

Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy

Yoichi Murakami ^a, Shohei Chiashi ^a, Yuhei Miyauchi ^a, Minghui Hu ^b, Masaru Ogura ^b,
Tatsuya Okubo ^{b,c}, Shigeo Maruyama ^{a,*}

^a *Department of Mechanical Engineering, The University of Tokyo*
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

^b *Department of Chemical System Engineering, The University of Tokyo*
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

^c *PRESTO, JST, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.*

Received 23 November 2003; in final form 5 December 2003

Abstract

Films of vertically aligned single-walled carbon nanotubes (SWNTs) with a few μm thickness were grown by catalytic chemical vapor deposition (CVD) on quartz substrates. Low-temperature CVD from ethanol was performed by using densely mono-dispersed Co-Mo catalyst of $\approx 1.0 - 2.0$ nm prepared on quartz substrates by a dip-coating method. Continuous reduction of catalysts with Ar/H₂ (3% H₂) during CVD was essential for generating dense enough SWNTs with vertical alignment. Vertical alignment was clearly demonstrated by anisotropic optical absorption and transmission characteristics in addition to observations by FE-SEM, TEM and resonance Raman scattering.

*Corresponding Author. Fax: +81-3-5800-6983.

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

1. Introduction

Single-walled carbon nanotubes [1] (SWNTs) have been the subject of focused multi-disciplinary studies due to their unique electrical, mechanical and thermal properties that promise wide applications [2]. The experimental studies of SWNTs have been facilitated by the development of selective generation by the laser furnace method [3], followed by that of more scalable CVD techniques such as the high-pressure CO (HiPco) method [4]. In addition to bulk synthesis, controlled positioning of carbon nanotubes on a substrate has been regarded as crucial for applications to field emission transistors [5] (FET), chemical sensors [6], optical devices for telecommunications [7] etc. Vertical alignment of multi-walled carbon nanotubes (MWNTs) has also been reported [6,8,9]. As for SWNTs, however, only those aligned *parallel* to a substrate surface has so far been achieved by application of a strong electric or magnetic field [10-12].

We demonstrate in this Letter that vertically aligned SWNTs, densely populated in a form of a “film” with thickness of a few μm , can be grown by a simple thermal CVD process and that the prepared specimen exhibits optical anisotropy due to this alignment.

2. Experiment

SWNTs were synthesized by the alcohol-CVD technique [13, 14]. Bimetallic Co-Mo catalyst was supported on a quartz substrate by dip-coating the substrate in an acetate solution [14]. As-delivered quartz substrate ($25 \times 25 \times 0.5 \text{ mm}^3$) was baked in air at $500 \text{ }^\circ\text{C}$ for 5 min in an electric furnace just before the supporting process. The substrate was first coated with an ethanol solution of Co and Mo acetates, each with a metal content of 0.01 wt%; then it was heated in air at $400 \text{ }^\circ\text{C}$ to convert the acetates to metal oxides and was reduced in the heat-up stage by flowing 300 sccm Ar/H₂ (3 % H₂) to retrieve its catalytic activity for the CVD reaction. When the electric furnace reached the SWNT growth temperature of $800 \text{ }^\circ\text{C}$, the supply of Ar/H₂ gas was either cut off or continued during the CVD reaction: The former resulted in random growth parallel to the substrate surface [14], while the latter led to dense growth of vertically aligned SWNTs on the surface, as reported below. All the CVD experiments were performed for 1 h with 10 Torr of ethanol used as a carbon source. The flow rate of Ar/H₂ (3% H₂) gas was fixed at 300 sccm, at 300 Torr during the heat-up stage and a partial pressure of 7 Torr during the CVD reaction, being controlled by a degree of evacuation. A quartz tube with an inner diameter of 26 mm and an annular electric furnace of 60 cm in length were used for our CVD apparatus. The substrate was placed down-stream of the furnace so as to let the gases passing over the specimen uniformly reach the furnace temperature. The background pressure of the CVD chamber was kept below 2×10^{-2} Torr to ensure reproducibility. SEM observation was performed at 4 kV with a Hitachi S-900 field emission SEM (for Fig. 1), and TEM

with a JEOL 2000EX at 120 kV (for Figs. 2a,b) and a JEM-4000EX at 400 kV (for Fig. 2c). Raman measurements were performed using a CHROMEX 501is spectrometer, an ANDOR Technology DV401-FI CCD system, and a SEKI TECHNOTRON Corp. STR250 optical system.

