CHEMISTRY OF MATERIALS

VOLUME 18, NUMBER 18 SEPTEMBER 5, 2006

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Communications

Preparation of Single-Walled Carbon Nanotube−Organosilicon Hybrids and Their Enhanced Field Emission Properties

Yutaka Maeda,[†] Yoshinori Sato,[‡] Masahiro Kako,[§] Takatsugu Wakahara,[∥] Takeshi Akasaka,*[,∥] Jing Lu,[⊥] Shigeru Nagase,*[,#] Yumiko Kobori,[†] Tadashi Hasegawa,*[,†] Kenichi Motomiya,[‡] Kazuyuki Tohji,*[,‡] Atsuo Kasuya,[⊗] Dan Wang,[○] Dapeng Yu,[⊥] Zhengxiang Gao,[⊥] Rushan Han,[⊥] and Hengqiang Ye[⊥]

Department of Chemistry, Tokyo Gakugei University, Tokyo 184-8501, Japan, Graduate School of Environmental Studies and Center for Interdisciplinary Research, Tohoku University, Sendai, 980-8579, Japan, Department of Chemistry, The University of Electro-Communications, Tokyo 182-8585, Japan, Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba 305-8577, Japan, Mesoscopic Physics Laboratory, Department of Physics, Peking University, Beijing 100871, People's Republic of China, Department of Theoretical Molecular Science, Institute for Molecular Science, Okazaki 444-8585, Japan, and Department of Physics, Capital Normal University, Beijing 100037, People's Republic of China

Received May 11, 2006
Revised Manuscript Received July 17, 2006

Since single-walled carbon nanotubes (SWNTs) were discovered in 1993,[1] their unique physical and electronic properties have attracted considerable interest. SWNTs have been used as field emission sources of field emission display devices because of their unique structures and prominent stability.[2] It is well-known that adsorption of various gases on SWNTs leads to different field emission characteristics. For example, exposure of SWNTs to oxygen gas increases the turn-on voltage and decreases the field emission current,[3] whereas intercalation of Cs atoms decreases the turn-on voltage by a factor of 2.1−2.8 and increases the field emission current by a factor of 10 to the power of 6.[4]

Organosilicon compounds, in which extensive delocalization of σ electrons takes place along the silicon chain, have many unique and interesting electronic properties.[5] In this account, we report novel hybrid materials prepared from SWNTs and organosilicon compounds. Interestingly, the hybrid materials exhibit significantly enhanced field emission efficiency compared with pristine SWNTs.

SWNTs produced by the pulsed laser vaporization method of a metal/carbon target in a furnace at 1100 °C and purified by a previously reported procedure were obtained as toluene suspension from the Tubes@Rice. For the addition of silyl radical, the SWNTs were dispersed in benzene by ultrasonication. Irradiation of a degassed benzene suspension containing SWNTs (2 mg) and 1,1,2,2-tetraphenyl-1,2-di-*tert*-butyl-

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* To whom correspondence should be addresseed. E-mail: akasaka@tara.tsukuba.ac.jp (T.A.), nagase@ism.ac.jp (S.N.), tadashi@u-gakugei.ac.jp (T.H.), tohjik@mail.kankyo.tohoku.ac.jp (K.T.).

[†] Tokyo Gakugei University.

[‡] Graduate School of Environmental Studies, Tohoku University.

[§] The University of Electro-Communications.

[∥] University of Tsukuba.

[⊥] Peking University.

[#] Institute for Molecular Science.

[⊗] Center for Interdisciplinary Research, Tohoku University.

[○] Capital Normal University.

