polymer films should reveal either horizontally laid network or vertically aligned feature. However, to build integrated carbon nanotube-polymer-based systems, it is necessary for one to have a state-of-the art ability of incorporating organized nanotube architectures.

The common methods of preparing CNTs/polymer composites are solution processing, melt processing and reaction processing. Among these methods, the solution processing is the most effective way to prepare composites

with homogeneously distributed CNTs [5]. However, it relies strongly on the efficient dispersion of nanotubes in the used solvent. CNTs, nevertheless, has an intrinsic problem of insolubility in most solvents [6]. In addition, the orientation of CNTs is uncontrollable in the solutions. These disadvantages brought us to propose a novel transfer method to fabricate CNT polymer composites.

This work reports how poly(3,4-ethylenedioxythiophene) polymerized poly(4-styrenesulfonate) (PEDOT:PSS) is used to link CNTs on a flexible substrate to keep high conductivity of CNT polymer composites. The relationship between the conductivity of CNT polymer composites and the degree of orientation of CNTs are discussed.

## 2 EXPERIMENTAL

### 2.1 Preparation of CNTs

The synthesis of CNTs started with the deposition of a 3-nm-thick nickel catalyst layer on an n-type silicon substrate of 10 mm x 10 mm by e-beam evaporation at room temperature. The Ni coated Si wafer was then surface treated with nitrogen (N<sub>2</sub>) plasma under a pressure of 1x10<sup>-2</sup> torr, at microwave power of 260 W for 40 s. After the plasma treatment, Ni film appeared to be individual particles spreading all over the substrate. The average particle size is around 20 nm - 30 nm. The presence of Ni catalytic particles is necessary for the growth of carbon nanotubes with chemical vapor deposition (CVD).

The vertically-aligned CNT films were prepared in an electron cyclotron resonance chemical vapor deposition (ECR-CVD) system with a base pressure below 10<sup>-6</sup> torr. In order to decrease the carbon feedstock, methane (CH<sub>4</sub>), in steady of ethylene (C<sub>2</sub>H<sub>2</sub>) was chosen as the reactive gas to mix with N<sub>2</sub>. The flow rates of CH<sub>4</sub>/N<sub>2</sub> were set to 20 sccm/20 sccm and the applied microwave power was fixed at 450W. In 20 min of deposition, the pressure was regulated at 1x10<sup>-2</sup> torr and the substrate was heated to 500°C with a halogen lamp.

The morphology and microstructure of CNTs films were analyzed using scanning electron microscopy (SEM) and field emission gun transmission electron microscopy (FEG-TEM), respectively. From the cross-sectional SEM images, the ECR-CVD grown CNTs revealed vertically-aligned characters and the average lengths of CNTs were 1.5 - 2.4µm.

## 2.2 Preparation of PEDOT:PSS

Indium tin oxide (ITO) coated PET (with resistance of  $80 \Omega/\text{sq.}$ ) was used as the flexible substrate, on which the conductive polymer PEDOT:PSS (CLEVIOS™ PH 1000, solid content 1.0 - 1.3 % from Heraeus) was coated. To enhance the wettability of PEDOT:PSS on PET substrate, ITO surfaces were pretreated by oxygen plasma under the pressure of 100 mtorr at RF power of 70W for 10min. The contact angle, measured by water drop test, dramatically decreased from  $100^\circ$  to  $20^\circ$  after the oxygen plasma treatment. The pretreated PET was immediately coated with PEDOT:PSS using a spin coater. In the spin coating process, the spin rate was fixed at 1000 rpm in the first step for 10s to yield a uniform PEDOT:PSS initial layer. The spin rate was set to various values ranging from 1,000 to 2,500 rpm for the 2<sup>nd</sup> step to obtain thickness of desired.

The thickness, sheet resistance, and optical transmittance of PEDOT:PSS films were characterized by  $\alpha$ -step, four-point probe, and UV-VIS spectrometry, respectively.

