Chem. Phys. Lett. (2006) in press.

# Detachment of vertically aligned single-walled carbon nanotube films from substrates and their re-attachment to arbitrary surfaces

Yoichi Murakami, Shigeo Maruyama*

*Department of Mechanical Engineering, The University of Tokyo*

*7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

Received 31 December 2005; in final form 20 February 2006

**Abstract**

A method for detachment of vertically aligned single-walled carbon nanotube (VA-SWNT) films from substrates simply using hot water has been developed. The VA-SWNT films were peeled off spontaneously by submersing the substrate into heated (larger than 60 °C) distilled water, and the detached films floated on the water surface. The detached films could readily be re-attached onto arbitrary solid surfaces, and conservation of the vertically aligned morphology after the re-attachment was confirmed based on measurements by field-emission scanning electron microscopy, resonant Raman scattering, and optical absorption spectroscopy. A possible mechanism for the process of film detachment is discussed.

* Corresponding author. FAX: +81-3-5800-6983.

*E-mail address:* maruyama@photon.t.u-tokyo.ac.jp (Shigeo Maruyama).

## 1. Introduction

Single-walled carbon nanotubes (SWNTs) [1] have been studied in a wide range of research fields due to their unique physical properties [2]. After development of the chemical vapor deposition (CVD) method for growth of SWNTs [3], various experimental studies have been explored in fundamental and applied sciences [4]. We have developed techniques of alcohol catalytic CVD (ACCVD) [5,6] and dip-coat catalyst supporting method [7,8], and on these bases a method for synthesizing vertically aligned SWNTs (VA-SWNTs) over a large area of the substrates [9-11]. Because of their aligned morphology, the VA-SWNT films [12-15] are thought to have potential for facilitating investigation of the fundamental properties of SWNTs [16-18] and for exploring applications of SWNTs.

However, we should point out that the CVD process has had major problems in itself for full utilization of the potential mentioned above: First, typical CVD is done at 700 - 900 °C and most materials including normal glasses, plastics, and electronic circuits cannot stand such high temperatures. Second, catalytic growth of SWNTs with supported catalyst has been limited on stable oxides such as $SiO_2$, $Al_2O_3$, and MgO, and is usually impossible on common metals like Cr, Ti, Al, Cu, and Au, to the best of our knowledge including our cases.

For resolution of these problems, we have developed a method for detaching VA-SWNT films from their substrates and re-attaching them to other non-heat-resistive surfaces, as we report in this Letter.

## 2. Experimental and results

### *2.1. Preparation of the films*

Details of the synthesis and characterizations of VA-SWNT films have been reported in Refs. [11] and [18]. The VA-SWNT films were synthesized by ACCVD on both sides of an optically polished quartz substrate (thickness: 0.5 mm), on which Co-Mo catalyst was supported by the dip-coat technique [9,11]. Observation of the sample by high-resolution transmission electron microscopy (HR-TEM) revealed that the diameter of our VA-SWNTs ranged from 0.8 to 3.0 nm (average diameter ≈2.0 nm), consisting of only clean SWNTs being free from multi-walled carbons or amorphous carbons [18]. The reproducibility of the results described in the following was tested by repeated measurements, and the validity was confirmed within the range of the film thicknesses, 500 nm – 20 μm. It was possible to handle these films equally in this range of thickness, because mechanical toughness of the films was not the essential requisite for the method proposed below.