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10.1021/cm061100s CCC: $33.50 © 2006 American Chemical Society
Published on Web 08/08/2006

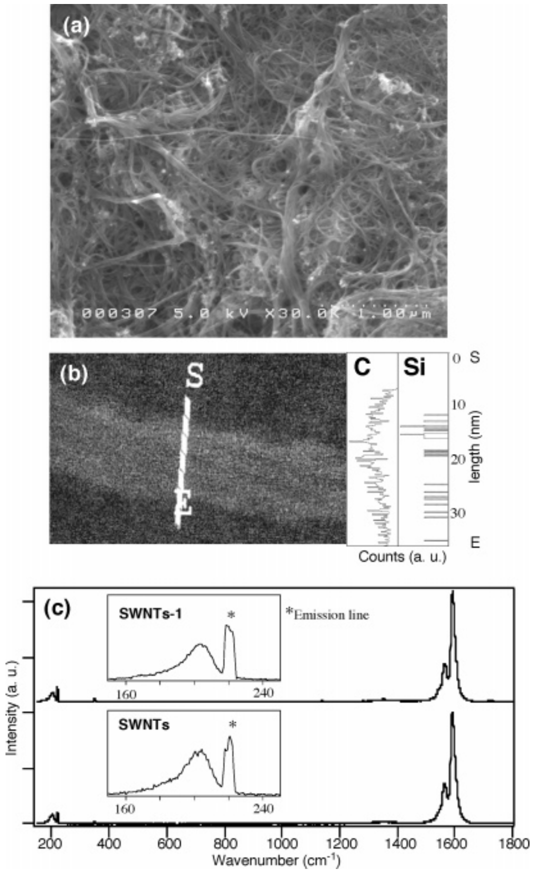

Figure 1. (a) SEM image of SWNTs-**1**. (b) EDS analysis of SWNTs-**1**. (c) Raman spectra of SWNTs and SWNTs-**1**.

1,2-disilane (**1**, 10 mg) with a low-pressure mercury-arc lamp resulted in formation of the silylated SWNTs (SWNTs-**1**). The SWNTs-**1** were collected and washed by toluene to remove residual silicon compounds. The SWNTs on which organosilicon compounds are adsorbed (SWNTs/**1**) were prepared from the ultrasonic treatment of a mixture of 2 mg of SWNTs and 10 mg of organosilicon compounds in 10 mL of benzene at room temperature. SWNTs/**1** were collected by filtration using a membrane filter, washed with benzene to remove free organosilicon molecules, and then dried. The carbene adduct of SWNTs (SWNTs-CH_2) was prepared from the reaction of SWNTs and diazomethane.[6] A SWNTs (50 mg) dispersion in toluene was added to the ether solution of diazomethane (large excess) at 0 °C and then stirred at room temperature under an Ar atmosphere in the dark. The reaction mixture was heated to 100 °C and then was collected and washed by toluene. The diazomethane was prepared from *p*-tolylsulfonylmethynitrosamide and Carbitor by the literature method.[7] (*Diazomethane is toxic and explosive.*)

Figure 1a is a scanning electron microscope (SEM) image of the SWNTs-**1**. SWNTs-**1** are clean and uniformly distributed in the form of bundles. The existence of silicon in the SWNTs-**1** was demonstrated clearly by energy dispersive X-ray spectrometry (EDS) line analysis, as shown in Figure 1b. Raman spectroscopy is useful for characterizing SWNT features.[8] As shown in Figure 1c, the typical Raman pattern of the SWNTs excited at 488 nm was observed. It shows the well-defined radial breathing mode at 200 cm^{-1}, a strong tangential mode at 1590 cm^{-1}, and a disorder mode with very low intensity at 1350 cm^{-1}. It is well-known that charge-transfer between SWNTs and dopant, such as alkali metals, shifts the tangential modes remarkably.[9] No significant difference in the tangential mode between pristine SWNTs and SWNTs-**1** was observed, although theoretical calculations (see below) reveal that about 0.7−0.8 electron is transferred from SiH_2 to SWNT. It may be due to the small number of silicon substituents on the sidewall of SWNTs bundles.

