

# Research of organic field effect transistors based on semi-conducting single-walled carbon nanotubes\*

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The metal-conducting single-walled carbon nanotubes (m-SWNTs) with small diameters (0.7 nm–1.1 nm) are selectively removed from the single-walled carbon nanotubes (SWNTs) by using HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixed solution. Semiconducting single-walled carbon nanotubes (s-SWNTs) can be separated efficiently from the SWNTs with high controllability and purity based on this novel method, and the outcome is characterized by Raman spectrum. Moreover, the organic field effect transistors (OFETs) are fabricated based on the poly (3-hexylthiophene-2, 5-diyl) (P3HT), and untreated SWNTs and separated SWNTs (s-SWNTs) are mixed with P3HT, respectively. It could be found that the P3HT/s-SWNT device exhibits a better field effect characteristic compared with the P3HT device. The current on/off ratio is increased by 4 times, the threshold voltage is also increased from -28 V to -22 V, and the mobility is increased from  $3 \times 10^{-3}$  cm<sup>2</sup>/Vs to  $5 \times 10^{-3}$  cm<sup>2</sup>/Vs.

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Carbon nanotubes (CNTs) possess unique physical, optical, thermal and electrical properties for their potential applications, such as sensors, transistors, nanostructured solar cells and double-layer capacitors. In 1991, Iijima<sup>[1]</sup> observed the multi-walled carbon nanotubes (MWNTs) in the transmission electron microscopy (TEM) studies for the first time. Two years later, Iijima<sup>[2]</sup> and Bethune<sup>[3]</sup> independently produced the single-walled carbon nanotubes (SWNTs) with small diameter distribution, fewer defects, better uniformity and consistency. Until now, lots of researches on nanotubes have attracted intensive attention due to their advantages in transistor applications<sup>[4-6]</sup>. The SWNTs are mixed by metal-conducting single-walled carbon nanotubes (m-SWNTs) and semiconducting single-walled carbon nanotubes (s-SWNTs). The s-SWNTs are highly demanded at present for the applications in field effect transistors (FETs) and thin film transistors (TFTs). Therefore, many different methods have been attempted to separate the s-SWNTs or the m-SWNTs from the mixture. Recently, several approaches have been reported to solve this problem. One of the methods is to grow s-SWNTs preferentially<sup>[7,8]</sup>, and this approach needs to improve the

growth selectivity and efficiency. Another method relies on the separation between s-SWNTs and m-SWNTs<sup>[9-11]</sup>, which involves complicated physical/chemical processes. The third method is based on existing nanotube devices composed of bridging source-drain electrodes, in which the metallic tubes then burn off<sup>[12]</sup>. In this paper, we adopt a selective removal of the m-SWNTs with small diameters, in which the contamination and degradation of the SWNTs can not be produced. This efficient removal method shows a simple and controllable process compared with the above methods in other works. We obtain s-SWNTs with high purity and verify the outcome by the Raman spectrum. Moreover, the s-SWNTs are applied into the fabrication of three different organic field effect transistors (OFETs), and the P3HT/s-SWNTs device exhibits a better field effect characteristic which can be found from the carrier mobility, current on/off ratio and threshold voltage.

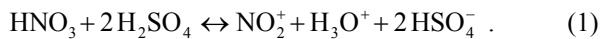
The SWNTs used in our experiment were purchased from sigma-aldrich, which were produced by catalytic chemical vapor deposition (CVD) process. The tube diameter of the SWNTs is about 0.7 nm to 1.1 nm, and the chirality (7,6)

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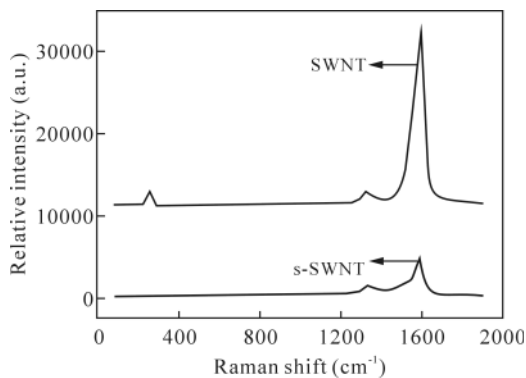
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distribution exceeds 50%. In the separation process, the 30 mg batches of SWNTs were immersed and stirred at room temperature in 30 ml mixture of HNO<sub>3</sub> (67%)/ H<sub>2</sub>SO<sub>4</sub> (97%) with the volume ratio of 1:9 for 36 h. This solution was diluted firstly for avoiding to break the membrane filter, then filtrated through the membrane filter with a pore diameter of 10 μm, and washed with deionized water for three times at last. The leftover nanotubes on the filter were dried and further heat-treated in Ar atmosphere for 1 h at 900 °C.