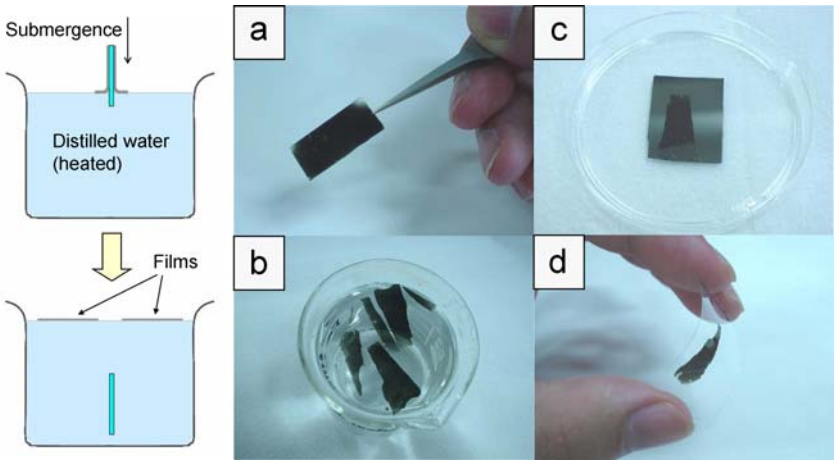


Fig. 1. Photos of the VA-SWNT films (a) before and (b) after detachment, and after re-attachment to (c) a Si substrate and (d) a transparent plastic film. All the films shown in (b-d) are the same as that in (a). The left figure shows schematic of the process.

### *2.2. Detachment of the films*

The procedure for the detachment of the VA-SWNT film was as follows: Distilled water (Wako Chemical Ltd, #047-16783) in a glass beaker set on a hot plate was heated up to 60 °C. A quartz substrate on which the films had been grown (hereafter called “the sample”), as shown in Fig. 1a, was perpendicularly submerged into the heated water (schematic in Fig. 1). The thickness of the film in the figure was 10 μm per side. As the sample was submerged slowly (roughly 2 ~ 5 mm/s), the films on both

sides started to depart from the substrate and moved laterally onto the water surface. In the end, the detached films floated on the water surface (Fig. 1b).

The key point of this technique was to use hot water above 60 °C. The films were hardly detached by water at room temperature (R.T.) (≡ 23 °C) with high reproducibility (only 1 out of more than 20 samples detached), whereas all of them were smoothly detached when the water was at 60 °C. The response of the VA-SWNT films to submersion into the water depended remarkably on the water temperature: When the water was at R.T., the films were not detached and the water was just repelled due to the hydrophobicity of vertically aligned carbon nanotube films [19]. At 40 °C, a part of the film fringes showed local detachment, and at 50 °C the films became detachable in the whole area though not smoothly. At 60 °C, the films were removed smoothly and wholly from the substrate.

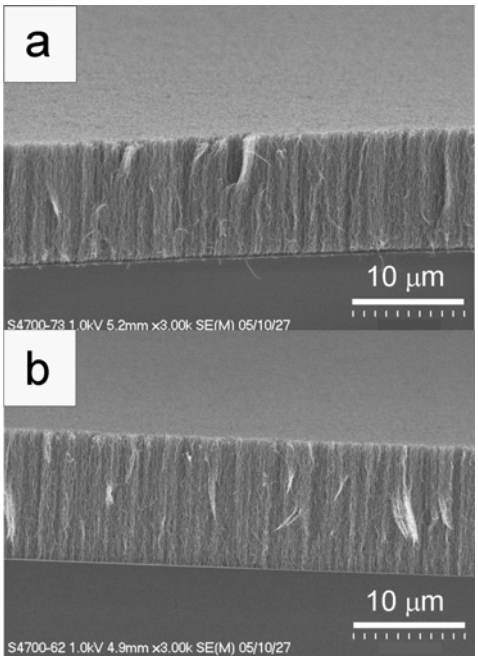


Fig. 2. FE-SEM image of the film cross-sections (a) before detachment on quartz and (b) after re-attachment on Si.

*2.3. Re-attachment of the films*

The detached VA-SWNT films could be re-attached to arbitrary surfaces. One could do this by simply submerging any plate into the water on which the detached film was floating (see Fig. 1b) and then by lifting up the plate with the film. Figures 1c and d show the pictures of VA-SWNT films re-attached to a silicon substrate and a transparent flexible plastic film, respectively. Adhesion of the VA-SWNT film in Fig. 1d was mechanically strong, as no detachment or fracture of the film occurred after 100

times-repeated bending with a radius of 10 mm. Formation of SWNT films on the surface of transparent flexible films have been reported for random [20] and laterally-aligned [21] morphologies.