## 2.3 Preparation of CNT/PEDOT:PSS Composites

The CNT/PEDOT:PSS composites were fabricated by transferring a vertically aligned carbon nanotube forest onto the oxygen-plasma-treated PEDOT:PSS/PET substrate. The transfer process was conducted at a temperature of  $120^\circ\text{C}$ . During the transfer process, a constant force of about 1 N was applied on CNT coated Si wafer in contact with PEDOT:PSS/PET substrate for 3 hours. This was followed by carefully peeling off vertically aligned CNT film from the Si substrate after the substrate was cooled down to room temperature. The vertically aligned CNT film was found well attached to the flexible PEDOT:PSS film to form the CNT/PEDOT:PSS composite. A schematic representation of the transfer method of CNTs on PET is shown in Fig. 1.

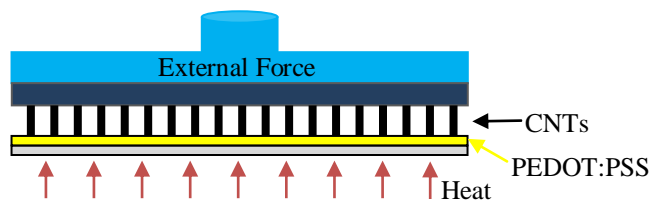


Figure 1: Schematic of the transfer method for fabricating CNT/PEDOT:PSS composites on PET.

## 3 RESULTS AND DISCUSSIONS

### 3.1 CNTs Forest

Fig. 2 (a) and (b) show the typical cross-section and top-view SEM images of CNTs films deposited on the Ni coated Si substrates. From Fig. 2 (a), one can see the

morphologies of deposited CNT films exhibit vertically aligned characters. Each of CNTs likes to stand alone on the substrate without forming a bundle. The average length of CNTs varied from 1.5 to  $2.4 \mu\text{m}$  over the whole surface of substrate. From the cross-sectional image, it is evident that the tip of CNTs is slightly bent especially when the length of CNT is over than  $1 \mu\text{m}$ . The bent CNTs tend to curl together as shown in top-view image Fig. 2(b).

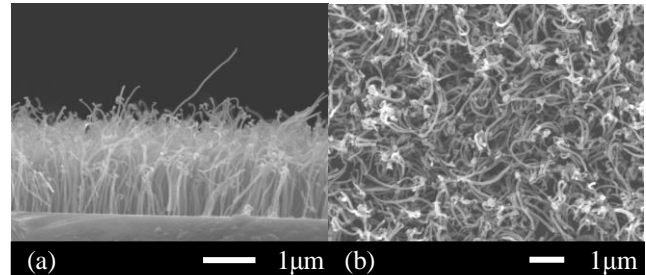


Figure 2: (a) cross-section (b) top view SEM images of ECR-CVD grown CNT films on the Ni coated Si substrate.

Fig. 3 is the TEM image of CNTs grown at the pressure of  $1 \times 10^{-2}$  torr. The CNT clearly shows a multi-walled structure. The outer diameter of the MWNT was measured to be in the range of 20 to 30 nm. Lin [7] reported that ECR-CVD generally provides a favorable condition for the formation of bamboo-like structure via the tip growth mode. In this study, the growth model of CNTs is supposed to be the base growth mechanism as shown in the insert of Fig.3. The bottom of CNT is constructed by the Ni particle having a cone shape, which is formed due to that the catalyst

