

## Improved field emission properties of thiolated multi-wall carbon nanotubes on a flexible carbon cloth substrate

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2007 Nanotechnology 18 395702

(<http://iopscience.iop.org/0957-4484/18/39/395702>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 140.113.38.11

This content was downloaded on 26/04/2014 at 03:53

Please note that [terms and conditions apply](#).

# Improved field emission properties of thiolated multi-wall carbon nanotubes on a flexible carbon cloth substrate

F T Chuang<sup>1</sup>, P Y Chen<sup>2</sup>, T C Cheng<sup>2</sup>, C H Chien<sup>3</sup> and B J Li<sup>4</sup>

<sup>1</sup> Department of Material Science and Engineering, National Chiao-Tung University, Hsinchu 30050, Taiwan, Republic of China

<sup>2</sup> National Nano Device Laboratories, Hsinchu 30078, Taiwan, Republic of China

<sup>3</sup> Department of Electronics Engineering, National Chiao-Tung University, Hsinchu 30050, Taiwan, Republic of China

<sup>4</sup> Industrial Technology Research Institute (ITRI), Hsinchu 30050, Taiwan, Republic of China

E-mail: [pychen@mail.ndl.org.tw](mailto:pychen@mail.ndl.org.tw)

Received 1 May 2007, in final form 22 July 2007

Published 4 September 2007

Online at [stacks.iop.org/Nano/18/395702](http://stacks.iop.org/Nano/18/395702)

## Abstract

In this paper we report the observation of enhanced field emission properties from thiolated multi-wall carbon nanotubes (MWCNTs) produced by a simple and effective two-step chemical surface modification technique. This technique implements carboxylation and thiolation on the MWCNTs synthesized by microwave plasma chemical vapor deposition (MPCVD) on the flexible carbon cloth substrate. The resulting thiolated MWCNTs were found to have a very low threshold field value of  $1.25 \text{ V } \mu\text{m}^{-1}$  and a rather high field enhancement factor of  $1.93 \times 10^4$ , which are crucial for applications in versatile vacuum microelectronics.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Since carbon nanotubes (CNTs) were discovered by Iijima in 1991 [1], there has been increased interest in the study of electron field emission of CNTs, in particular for potential applications in field emission displays (FEDs), vacuum flat lamps, vacuum microelectronic sources, etc. [2–4]. Some unique physical properties, such as high aspect ratio, a whisker-like shape for optimum geometrical field enhancement, high electrical conductivity and extraordinary environmental stability, make CNTs promising candidates for cold cathode materials. In the past, field emission from patterned CNT thin films on silicon and various types of rigid substrates had been extensively studied [5–8]. However, these sorts of substrates are vulnerable to breaking. Therefore, the lighter, more durable and longer lifespan field emitters made on flexible substrates have recently attracted significant attention.

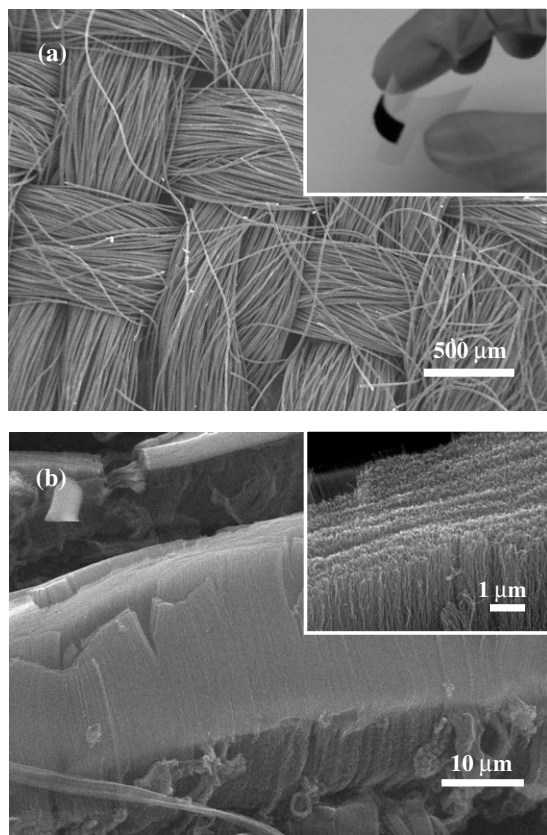
In 2004, Jo *et al* [9] and Banerjee *et al* [10] reported, respectively, the growth of CNTs or ZnO nanowires (ZnO NWs) on carbon cloth by thermal chemical vapor deposition (thermal CVD). We find that carbon cloth is intrinsically