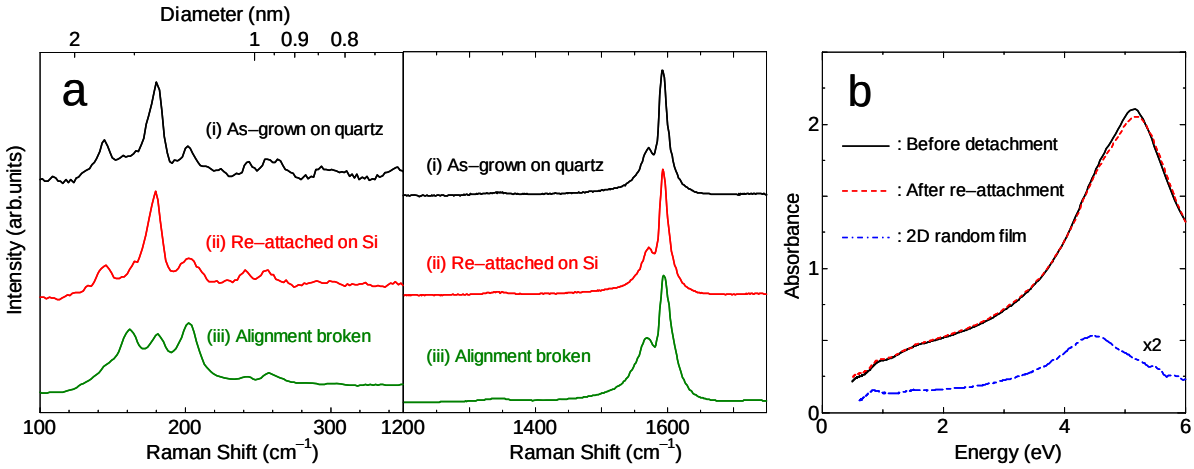


Fig. 3. (a) Resonant Raman scattering spectra measured by 488 nm laser light of the vertically aligned SWNT films (i) before detachment from a quartz substrate, (ii) after detachment and re-attachment to a Si substrate, and (iii) after destruction of the aligned morphology by wetting with ethanol and subsequent desiccation in vacuum at 200 °C. The right panel shows high-frequency region including the G- and D-bands. The left panel shows low-frequency RBM spectra, on top of which a diameter scale based on the relationship "$d$/nm = 248/($\nu$/cm$^{-1}$)" is presented. (b) Optical absorption spectra of the same VA-SWNT film before detachment from the quartz substrate (solid line) and after re-attachment to other quartz substrate and desiccation in vacuum at 200 °C (dotted line). The dot-dash line shows a typical absorption spectrum of 2D random SWNT film, with its ordinate doubly magnified.

*2.4. Characterization of the re-attached films*

2.4.1. FE-SEM. Figures 2a and b show field-emission scanning electron microscopy (FE-SEM) images of the sample before detachment (the same sample as shown in Fig. 1a) and after re-attachment onto Si (the same sample as shown in Fig. 1c), respectively. The figures indicate that the vertically aligned morphology is highly conserved throughout the attachment/re-attachment process. It is noted that most of the SWNTs in the VA-SWNT film form bundles with diameters of 5 - 20 nm, as displayed by each string seen in Fig. 2.

2.4.2. Raman scattering. Figure 3a shows resonant Raman scattering spectra of the VA-SWNT films before detachment (the sample shown in Fig. 1a) and that after re-attachment to Si substrate (that shown in Fig. 1c), respectively, measured by 488 nm laser light with light perpendicularly incident to the substrates. It has been known that the resonant condition, as well as resultant spectral shape of the radial

breathing mode (RBM) shown in the left panel of Fig. 3, is highly sensitive to the morphology of SWNT films [16,18]. Specifically, the vertically aligned morphology is indicated by the dominance of RBM peak at $\approx 180$ cm$^{-1}$, as it is resonantly excited when polarization direction of an incident light is perpendicular to the direction of SWNT alignment [16]. Figure 3a-(iii) exemplifies the spectra of the sample whose vertical alignment had been destroyed (i.e., SWNTs had been deposited onto the substrate surface with spaghetti-like morphology) by being immersed into ethanol and subsequently dried in vacuum at 200 °C. The observed invariance of the RBM spectra, observed in Figs. 3a-(i) and (ii), presents a spectroscopic evidence for complete conservation of the aligned morphology throughout the detachment/re-attachment process.