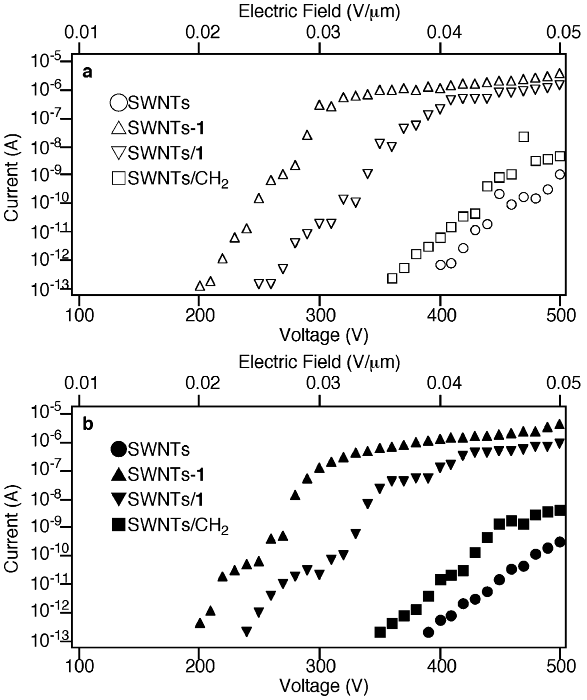

Figure 2. Plots of the field emission current vs voltage of SWNTs, SWNTs-**1**, and SWNTs-CH_2. (a) First scan. (b) Second scan.

The field emission currents were measured as a function of applied voltage at a pressure of 1.0×10^{-7} Torr for a spacer of 10 mm between a cathode of the SWNTs tips and an anode of the Faraday cup. Isosceles triangle-shaped SWNTs tips were cut out from the mats of SWNTs, SWNTs-**1**, and SWNTs/**1** using a razor and were fixed on top of hair-pin shaped wires using Ag paste to measure the field emission properties, respectively. The anode was electrically grounded, and the negative bias was applied to the cathode (up to 500 V). Weak and unstable currents were observed for each sample only at the first rising of the voltage around 150−200 V; these suggest removal of adsorbates. Current−voltage ($I-V$) properties were measured from 500 to 0 V.[9] From the $I-V$ characteristics (Figure 2a), the turn-on voltage decreases from 400 to 200 V/0.1 pA by silylation, and the

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field emission current increases from 10^{-8} to 10^{-6} A at a voltage of 500 V. SWNTs-CH_2 also show a lower gate voltage (350 V/0.1 pA) than SWNTs.[10] These results suggest that the chemical functionalization improves field emission properties of SWNTs significantly. The second measurements of the same SWNT tips showed the result similar to the $I-V$ properties of the first measurements, as shown in Figure 2b.

We have reported that the covalent combination of C_{60} and organosilicon compounds produces a new class of silylfullerene. The combining π and σ conjugated compounds have interesting characteristics, and the silylfullerene has lower oxidation and higher reduction potentials than the analogous carbon substituted derivatives as well as C_{60} itself.[11] This unique electrochemical property is the electron-releasing nature of silicon relative to carbon. In addition to the covalent combination, a noncovalent combination of C_{60} and organosilicon compounds was realized by Wang et al., who reported that doping of fullerene into polysilane enhances its charge-generation efficiency significantly.[12] We compared the field emission properties between SWNTs and the adsorbed adduct (SWNTs/**1**). SWNTs/**1** shows a lower gate voltage (250 V/0.1 pA) than SWNTs, suggesting that the intermolecular $\sigma-\pi$ interaction between SWNTs and the organosilicon compound also enhances effectively the field emission of SWNTs.

