Separation and ink formulation of high purity semiconducting single-walled carbon nanotubes with polymers for printed thin film transistors

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ABSTRACT

In this work, a new approach to selectively sort semiconducting single-walled carbon nanotubes (sc-SWCNTs) by regioregular poly(3-dodecylthiophene) (rr-P3DDT) has been reported. Effective separation of sc-SWCNTs has been demonstrated by tuning the types of solvent, temperature and centrifugation rate. Thin-film transistors (TFTs) using rr-P3DDT sorted sc-SWCNTs as semiconducting ink were fabricated on the SiO_2/Si substrate by inkjet printing technique. Printed TFTs showed good electrical properties with effective mobility up to 1.2 $cm^2V^{-1}s^{-1}$ and on/off ratio of 10^7. It is expected to use sorted sc-SWCNTs to fabricate printable logic circuits and other printable electronics.

Keywords: SWCNTs, thin-film transistors, rr-P3DDT, inkjet printing

1 INTRODUCTION

Printed thin film transistors (TFTs) have become one of the hot topics because they enable large-scale and flexible electronic systems to be produced without using complicated and costly lithography process.[1-7] The main chanllenge in printed high-performance TFTs is to fabricate printable inks with excellent properties. Semiconducting single-walled carbon nanotubes (sc-SWCNTs) have been regarded as one of the most important materials for preparing high-quality printable inks due to their excellent electrical properties, and stable chemical and physical properties.[8-17] Some reports have demonstrated that TFTs based on printed SWCNT inks showed good electrical properties with high on/off ratio and excellent charge mobility.[18-29] However, The undesired presence of metallic nanotubes along with semiconducting nanotubes is the major hurdle to obtain ideal semiconducting devices. In order to obtain high-purify sc-SWCNTs, various approaches have been developed to selectively remove or eliminate metallic species in commercial SWCNTs, including dielectrophoresis, selective oxidation, aromatic extraction, surfactant extraction, amine extraction, surface alignment, and selective polymer wrapping. It has been found that some polymers can selectively wrap sc-SWCNTs which separate the metallic tubes from semiconducting tubes. The sorted sc-SWCNTs exhibit excellent electrical properties.[30] However, very few work were reported on the electrical properties of TFTs made by printing the ink form of sc-SWCNTs sorted with polymers.

In the present work, we found that regioregular poly(3-dodecylthiophene) (rr-P3DDT) could be used to sort sc-SWCNTs from commercial CG 200 SWCNTs by tuning the types of solvent, temperature and centrifugation rate. Thin-film transistors (TFTs) using rr-P3DDT sorted sc-SWCNTs as semiconducting ink were fabricated on the SiO_2/Si substrate by inkjet printing technique, and effective mobility up to 1.2 $cm^2V^{-1}s^{-1}$ and on/off ratio of 10^7 has been achieved after annealing at 200 ^oC for 30 min. (the ratio of channel width and channel length is 30).

2 EXPERIMENT

2.1 Materials and Instrument

The purified CG 200 SWCNTs (diameter ~ 0.9 nm) were purchased from SouthWest Nanotechnologies (USA). Regioregular poly(3-dodecylthiophene) (rr-P3DDT) (M_w=50000-70000 $gmol^{-1}$) were purchased from Rieke Metals, Inc.. The materials were directly used without further purifications. A confocal Raman microscope (WITec CRM200) equipped with 633 nm lasers was used for Raman measurements. Optical absorption measurements were performed in a Perkin Elmer Lambda 750 UV-Vis-Nir spectrometer. All electrical measurements were carried out in ambient using a Keithley semiconductor parameter analyzer (model 4200-SCS). A NSCRIPTOR DPN system (NanoInk inc., IL, USA) and Dimension 3100 AFM (Veeco, CA, USA) was used in AFM imaging. The dielectric layer was a 300-nm SiO_2 layer on a heavily n-doped Si substrate as the bottom gate. The pre-patterned interdigitated electrode arrays with 3 fingers (finger dimensions: width 200 μm, length 20 μm, interfinger spacing 20 μm, ie. channel length and width are 20 μm and 600 μm, respctively.) were fabricated on SiO_2/Si substrates by lithography. Sorted sc-SWCNT solutions were printed by using a Dimatrix 2831 inject printer.