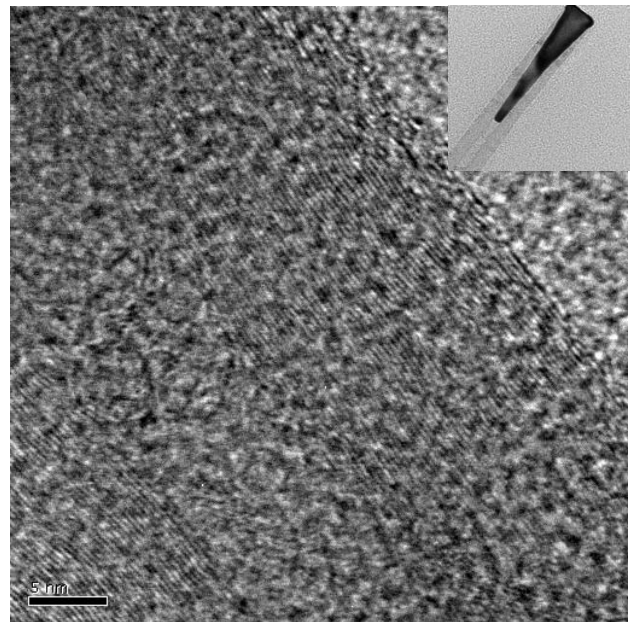


Figure 3: High resolution TEM image of CNTs grown on Ni coated Si substrate at pressure of  $1 \times 10^{-2}$  torr. The insert shows the CNT with the base of a Ni particle.

particle is in liquid or semi-liquid state during the growth process [8]. The hypothesis of base growth mechanism agrees with the previous interpretation on the carbon layer formation.

### 3.2 PEDOT:PSS on ITO Coated PET

Fig.4 (a) and (b) show the optical images of PEDOT:PSS coated on the non-pretreated and the oxygen plasma treated flexible substrate, respectively, using Confocal Laser Scanning Microscope. One can see that the substrate without pretreatment exhibits a rainbow-like image, which is attributed to the non-uniformity of coated PEDOT:PSS. The uniformity of PEDOT:PSS was improved by oxygen plasma treatment due to the improved wetting between PEDOT:PSS and ITO/PET. The decrease in the contact angle from  $100^\circ$  to  $20^\circ$  gives the evidence. The sheet resistance of ITO coated PET remains unchanged when the RF power of  $O_2$  plasma is kept below 300 W. Interestingly, coating of PEDOT:PSS was observed to improve the conductivity of PET substrate with a slight sheet resistance drop from  $80\Omega/sq.$  to  $72\Omega/sq.$

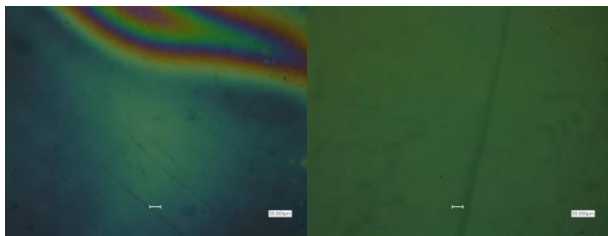


Figure 4: The optical images of PEDOT:PSS coated on PET (a) as deposited, (b) with oxygen plasma treatment.

Fig. 5 shows the transmittance and thickness of PEDOT:PSS layer as function of the spin rate of the second spin coating step at a constant time of 10s. The time and spin rate of the first step were fixed. The thickness of layer

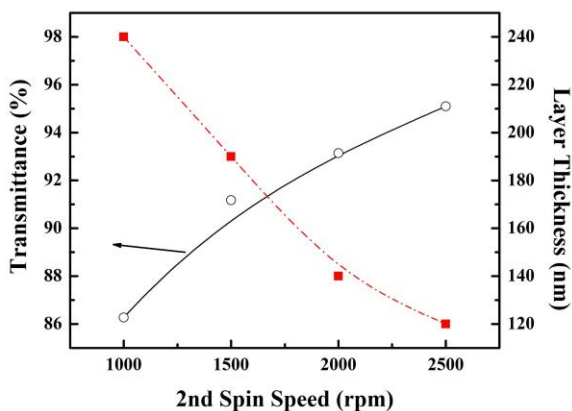


Figure 5: The transmittance and thickness of PEDOT:PSS layer vs. 2<sup>nd</sup> step spin rate.

is decreased from 240 nm to 120 nm when the spin rate is increased from 1000 rpm to 2500 rpm. Accordingly, the transmittance is increased with the decrease in the thickness. A high transmittance of 95% has been achieved for the PEDOT:PSS layer with a thickness of 120nm.