To understand the above experimental results, we have studied the interaction of SiH_2 and Si_2H_6 with the semiconducting (10,0) SWNT and that of SiH_2 with the metallic (5,5) SWNT by using local density functional theory. In the case of Si_2H_6-(10,0), a supercell containing double unit cells of the (10,0) SWNT is constructed, while in the case of SiH_2-(5,5), a supercell containing three unit cells of the (5,5) SWNT is constructed. Full geometry optimization was performed for both the atomic positions and lattice lengths by using the ultrasoft pseudopotential plane-wave program,[13] CASTEP,[14] with a cutoff energy of 240 eV. The convergence tolerance of force on each atom is 0.01 eV/Å. Static total energies of the relaxed structures are calculated with a larger 310 eV cutoff energy. An all-electron double numerical atomic orbital basis set[13] is employed to calculate the electronic energy bands. SiH_2 is adsorbed on the sidewall of the (10,0) SWNT (Figure 3a), and the adsorption energies are 2.11, 4.34, and 8.02 eV for one , two, and four SiH_2 groups per super cell, respectively (the corresponding ratio of Si:C is 2.5%, 5%, and 10%, respectively). The band gap of the (10,0) SWNT is reduced from 0.81 to 0.73, 0.53, and 0.23 eV, respectively, as a result of the formation of new bands in the band gap by SiH_2 addition (Figure 3b). Each SiH_2 group induces a new band in the band gap of the nanotube and donates about 0.7−0.8 electrons to the nanotube. Notably, the Fermi level of the (10,0) SWNT is elevated by 0.24, 0.46, and 1.06 eV, respectively, by one, two, and four SiH_2 additions per unit cell, suggesting a corresponding reduction of 0.24, 0.46, and 1.06 eV in the work function (in the first approximation, the work function is equal to the negative Fermi level).[15] Similarly, the Fermi level of the (5,5) SWNT is elevated by 0.10 and 0.50 eV by one and six SiH_2 additions per supercell (the corresponding ratio of Si:C is 1.7% and 10%, respectively). These remarkable reductions in the work function are in agreement with the measured remarkable reduction in turn-on voltage of field emission of SWNT upon silylation.

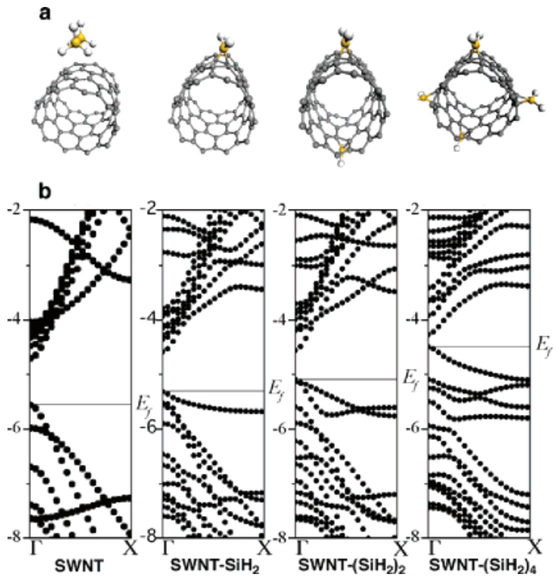

Figure 3. (a) Optimized structures of Si_2H_6-physisorbed (10,0) and SiH_2-adsorbed (10,0) SWNTs with one, two, and four SiH_2 per unit cell. (b) Electronic band structures of pure and SiH_2-adsorbed (10,0) SWNTs with one, two, and four SiH_2 per unit cell.

Covalent functionalization by CH_2 elevates the Fermi level of SWNTs in a less significant way than that by SiH_2. The Fermi level of the (10,0) SWNT is only elevated by 0.59 eV upon four CH_2 additions per unit cell, half the value of SiH_2 addition. This appears qualitatively consistent with the observed smaller enhancement in field emission upon CH_2 addition than organosilicon addition as shown in Figure 1. Si_2H_6 is physisorbed on the surface of the nanotube (Figure 3a) with an adsorption energy of 0.19 eV. The shortest atom-to-atom distance between Si_2H_6 and the (10,0) SWNT is 2.88 Å. No significant shift of the Fermi level is found at this concentration, but 0.01 electrons are transferred from Si_2H_6 to the nanotube. If the concentration of Si_2H_6 is increased by a factor of 10, the number of transferred electrons would be increased to about 0.1. These transferred electrons are likely to fill the conduction band rigidly and elevate the Fermi level as in the case of Cs doping.[16] Therefore, the mechanism of enhanced field emission upon physisorption of organosilicon can be understood in terms of a simple electron-transfer picture.