a plastic and electrically conducting substrate, allowing the practical implementation of flexible electron sources for versatile vacuum microelectronics applications. In addition, carbon cloth is also considered to be a good cathode substrate due to its woven geometry, which provides an additional geometric enhancement effect to the overall field emission properties [9].

In this work, we report a study on surface chemical modifications on MWCNTs with the aim of improving the field emission properties of the MWCNTs grown on the flexible carbon cloth. Our experimental results obtained using a two-step chemical process show that thiolation of MWCNTs could significantly improve the field emission efficiency, and thus be very promising for the fabrication of low turn-on field and highly efficient electron emitters for flexible electronics.

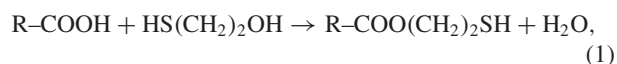
## 2. Experimental details

All MWCNT samples were grown by MPCVD on the flexible carbon cloth substrate [11]. A Fe film of 20 nm was used as a catalyst and patterned with a size of  $0.5 \times 0.5 \text{ cm}^2$ . The



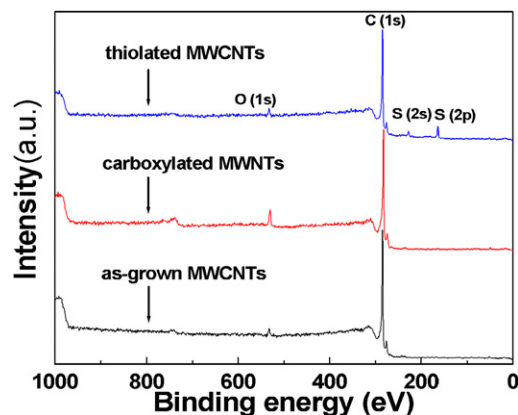
**Figure 1.** SEM images of (a) the pristine carbon cloth, the inset showing the bent flexible MWCNT field emission cathode and (b) MWCNTs thin film grown on carbon cloth.

reactant gases were a mixture of  $H_2$  and  $CH_4$  with a ratio of 90:30 sccm at a pressure of 10 Torr. The microwave power of 300 W was applied to generate the plasma. After heating at  $550^\circ C$  for 20 min with a bias of  $-50$  V, vertically aligned MWCNTs with similar height were uniformly grown over the carbon cloth. These as-grown MWCNTs then underwent a two-step chemical surface modification procedure. In step 1, MWCNTs were modified by 14 M  $HNO_3$  at  $90^\circ C$  for 12 h for the carboxylation of MWCNTs [12], i.e. caps of closed MWCNTs were removed, forming an open-ended shape. In step 2, the thiolation of MWCNTs was introduced by a method based on the pre-formation of carboxylic bonds of MWCNTs. After refluxing with deionized water to remove residual  $HNO_3$ , thiolated MWCNTs were obtained by reacting with 2 M 2-mercaptoethanol ( $C_2H_6OS$ ) in a dehydration reaction [13]:



at  $90^\circ C$  for 12 h. Finally, the residual  $C_2H_6OS$  was removed by ethanol.