2.4.3. Absorption spectroscopy. Figure 3b provides support in terms of optical absorption spectroscopy, in which the solid curve denotes the spectrum of an as-grown VA-SWNT film on one side of the quartz substrate, while the dotted curve denotes that of the same sample re-attached to another quartz substrate. These spectra were taken in the direction normal to the substrates (i.e., direction of SWNT alignment), and therefore absorption structures for inter-subband transitions in IR-vis region are only weakly recognizable. Since optical absorption of SWNTs is highly anisotropic [17], the absence of any significant difference between the spectra implies that the deterioration of alignment is inessential throughout the process. The vertical alignment after the re-attachment is also recognized by the dominance of perpendicularly-excited $\pi$ plasmon excitation at $\approx 5.2$ eV that would be suppressed when SWNTs are 2-dimensionally random [17,18], as exemplified by a dot-dash curve in Fig. 3b, where $\pi \rightarrow \pi^*$ excitation at $\approx 4.5$ eV [17] is dominant instead.

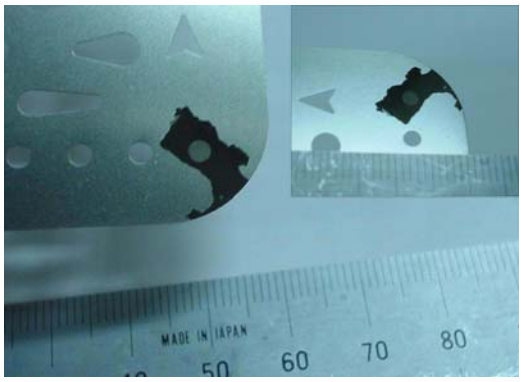


Fig. 4. A photo of self-standing VA-SWNT film suspended over $\phi = 2.5$ mm hole of an erasing shield taken from its normal direction. Inset shows the photo taken from a tilted angle ($\approx 45°$ from normal).

*2.5. Self-standing membrane of VA-SWNTs*

There are other possible applications of this technique besides aforementioned re-attachment to flat surfaces. One example is shown in Fig. 4, where a self-standing VA-SWNT film (thickness $\approx 15$ μm) is

suspended over a $\phi$ = 2.5 nm hole of an erasing shield (STAEDTLER, #529-50), which is a thin flexible stainless-steel plate with holes of various shapes, taken from the direction normal to the shield. The inset shows a photo of the same suspended film taken from a tilted angle ($\approx$45°), from which the optical anisotropy [17,18] of the self-standing area is evident. Such a self-standing membrane of aligned SWNTs should be applicable to spectroscopic studies of SWNTs, where an elimination of optical absorptions by substrates or matrix polymers is highly desirable.

Table 1

Dependence of detachment on the sample and temperature of distilled water

| Sample | 23 °C | 23 °C | 60 °C | -15 °C | 60 °C |
|---|---|---|---|---|---|
| Water | 23 °C | 60 °C | 60 °C | 23 °C | 23 °C |
| Detachment | No | Yes | No | Yes | No |
| Rate [a] | ≈ 1/25 | ≈ 30/30 | 0/4 | 4/4 | 0/4 |

[a] (No. of detached samples) / (no. of tested samples).

**3. Possible mechanism of film detachment**

We have gained the following experimental findings (i) ~ (iii), summarized in Table 1, each repeatedly confirmed with several samples: (i) Submersion of the VA-SWNT samples heated to $\approx$60 °C into 60 °C water causes no detachment. (ii) Submersion of the samples chilled to -15 °C into R.T. water causes the detachment. (iii) Submersion of the sample heated to $\approx$60 °C into R.T. water causes no detachment.