In the mixing procedure of HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>, the nitronium ions (NO<sub>2</sub><sup>+</sup>) can be produced in this solution, which is depicted as



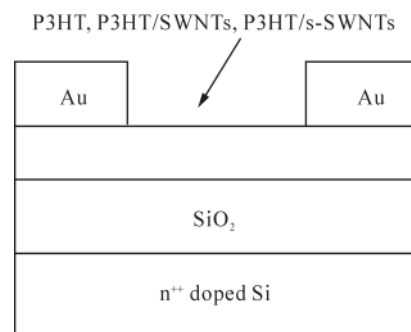
When dissolving the SWNTs in HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixture, different reactions will take place to m-SWNTs and s-SWNTs. NO<sub>2</sub><sup>+</sup> obtained from Eq.(1) preferably attacks the m-SWNTs, on which more available electron densities are at the Fermi level. After the reaction process, m-SWNTs were removed effectively, which are the SWNTs with small diameters less than 1.1 nm, especially in the range from 0.9 nm to 1.1 nm. In order to testify the purity, the production is characterized by the Raman spectra which are shown in Fig.1. From the spectra, the peak at 260 cm<sup>-1</sup> disappears compared with the m-SWNTs parts after the treatment of the mixed acids, in which NO<sub>2</sub><sup>+</sup> preferably attacks the m-SWNTs but not the s-SWNTs, which is consistent with the previous report<sup>[13]</sup>. Moreover, this removal process of acids treatment is also confirmed by the effects of the fabricated OFETs.



**Fig.1 Raman spectra of the SWNTs and s-SWNTs**

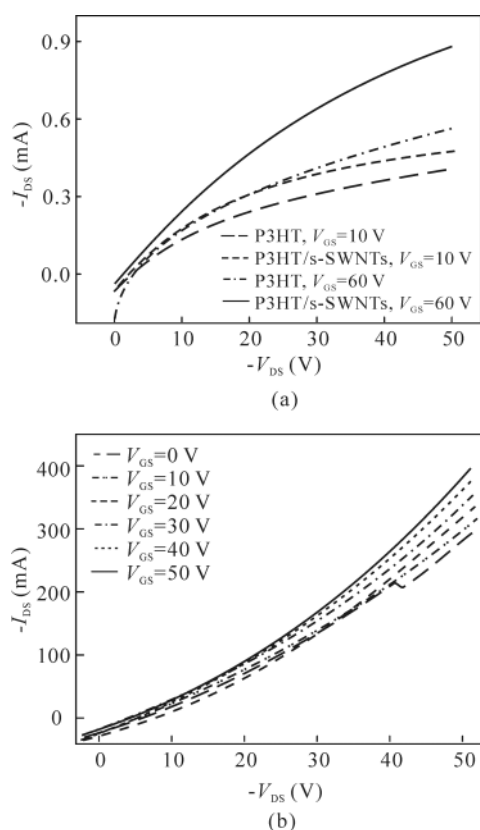
On the other hand, OFETs were fabricated using the top-contact OFET structure with an inorganic silicon dioxide (SiO<sub>2</sub>) gate insulator<sup>[14]</sup>, which is shown in Fig.2. The silicon wafer was etched with hydrofluoric acid and subsequently washed with deionized water, then dried in the vacuum oven for 3 h. Three devices were prepared with different kinds of

semiconductor layers, using the P3HT as the control device, the P3HT doped with SWNTs and the P3HT doped with s-SWNTs, respectively. In the first device (the control device), the concentration of P3HT is 2 mg/ml in o-dichlorobenzene solution. For the P3HT/SWNTs device (the P3HT doped with SWNTs) and the P3HT/s-SWNTs device (the P3HT doped with s-SWNTs), both SWNTs and s-SWNTs were firstly ultrasonicated for 12 h with the concentration of 1 mg/ml in o-dichlorobenzene solution, then stirred together with P3HT (2 mg) for 12 h. The films were spin-coated onto the silicon at a low speed of 800 r/min for 6 s and a high speed of 1500 r/min for 20 s successively. After that these devices were dried at 120 °C in the vacuum oven for 2 h so as to reduce the residual solvents. Subsequently, the Au (50 nm) electrodes were thermally evaporated by the self-made shadow mask under the pressure of about 3×10<sup>-4</sup> Pa in the glove box under Ar ambience. The evaporation rate is about 3 nm/s. The channel length (*L*) and width (*W*) in all devices are 50 μm and 5000 μm, respectively.