The morphologies of as-grown and chemically modified MWCNTs were characterized by scanning electron microscopy (SEM, JEOL JSM-6500F) and transmission electron microscopy (TEM, JEOL JEM-4000). X-ray photoelectron spectroscopy (XPS, PHI 1600) measurement nets were employed to identify the chemical natures of MWCNTs before and after the carboxylation and thiolation processes.



**Figure 2.** XPS spectra of three types of MWCNTs. S 2s and S 2p emission peaks were revealed from the sample after surface thiolation.

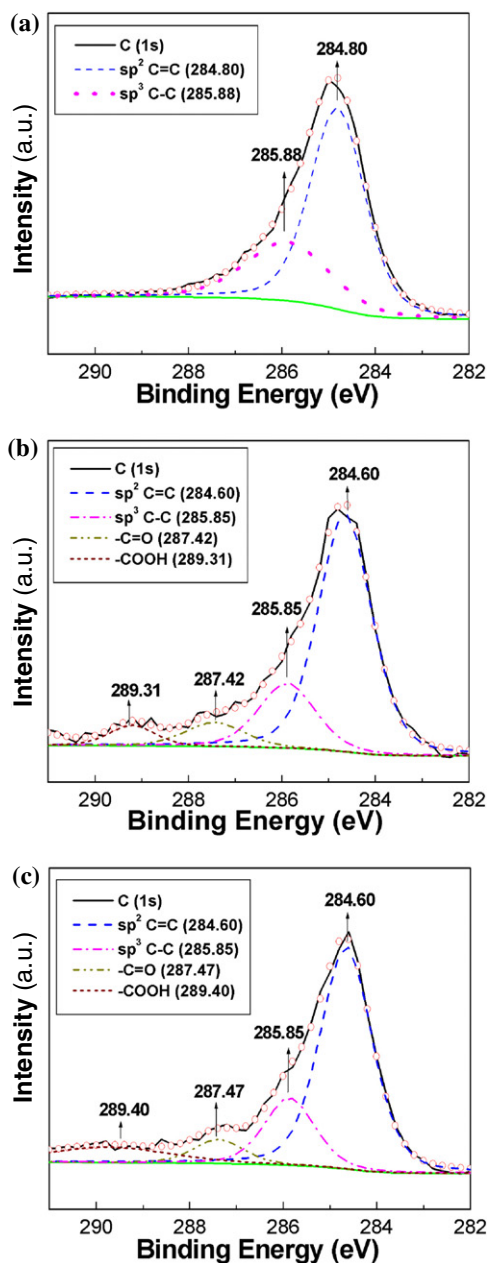
The field emission properties of the three types of MWCNTs (as-grown, carboxylated and thiolated) were measured using a planar diode in the vacuum chamber at a pressure of  $\sim 5 \times 10^{-7}$  Torr at room temperature. All samples with the same emission area of  $0.5 \times 0.5$   $cm^2$  were mounted on a stainless-steel plate as a grounded cathode. The anode was another stainless-steel plate with a much larger area than the cathode, in order to collect all emitted electrons. The distance between the anode and cathode was fixed at  $550 \mu m$  during the field emission measurement. The voltage applied on the anode was varied from 0 to 1 kV, to supply an electric field for extraction of the electrons from the MWCNTs. The emission current was monitored using a Keithley 237 picoammeter.

### 3. Results and discussion

Shown in figures 1(a) and (b) are the SEM images of a piece of the pristine carbon cloth composed of smooth textured carbon fibers and the MWCNT thin film grown on the carbon cloth, respectively. The inset of figure 1(b) is a magnified SEM image at the apex of the MWCNTs. It is seen that dense, extremely long (approximately  $20 \mu m$ ) and well-aligned MWCNTs adhered very well to the carbon cloth. The inset of figure 1(a) demonstrates the flexibility of MWCNT thin films grown on the carbon cloth, which was attached to the flexible indium-tin-oxide (ITO) template by the use of copper tape.