2.2 Preparation of printable SWCNT inks

To obtain sc-SWCNT inks, 2.5 mg of CG-200 SCNT was dispersed in 20 mL toluene with 5 mg rr-P3DDT using probe-ultrasonication for 30 min (Sonics ＆ Materials Inc., Model： VCX 130， 60W). The resultant mixture was then centrifuged at 21000 g for 3 h to remove metallic species and big bundles. The supernant was carefully collected and used to fabricate TFT devices without any other purification. Figure 1 showed the optical images of the resulting SWCNT inks before and after centrifugation.

Figure 1. the optical pictures of sorted sc-SWCNTs in toluene before (a) and after (b) centrifugation.

2.3 Fabrication of TFT Devices

Sorted sc-SWCNT solutions were printed onto the pre-treated devices, followed by drying at room temperature and washing with toluene for 3 times. The procedure was repeated 9 times until the density of sorted sc-SWCNTs was high enough to form a percolation path and to reach the desired current level. The prepared TFT devices were annealed at 200 °C for 30 min in vacuum oven, and then the electrical properties of SWCNT TFTs were measured.

The mobilities of SWCNT TFTs are estimated by $\mu = \left(\frac{dI_d}{dV_g}\right) \times \frac{L}{W} \times \frac{1}{C_i V_{ds}}$. Here, C_i is the oxide capacitance per unit area, which is determined by $\varepsilon_0 \varepsilon_r A/d$, where ε_0 is permittivity of free space (8.85×10^{-12}), ε_r is relative permittivity (3.9), A is unit area and d is the gate silicon oxide thickness (3×10^{-7}). L and W represent the channel length and width, respectively.

3 RESULTS AND DISCUSSION

In order to demonstrate that sc-SWCNT were selectively sorted from CG 200 by rr-P3DDT, the resulted solutions were characterized by UV-Vis-NIR spectroscopy. Figure 2a represented the adsorption spectra of CG 200 SWCNTs before and after sorting by rr-P3DDT. As shown in Figure 2a, the sc-SWCNT peaks in the range of 700 nm-1300 nm became very sharp, which indicates that sc-SWCNTs disperse well in toluene after reaction with rr-P3DDT.

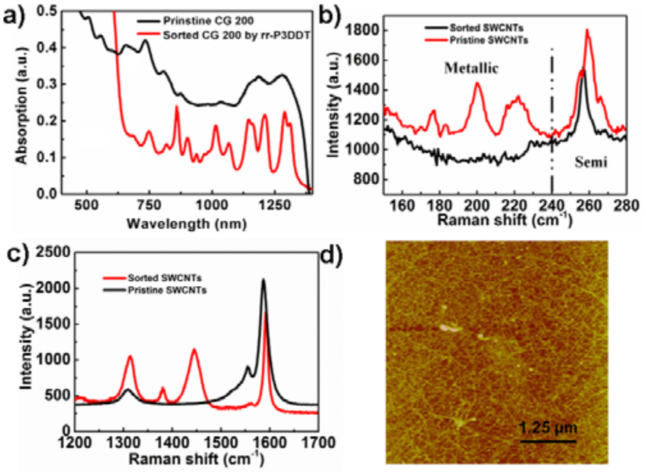

Figure 2. (a) Absorption spectra, and (b), (c) Raman spectra of SWCNTs before and after sorting by rr-P3DDT after centrifugation at 21000 g for 2 hours, (d) AFM image of sorted SWCNT by rr-P3DDT.

To further confirm the results, Raman spectra of pristine SWCNTs and the sorted SWCNTs were measured by a confocal Raman microscope (WITec CRM200) with the excitation energy of laser 633 nm (1.96 eV) wavelength. As shown in Figure 2b, the metallic peaks at about 175 cm^{-1}, 200 cm^{-1} and 220 cm^{-1} are observed in pristine SWCNTs under the 633 nm excitation. Furthermore, the corresponding G^- peaks (from metallic SWCNTs) at 1550-1580 cm^{-1} and G^+ peaks (from sc-SWCNTs) at 1590 cm^{-1} of pristine CG 200 and sorted SWCNTs were also measured. As shown in Figure 3c, the G^- band in pristine SWCNTs is noticeably broadened due to strong coupling of phonons to the electronic continuum of the metallic carbon nanotubes, however, it becomes sharp and integrated area of G^+/G^- ratio is higher than that of pristine samples after interaction with rr-P3DDT and centrifugation, indicating that metallic species are selectively removed. However, they are disappeared after interaction with rr-P3DDT in toluene and centrifugation. As described above, the semiconducting species with certain chiralities can be preferentially sorted from CG 200 SWCNTs by rr-P3DDT with the aid of sonication and centrifugation.