Extensive delocalization of σ electrons takes place along the silicon chain, giving rise to many interesting electronic

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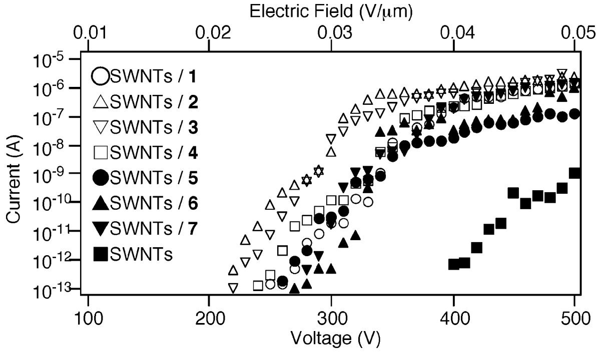

Figure 4. Plots of the field emission current vs voltage.

properties. For example, because of this σ-conjugation, the ionization potential is very sensitive to the silicon backbone. We attempted to expand this approach to other oligosilanes and polysilanes. The $I-V$ characteristic of the absorptive adducts SWNTs/**1**−**7** under the same condition also has an enhanced emission when compared to pristine SWNTs, as shown in Figure 4. All organosilicon compounds have improved the filed emission property of SWNTs. But the field emission property of these hybrid materials was not sensitive to the oxidation potential of the organosilicon compounds (Table 1). It was reported that not only oxidation potential but also the structures of the organosilicon compounds are important for the charge-generation efficiency of fullerene toward polysilane.[12]

In conclusion, the SWNT−organosilicon hybrids were prepared. In accordance with the significantly reduced work function found by density functional theory calculations, silylation of SWNTs significantly increases the field emission properties of SWNTs. The physisorption of organosilicon compounds on the surface of SWNTs is also effective for improvement of the field emission properties of SWNTs. Unlike the classical alkali metal doping, the hybrid materials of SWNTs with organosilicon compounds are stable under oxygen. This simple modification suggests a great potential industrial utilization as building blocks for field emission sources.

Table 1. (a) Turn-On Voltages for Various Film Field Emitters and (b) the Anodic Peak Potentials of Organosilicon Compounds[a]

a. Turn-On Voltages

compound	*V* (*V*)	compound	V (*V*)
SWNTs/*c*-$(Et_2Si)_5$ (**2**)	220	SWNTs/$Ph(SiPh_2)_3Ph$ (**5**)	260
SWNTs/$(Hex_2Si)_n$ (**3**)	220	SWNTs/*c*-$(Ph_2Si)_5$ (**6**)	270
SWNTs/$Ph_3Si(SiMe_2)_2$-$SiPh_3$ (**4**)	240	SWNTs/$(PhMeSi)_n$ (**7**)	280
SWNTs/$(t BuPh_2Si)_2$ (**1**)	250	SWNTs	400

b. Anodic Peak Potentials[a]

compound	*V* vs SCE	compound	*V* vs SCE
c-$(Et_2Si)_5$ (**2**)	1.62	$Ph(SiPh_2)_3Ph$ (**5**)	1.74
$(Hex_2Si)_n$ (**3**)	1.60[b]	*c*-$(Ph_2Si)_5$ (**6**)	1.61
$Ph_3Si(SiMe_2)_2SiPh_3$ (**4**)	1.76	$(PhMeSi)_n$ (**7**)	1.00[b]
$(t BuPh_2Si)_2$ (**1**)	1.90		

[a] The first anodic peak potentials scan rate; 50 mV/s, 0.1 M TBAP of a CH_2Cl_2 solution. [b] Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

Acknowledgment. This work was supported in part by the Kurata Memorial Hitachi Science and Technology Foundation and NEDO of Japan, and by a Grant-in-Aid, Nanotechnology Support Project and the 21st Century COE Program from MEXT of Japan. This work was also supported by NSFC and national 973 projects from MOST of China.

Supporting Information Available: Characterization of SWNTs-CH_2 (PDF). This material is available free of charge via the Internet at http://pubs/acs.org.

CM061100S