The effects of chemical modification were verified by the XPS measurements. Figure 2 depicts the overall spectra of XPS from three types of MWCNT samples. Besides some common features relating to C 1s and O 1s emissions, as marked in the spectra, two distinct peaks assigned due to S 2p ( $\sim 163.94$  eV) and S 2s ( $\sim 228.23$  eV) emissions were revealed from the sample after thiolation [13].

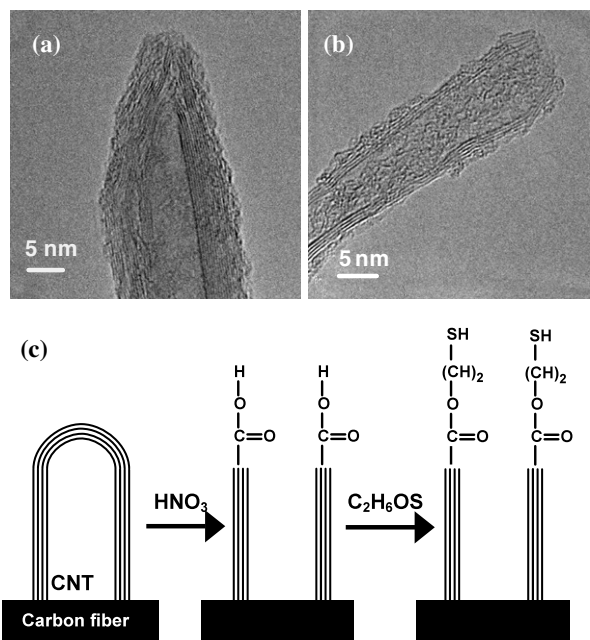
It is a bit difficult to analyze the bond configurations from the O 1s peak, since as a known effect, physically adsorbed oxygen molecules from ambient also contribute to all XPS spectra of MWCNTs. We therefore made a detailed analysis of the C 1s core-level peak shape on these three samples. Figure 3(a) shows that, for the as-grown samples, the C 1s emission was mainly composed of two components at 284.80 eV and 285.88 eV, respectively, as were obtained



**Figure 3.** C 1s core-level spectra of (a) as-grown, (b) carboxylated and (c) thiolated MWCNTs.

using deconvolution of the C 1s overall emission peak. These two components are known to be due to  $sp^2$  single-bond (C–C) and  $sp^3$  double-bond (C=C) carbon molecules, respectively, with one eV energy separation [14]. After carboxylation, the measured C 1s peak depicted some low-count intensity at the high-energy side (figure 3(b)). These features could be fitted by adding contributions due to C=O ( $\sim 287.42$  eV) and COOH ( $\sim 289.31$  eV) in peak deconvolution, indicating that the carboxyl groups were successfully introduced to the surface of MWCNTs via the oxidation of  $HNO_3$  [15].

Finally, after thiolation, the COOH peak intensity became lower, as illustrated in figure 3(c); at the same time, there was a slight decrease of the C=O peak intensity. Both observations imply that the chemical circumstance of C=O in the carboxyl



**Figure 4.** TEM images of (a) as-grown MWCNT and (b) MWCNT after oxidation by  $HNO_3$  (carboxylation), revealing an open-ended structure; (c) a schematic illustration of the sequence of chemical surface modifications on MWCNTs: as-grown, carboxylation and thiolation.

groups was changed due to the formation of thiol groups on top [13].