These facts give us further insight on the origin of the spontaneous film detachment. They indicate that positive temperature difference "$\Delta T \equiv T_{\mathrm{sample}} - T_{\mathrm{water}} \geq 40$ °C" is the important criterion for smooth detachment. The changes in the properties of water, such as the Brownian force ($\propto k_{\mathrm{B}}T$, 12.5 % increase from R.T. to 60 °C) or surface tension (7.6 % decrease from R.T. to 60 °C [22]) do not seem to be essential in our hot water-assisted detachment method. Similarly, the separation at an interface between the film and the substrate by thermally induced shear stress ($\propto |T_{\mathrm{sample}} - T_{\mathrm{water}}|$) is less plausible for the detachment. We note that no detachment was observed by submersion of the samples into liquid nitrogen, and that all the samples tested had been prepared at 800 °C.

Our interpretation of the main mechanism of the film detachment is as follows: First, the VA-SWNT films that we prepared are highly water-repellent (contact angle $\theta \approx$145°), as typically shown in Fig. 5a, whereas the surface of quartz ($SiO_2$) is water-wetting ($\theta \approx$30°). In addition, intrusion of water into the [VA-SWNT film]–[$SiO_2$ substrate] interface takes place at least during the detachment, as schematized in Fig. 5b. In one of our test experiments, a sample whose lower half had been lifted-off by hot water exhibited no further detachment by subsequent submersion into RT. water. This implies that the scissors that opens the edge of the film-substrate interface is identical to those that detach the entire film from the

substrate. Therefore, the problem here is the driving force of water intrusion into the film-substrate interface.

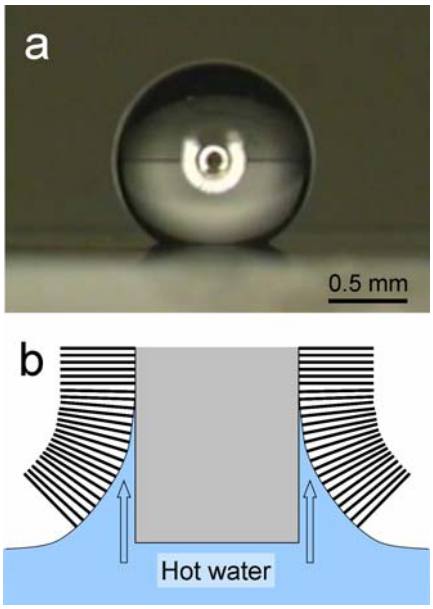


Fig. 5. (a) Typical picture of a water drop positioned on the surface of VA-SWNT film. (b) intrusion of hot water through the film-substrate interface during the detachment (schematic).

It is a well-studied phenomenon that a liquid thin film climbs up a vertical cold wall from hot liquid reservoir placed underneath driven by a force induced by the surface tension gradient due to the temperature gradient along the liquid-air interface [23,24], known as thermocapillary effect. Since water wets the quartz surface and a steep temperature gap exists between the substrate and the water ($\Delta T \approx 40$ K), the water is expected to move up on the quartz surface being driven by the thermocapillary force. At the same time, the thin film of water climbing on the quartz surface exerts a significant repulsive force on the VA-SWNTs to lift up the film, due to the hydrophobicity of vertically aligned carbon nanotube films.

**4. Concluding remarks**

We have developed an efficient technique for spontaneous detachment of CVD-grown VA-SWNT films from their substrates using hot water. The positive temperature difference, $\Delta T \geq 40$ °C, between the water and the substrate is found to be a key condition for smooth detachment, which may be accounted for in terms of the thermocapillary effect. The detached films are readily re-attached to arbitrary surfaces while preserving their aligned morphology. We have also prepared self-standing membranes of VA-SWNT films based on this technique. The proposed environment-friendly technique may broaden possible applications of VA-SWNT films in materials science and engineering.

Although all experiments in this paper were shown for the detachment from fused quartz substrates, we have confirmed that the technique is completely applicable also to the case of VA-SWNT films grown by the same method on silicon substrates with $\approx$10 nm oxidation layer.