**Fig.2 Configuration of the OFET with top-contact structure**

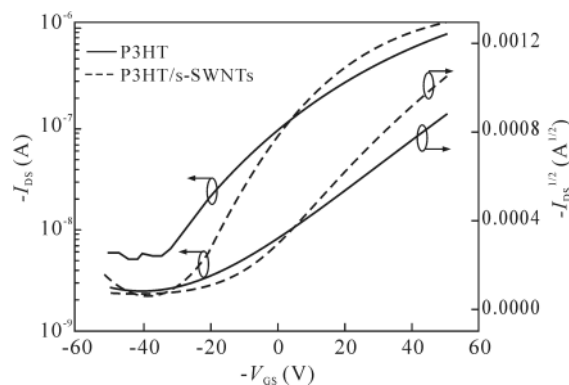
From the *I-V* measurement, the OFET device based on P3HT/SWNTs does not present any field effect, which is obviously shown in the Fig.3(b). The local current between the source and the drain is extremely high, because the SWNTs contain parts of the m-SWNTs which dominate the conducting property. However, the mono-doped device based on P3HT/s-SWNTs exhibits a preferable characteristic of field effect than the control device based on P3HT shown in Fig.3(a). For s-SWNTs, as a result of carrier confinement, most carriers can move in the single-layer graphite film along the axis of SWNTs rather than in the radial direction. So in the P3HT/s-SWNTs device, the carriers not only move in the directions of three-dimension for the P3HT film, but also transfer in one-dimensional structure<sup>[15,16]</sup>, when limited in the axial space of s-SWNTs. The carrier transport ability can be improved efficiently so as to enhance the device performance compared with the P3HT device.



**Fig.3 Output characteristics of (a) P3HT-based and P3HT/s-SWNTs-based OFETs and (b) P3HT/SWNTs-based OFETs**

Moreover, the analysis is put forward based on the improvement of carrier transport ability from the aspect of energy levels. The highest occupied molecular orbital (HOMO) level of P3HT is about -4.9 eV<sup>[17]</sup>, and the work function of s-SWNTs is about -4.7 eV<sup>[16]</sup>, which are consistent with the relevant reports. The HOMO of P3HT are slightly lower than the work function of s-SWNTs, and with the better carrier transport characteristic, the work function of s-SWNTs can act as a donor level of electrons in this host/dopant system (P3HT/s-SWNTs). It is universally acknowledged that the p-type organic semiconductor is apt to provide the free-electrons when the electrode applied with the high potential, which also means that the semiconductor favors the injection and trap for holes. The donor level of s-SWNTs provides another routine for electrons injected from this energy level to the HOMO of P3HT, which eventually offers more chances for the electrons to inject from the HOMO of P3HT to the work function of the Au (5.1 eV)<sup>[18]</sup>. It also means that the counterpart process facilitates the holes transport around the degenerate energy levels between the HOMO of P3HT and the donor level of the s-SWNTs. As a result, the carrier mobility can be enhanced in the device of P3HT/s-SWNTs. The threshold voltage ( $V_t$ ) is increased from -28 V to -22 V, the current on/off ratio ( $I_{on/off}$ ) is increased from  $1.38 \times 10^2$  to  $5.52 \times 10^2$ , and

the mobility is increased from  $3 \times 10^{-3} \text{ cm}^2/\text{Vs}$  to  $5 \times 10^{-3} \text{ cm}^2/\text{Vs}$ , which can be found in the transfer characteristics curves as shown in Fig.4.



**Fig.4 Transfer characteristics of the P3HT-based and P3HT/s-SWNTs-based OFETs at  $V_{DS} = -50 \text{ V}$**

In conclusion, we use an effective removal of the m-SWNTs with small diameters from 0.7 nm to 1.1 nm in the SWNTs by using  $\text{HNO}_3/\text{H}_2\text{SO}_4$  (1:9) mixed solution, and the outcome obtained by the removal method is characterized by the Raman spectrum which testifies the feasible removal of m-SWNTs from SWNTs. Three types of devices were successfully fabricated based on different semiconductors. It can be found that the P3HT/SWNTs device does not present any field effect characteristic, because the SWNTs have both s-SWNTs and m-SWNTs, in which the latter ones dominate the conducting property. Whereas the P3HT/s-SWNTs device exhibits a better field effect characteristic compared with the P3HT device. Meanwhile, the physical analyses are presented based on the configuration of device's energy levels. As a result, the transfer performance of  $I_{on/off}$  is increased by 4 times in the P3HT/s-SWNTs device,  $V_t$  is increased from -28 V to -22 V, and the mobility is increased from  $3 \times 10^{-3} \text{ cm}^2/\text{Vs}$  to  $5 \times 10^{-3} \text{ cm}^2/\text{Vs}$ . From this work, pure s-SWNTs could be obtained by effective removal method, and the field effect performance can be enhanced by doping s-SWNTs into P3HT semiconductors, which indicates that the performance of OFETs based upon the conventional materials can be improved by doping s-SWNTs for versatile applications.

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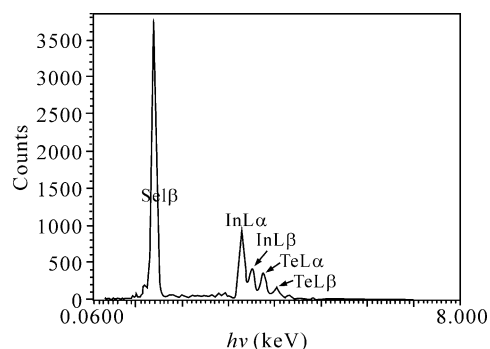
## Correction and Supplement

**Author: Abhay Kumar Singh**

**Title: Amorphous and nanophase microstructures of bulk Se-based chalcogenide alloys (Published on Vol.8 No.3)**

### ● Correction of figure

Fig.4(b) on page-0167 is corrected as follows:



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