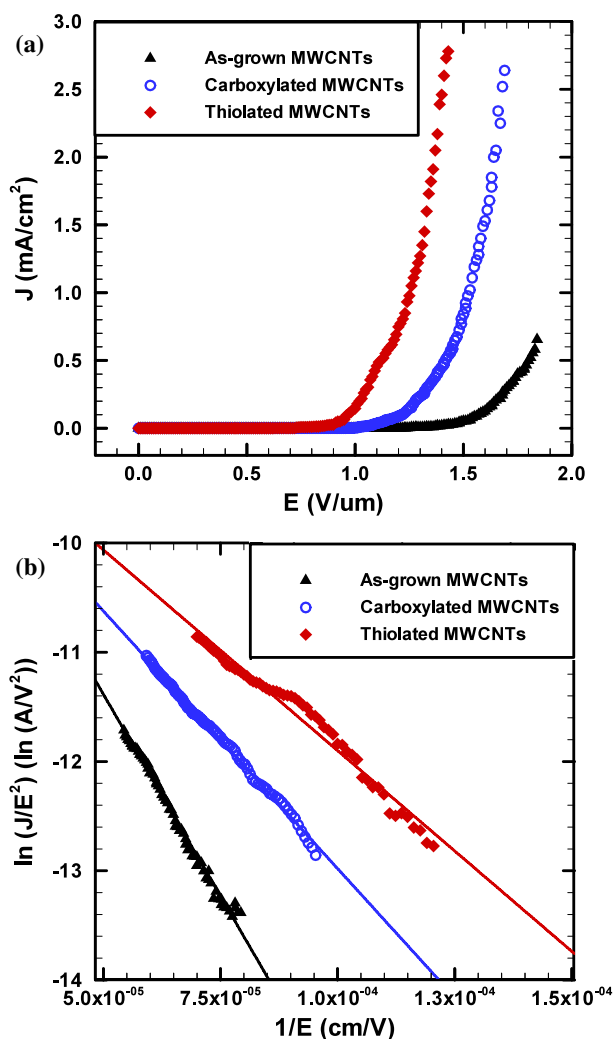
Figures 4(a) and (b) are the TEM images of the as-grown and carboxylated MWCNTs. One can clearly observe that there was an amorphous layer outside the crystalline structures of as-grown MWCNTs. After oxidation by  $HNO_3$ , the closed caps were etched away, accompanied by the partial removal of amorphous layers of MWCNTs [16]. The MWCNTs remain open-ended after thiolation (not shown). Figure 4(c) is a schematic presentation of how carboxyl and thiol functional groups were attached on top of MWCNTs using the surface chemical modification technique.

Figure 5(a) shows the measured emission current density versus the electric field ( $J$ – $E$  curves) of three MWCNT samples before and after surface chemical modifications. Obviously, the thiolated MWCNTs depict the lowest turn-on field of  $0.2 \text{ V } \mu\text{m}^{-1}$  and threshold field of  $1.25 \text{ V } \mu\text{m}^{-1}$ , which are defined as the value of macroscopic fields producing the emission current density of  $10 \mu\text{A cm}^{-2}$  and  $1 \text{ mA cm}^{-2}$ , respectively.

The detailed field emission properties of the three samples in this study are summarized in table 1. Field emission characteristics are analyzed using the Fowler–Nordheim (FN) equation [9]:

$$J = \frac{A\beta^2 E^2}{\phi} \exp(-B\phi^{3/2}/\beta E), \quad (2)$$

where  $J$  is the emission current density ( $\text{A cm}^{-2}$ ),  $E$  is the applied field ( $\text{V cm}^{-1}$ ),  $\phi$  is the work function of the MWCNTs,  $\beta$  is the field enhancement factor, which determines the amplification of the applied field, and  $A$  and  $B$  are



**Figure 5.** (a) Dependences of the measured field emission current density on applied field for as-grown MWCNTs ( $\blacktriangle$ ), carboxylated MWCNTs ( $\circ$ ) and thiolated MWCNTs ( $\blacklozenge$ ) grown on carbon cloth; (b) the corresponding Fowler-Nordheim plots.

**Table 1.** Field emission characteristics of three MWCNTs studied in this work.

Sample	Morphological feature	Turn-on field ( $V \mu m^{-1}$ )	Threshold field ( $V \mu m^{-1}$ )	Field enhancement factor
As-grown MWCNTs	Capped	0.5	—	$0.7 \times 10^4$
Carboxylated MWCNTs	Open-ended	0.34	1.52	$1.37 \times 10^4$
Thiolated MWCNTs	Open-ended	0.2	1.25	$1.93 \times 10^4$

constants with values of  $1.56 \times 10^{-6}$  ( $A eV V^{-2}$ ) and  $6.83 \times 10^7$  ( $V eV^{-3/2} cm^{-1}$ ).