In order to ensure that sc-SWCNTs have been selectively sorted, the sorted SWCNT solutions were deposited on SiO_2/Si substrates with pre-patterned gold electrodes by inkjet printing method and the electrical properties of printed TFTs were then measured using Keithley 4200-SCS semiconductor parameter analyzer. Figure 3 shows the typical transfer and output characteristics of printed TFTs based on sc-SWCNTs before and after annealing 200 ^{o}C for 30 min. As shown in Figure 3, the device fabricated via inkjet printing exhibited high on/off ratio up to 10^7 and high charge mobility up to 1.2 $cm^2V^{-1}s^{-1}$. Figure 2d represents the typical AFM image of sorted CG 200 SWCNTs. As shown in Figure 2d, SWCNT density is very high and the diameters and lengths of sc-SWCNTs are about 2 nm and 1-4 µm, respectively.

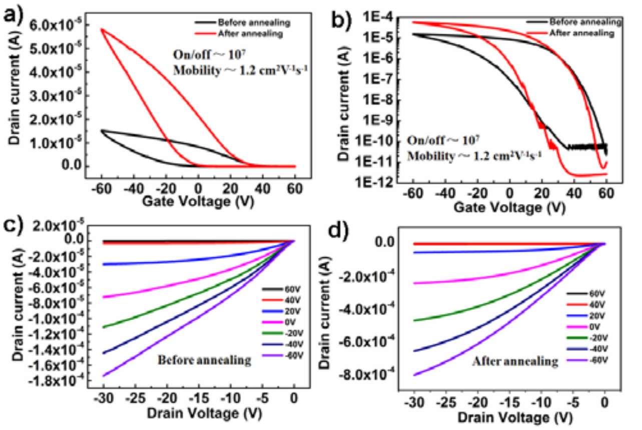

Figure 3. (a, b) Typical transfer and (c, d) outputcharacteristics of printed TFTs based on sorted sc-SWCNTs before and after annealing at 200 °C for 30 min.

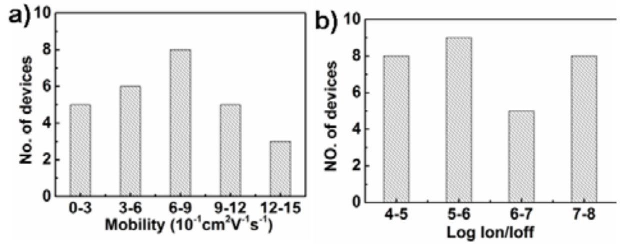

Figure 4. The histogram of (a) the mobility and (b) on/off ratios of TFT devices based on sorted sc-SWCNTs after annealing at 200 °C for 30 min.

Figure 4 showed the histogram of the mobility and on/off ratios of TFT devices made with sc-SWCNTs sorted with rr-P3DDT. The statistics was obtained from the printed devices after annealing at 200 °C for 30 min. As shown in Figure 4, all devices showed high on/off ratios ranging from 10^4 to10^8 and effective mobilities up to 1.5 cm^{2}V^{-1}s^{-1}.

4 SUMMARY

In summary, we have reported an effective approach to selectively sort and disperse sc-SWCNTs from CG 200 using rr-P3DDT in toluene. The absorption spectra, Raman spectra and electrical properties of SWCNT TFT devices demonstrated that semiconducting species of CG-200 SWCNTs were selectively sorted after interaction with rr-P3DDT in toluene with the aid of sonication and centrifugation. The sorted sc-SWCNT solutions were used as printable inks to fabricate SWCNT TFTs, and printed TFTs showed good electrical properties with mobility and on/off ratio up to 1.2 cm^{2}V^{-1}s^{-1} and 10^7, respectively. Furher work is underway to optimize the ink formulation and printing process to improve the performance of printed TFTs.

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