### 3.3 CNT/PEDOT:PSS Composites

The SEM images of CNT/PEDOT:PSS composites with various thickness of PEDOT:PSS prepared using transfer method are shown in Fig.6. Fig. 6(a) reveals the composite prepared from the use of droplet of PEDOT:PSS (without spinning). The thickness of the PEDOT:PSS droplet was not identified but was expected to be a few micrometers. It was observed that the CNT forests are entirely immersed in PEDOT:PSS solution in the course of transferring process. From the figure, the CNT/PEDOT:PSS composite shows a crown-like networking morphology with CNTs vertically aligned on the surface. The crown-like networking morphology may be caused by the inhaled micro-bubbles in PEDOT:PSS solution. However, in this case only part of CNTs was transferred. When the thickness of PEDOT:PSS is reduced to 120 nm by spinning, the CNTs grown on the silicon wafer could be completely transferred as shown in Fig 6 (b). The cross-sectional image (Fig.6 (c)) discovers that a 2.5  $\mu m$  thick vertical aligned CNT forest film has homogeneously grown on the top of the PET substrate. The

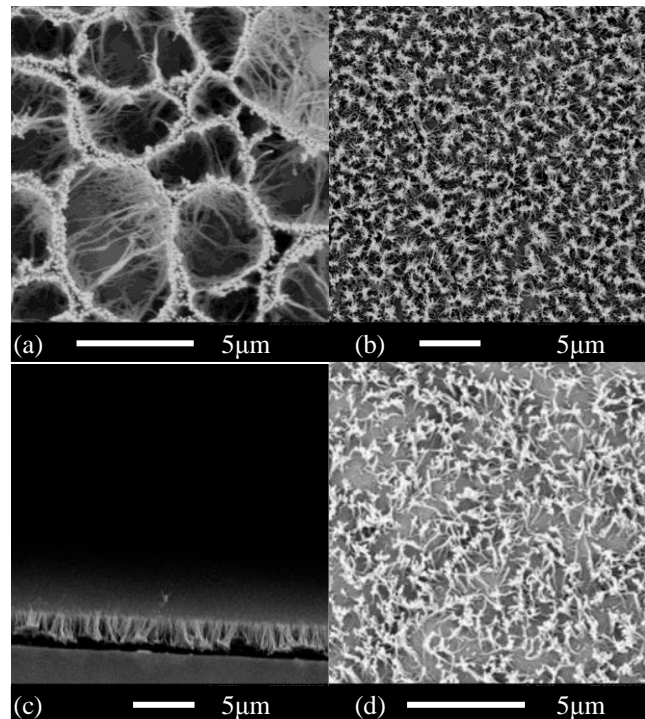


Figure 6: SEM images of CNT/PEDOT:PSS composites prepared with different thickness of PEDOT:PSS. (a) PEDOT:PSS droplet (b) PEDOT:PSS with 120 nm thick (top-view) (c) PEDOT:PSS with 120 nm thick(cross-section) (d) thickness of PEDOT:PSS < 100 nm.

surface of CNTs, however, appeared to be coated with polymer after the transfer process. As a result, the diameter of CNTs has been enlarged to 40 - 70 nm. This is believed due to that the PEDOT:PSS aqueous solution permeated into MWNTs film by capillary action during the transfer process. When the thickness of PEDOT:PSS is further decreased below 100 nm, the density of CNT transferred onto the PEDOT:PSS/PET surface is reduced again, as unveiled in Fig. 6(d). Such a result is suspected to be caused by the deficit of the incorporated PEDOT:PSS in CNT composite. In consequence, the transferred CNTs are lack of the support from PEDOT:PSS and would thus fail to construct the vertically aligned feature.

## 4 CONCLUSIONS

In conclusion, we have fabricated CNT/PEDOT:PSS composites in various morphologies through the proper controlled thickness of PEDOT:PSS. Results from micro-imaging of the composites reveal that the distribution and orientation of carbon nanotubes in CNT/polymer composites are controllable using the transfer printing approach. The most dense CNTs with vertically aligned feature was obtained for PEDOT:PSS films with a thickness of around 120 nm in this study. By controlling the orientations of CNTs in composites, the composite could possibly be applied to various fields.

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