The calculated FN plots of  $\ln(J/E^2)$  versus  $1/E$  are shown in figure 5(b) together with the experimental data. The linear relationship implies that the field emission of all three MWCNT samples in this work was dominated by the FN tunneling mechanism. Assuming the work function of CNTs

**Table 2.** A comparison of the threshold field (the emission current density is defined as  $1 mA cm^{-2}$ ) and field enhancement factor for various field emitters in the literature.

Emitters	Threshold field ( $V \mu m^{-1}$ )	Field enhancement factor	Ref.
ZnO nanowires on carbon cloth	0.7	41 100	[10]
SWNTs on silica	1.8	15 000	[20]
CNTs films	2.3	6 800	[21]
GaAs nanowires	6.5	3 500	[22]
Si nanowires	3.4	—	[23]
ZnO nanoneedle	6.5	1 464	[24]
ZnO nanocavity	11.6	1 035	[24]
ZnO nanotubes	17.8	910	[25]
ZnO nanorods	4.5	3 109	[26]
As-grown MWNTS on carbon cloth	—	7 000	This work
Carboxylated MWNTs on carbon cloth	1.52	13 700	This work
Thiolated MWNTs on carbon cloth	1.25	19 300	This work

is 5.0 eV, which seems appropriate for most MWCNTs [9], the field enhancement factor values  $\beta$  were determined by fitting to the slope of the FN plot, which were  $0.7 \times 10^4$ ,  $1.36 \times 10^4$  and  $1.93 \times 10^4$ , respectively, for the as-grown, carboxylated and thiolated MWCNTs. Again, the thiolated CNTs display the highest field enhancement factor among the three sample groups.

The fact that the field emission performance of the MWCNTs could be dramatically improved by the surface modification techniques employed in this work has been interpreted due to the combined effects of geometric enhancement of open-ended configuration and a lower electron affinity after surface thiolation. The effect that the circular sharp edge of open-ended MWCNTs could result in higher field amplification at the emission area was already demonstrated in [17–19]. Different from the previous work all using plasma post-treatment (PPT) with etchant gas (e.g. oxygen in [18, 19]), our approach is a wet chemical method that is very easy to process and cheaper in cost. In addition, the MWCNTs could be sharpened due to the removal of the surrounding amorphous carbon layer during the wet chemical process, which further improved the field emission properties. Moreover, the surface electron affinity in the thiol group is much smaller than that in C=C bonds [13]. Therefore, the electrons could be more readily emitted from the surface of the thiolated MWCNTs, which in turn leads to another significant enhancement of electronic field emissions. For a comparison, table 2 summarizes some results of the previously reported field emitters together with ours, at an emission current density level of  $1 mA cm^{-2}$  as the common reference. Our fabricated thiolated MWCNTs depict evidently a very low threshold field and a rather high field enhancement factor, compared with various field emitters in the literature.

#### 4. Conclusion

In summary, we have reported a simple, but very effective, two-step chemical modification technique that could produce

MWCNTs with excellent field emission properties on carbon cloth by thiolation. Our fabricated thiolated MWCNTs reveal a very low threshold field value of  $1.25 \text{ V } \mu\text{m}^{-1}$  and a rather high field enhancement factor of  $1.93 \times 10^4$ . The improved field emission properties of the thiolated MWCNTs were attributed to the combined effects of geometric enhancement of open-end MWCNTs and a lower electron affinity after thiolation, which have thus offered a useful solution with a large potential to fabricate low-threshold and high-efficiency field emitters for practical applications in flexible vacuum microelectronics.