Our attention has been called to a recent report [15] that vertically aligned SWNT films grown on $Si/SiO_2$ substrates were detached by etching-off of the $SiO_2$ layer using HF and were re-attached to other surfaces. The final products may be similar, but the chemicals and processes involved are clearly different, and perhaps the detailed mechanisms too.

**Acknowledgment**

Part of this work was supported by Grant-in-Aid for Scientific Research #16360098 and #1610754 from Japan Society for the Promotion of Science, and by Grant-in-Aid for Scientific Research #13GS0019 from Ministry of Education, Culture, Science and Technology.

**References**

[1] S. Iijima, T. Ichihashi, Nature 363 (1993) 603.

[2] R. Saito, G. Dresselhaus, M.S. Dresselhaus, Physical Properties of Carbon Nanotubes, Imperial College Press, London, 1998.

[3] H. Dai, A.G. Rinzler, P. Nikolaev, A. Thess, D.T. Colbert, R.E. Smalley, Chem. Phys. Lett. 260 (1996) 471.

[4] M.S. Dresselhaus, G. Dresselhaus, P. Avouris (Eds.), Carbon Nanotubes, Springer, Berlin, 2001.

[5] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, M. Kohno, Chem. Phys. Lett. 360 (2002) 229.

[6] Y. Murakami, Y. Miyauchi, S. Chiashi, S. Maruyama, Chem. Phys. Lett. 374 (2003) 53.

[7] Y. Murakami, Y. Miyauchi, S. Chiashi, S. Maruyama, Chem. Phys. Lett. 377 (2003) 49.

[8] Y. Murakami, S. Chiashi, Y. Miyauchi, S. Maruyama, Jpn. J. Appl. Phys. 43 (2004) 1221.

[9] Y. Murakami, S. Chiashi, Y. Miyauchi, M. Hu, M. Ogura, T. Okubo, S. Maruyama, Chem. Phys. Lett. 385 (2004) 298.

[10] M. Hu, Y. Murakami, M. Ogura, S. Maruyama, T. Okubo, J. Catalysis 225 (2004) 230.

[11] S. Maruyama, E. Einarsson, Y. Murakami, T. Edamura, Chem. Phys. Lett. 403 (2005) 320.

[12] K. Hata, D.N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, Science 306 (2004) 1362.

[13] G. Zhong, T. Iwasaki, K. Honda, Y. Furukawa, I. Ohdomari, H. Kawarada, Chem. Vap. Depo. 11 (2005) 127.

[14] S. Noda, H. Sugime, T. Osawa, Y. Tsuji, S. Chiashi, Y. Murakami, S. Maruyama, Carbon, in press.

[15] G. Zhang, D. Mann, L. Zhang, A. Javey, Y. Li, E. Yenilmez, Q. Wang, J. McVittie, Y. Nishi, J. Gibbons, H. Dai, cond-mat/0511035.

[16] Y. Murakami, S. Chiashi, E. Einarsson, S. Maruyama, Phys. Rev. B 71 (2005) 085403.

[17] Y. Murakami, E. Einarsson, T. Edamura, S. Maruyama, Phys. Rev. Lett. 94 (2005) 87402.

[18] Y. Murakami, E. Einarsson, T. Edamura, S. Maruyama, Carbon 43 (2005) 2664.
[19] H. Li, X. Wang, Y. Song, Y. Liu, Q. Li, L. Jiang, D. Zhu, Angew. Chem. 113 (2001) 1793.
[20] Z. Wu, Z. Chen, X. Du, J.M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J.R. Reynolds, D.B. Tanner, A.F. Hebard, A.G. Rinzler, Science 305 (2004) 1273.
[21] T. Takenobu, T. Tanahashi, T. Kanbara, K. Tsukagoshi, Y. Aoyagi, Y. Iwasa, Appl. Phys. Lett. 88 (2006) 033511.
[22] D. R. Lide (Ed.), Handbook of Chemistry and Physics, 82nd Ed., CRC Press, Boca Raton, 2001.
[23] V. Ludviksson, E.N. Lightfoot, AIChE J. 17 (1971) 1166.
[24] P. Carles, A.M. Cazabat, J. Coll. Interf. Sci. 157 (1993) 196.