### Acknowledgments

We thank Professor C F Chen of the Material Science Engineering Department, National Chiao-Tung University, Taiwan, Republic of China and C Chiu of Engineering Physics, Queen's University, Canada for fruitful discussions.

### References

- [1] Iijima S 1991 *Nature* **354** 56
- [2] Choi W B *et al* 1999 *Appl. Phys. Lett.* **75** 3129
- [3] Gangloff L *et al* 2004 *Nano Lett.* **4** 1575
- [4] Pirio G, Legagneux P, Pribat D, Teo K B K, Chhowalla M, Amaratunga G A J and Milne W I 2002 *Nanotechnology* **13** 1
- [5] Rinzler A G, Hafner J H, Nikolaev P, Lou L, Kim S G, Tomanek D, Nordlander P, Colbert D T and Smalley R E 1995 *Science* **270** 1179
- [6] Fan S, Chapline M G, Franklin N R, Tomblor T W, Cassell A M and Dai H 1999 *Science* **283** 512
- [7] Bonard J M, Kind H, Stockli T and Nilsson L O 2001 *Solid-State Electron.* **45** 893
- [8] Rao A M, Jacques D, Haddon R C, Zhu W, Bower C and Jin S 2000 *Appl. Phys. Lett.* **76** 3813
- [9] Jo S H, Wang D Z, Huang J Y, Li W Z, Kempa K and Ren Z F 2004 *Appl. Phys. Lett.* **85** 810
- [10] Banerjee D, Jo S H and Ren Z F 2004 *Adv. Mater.* **16** 2028
- [11] Chen C C, Chen C F, Hsu C H and Li I H 2005 *Diamond Relat. Mater.* **14** 770
- [12] Rajalakshmi N, Ryu H, Shaijumon M M and Ramaprabhu S 2005 *J. Power Sources* **140** 250
- [13] Kim Y T and Mitani T 2006 *J. Catal.* **238** 394
- [14] Okpalugo T I T, Papakonstantinou P, Murphy H, McLaughlin J, Brown N M D and McNally T 2005 *Fullerenes, Nanotubes, Carbon Nanostruct.* **13** 47
- [15] Xie J, Zhang N, Guers M and Varadan V K 2002 *Smart Mater. Struct.* **11** 575
- [16] Chen C M, Chen M, Peng Y W, Lin C H, Chang L W and Chen C F 2005 *Diamond Relat. Mater.* **14** 798
- [17] Pan Z W, Au F C K, Lai H L, Zhou W Y, Sun L F, Liu Z Q, Tang D S, Lee C S, Lee S T and Xie S S 2001 *J. Phys. Chem. B* **105** 1519
- [18] Saito Y and Uemura S 2000 *Carbon* **38** 169
- [19] Tanaka H, Akita S, Pan L and Nakayama Y 2004 *Japan. J. Appl. Phys.* **43** L427
- [20] Zhang L, Balzano L and Resasco D E 2005 *J. Phys. Chem. B* **109** 14375
- [21] Kumar A, Pushparaj V L, Kar S, Nalamasu O, Ajayan P M and Baskaran R 2006 *Appl. Phys. Lett.* **89** 163120
- [22] Zhi C Y, Bai X D and Wang E G 2005 *Appl. Phys. Lett.* **86** 213108
- [23] Zeng B, Xiong G, Chen S, Jo S H, Wang W Z, Wang D Z and Ren Z F 2006 *Appl. Phys. Lett.* **88** 213108
- [24] Zhao Q, Zhang H Z, Zhu Y W, Feng S Q, Sun X C, Xu J and Yu D P 2005 *Appl. Phys. Lett.* **86** 203115
- [25] Wei A, Sun X W, Xu C X, Dong Z L, Yu M B and Huang W 2006 *Appl. Phys. Lett.* **88** 213102
- [26] Li C, Fang G, Yuan L, Liu N, Ai L, Ziang Q, Zhao D, Pan C and Zhao X 2007 *Nanotechnology* **18** 155702