3. Results

3.1. SEM and TEM observations and Raman scattering for vertically aligned SWNTs

The SEM micrographs of the as-grown SWNTs at a fractured edge of the quartz substrate, shown in Fig. 1, demonstrates the vertical alignment of SWNTs with $\approx 1.5 \mu\text{m}$ as well as its spatial uniformity. This alignment can be ascribed to high enough density of SWNTs, as discussed below. The inset of Fig. 1 shows that the substrate covered with catalyst, which retained full transparency, was blackened by the growth of SWNTs.

For TEM observation, the substrate was sonicated in methanol for 15 s and the suspension was dripped onto a microgrid. In addition to unraveled SWNT bundles, an apparent vestige of the alignment was occasionally observed (Fig. 2a). Its magnified picture (Fig. 2b) confirmed that the aligned bundles were composed of SWNTs, in which catalytic particles with a few nm diameter (presumably metal carbide) were sparsely scattered. Such a flake structure with aligned SWNT bundles was often observed during TEM observations. Since the widths of the flakes were nearly identical with the film thickness, they were probably produced by direct decomposition of the SWNT film. This accounts for that the lengths of the SWNTs in the TEM images are nearly equal to the thickness of the SWNT film observed in Fig. 1. No MWNTs were found in repeated TEM observations.

We further investigated the catalyst morphology on the quartz surface. Figure 2c displays a TEM image of catalyst particles (black circles) on a quartz surface formed by heating the substrate in the CVD chamber with a flow of Ar/H₂, which indicates the morphology just before the CVD reaction. Here, the catalyst-supporting quartz substrate was heated up in the CVD chamber with a flow of Ar/H₂, and then brought back to room temperature without undergoing CVD. These finely dispersed particles (oxidized Co) with 1.0 – 2.0 nm diameters were self-formed on the surface and were stabilized by CoMoO_x layers [15]. In addition to TEM, the quality of SWNTs was also confirmed by a Raman scattering analysis by 488 nm laser excitation (Fig. 2d). The Raman spectra in this report are an average of 5 measurements at different locations on the specimen surface. The sharp “G-band” peak at 1590 cm⁻¹ corresponds to the in-plane oscillation of carbon atoms in the graphene wall of SWNTs, and the less remarkable “D-band” peak at 1350 cm⁻¹ represents the degree of defects or dangling bonds [2]. The large ratio of G to D peaks observed here confirms the TEM observations of the absence of MWNTs and amorphous carbon in this sample. The diameter was

estimated from the resonant peaks of the radial breathing mode (RBM) of SWNTs by the correlation ' d (nm) = 248 / ν (cm⁻¹)' (d : diameter, ν : Raman shift) [16], from which the diameter distribution of SWNTs was estimated to range 1.0 - 2.0 nm. For comparison, the morphology of the unaligned case where no Ar/H₂ flow was used in the CVD process is shown in Fig. 3a, where a partial peeling of the film was intentional. The thickness was measured by AFM to be 200 - 300 nm. The Raman spectrum of the unaligned SWNTs, displayed in Fig. 3b, has a significantly narrower diameter distribution than that of the vertically aligned case (Fig. 2d).

3.2. Optical anisotropy

Optical absorption spectra were measured for unaligned and aligned specimens with randomly polarized light (Figure 4a). For unaligned SWNTs shown in Fig. 3, an absorption peak corresponding to the semiconducting band gap E_s^{11} was observed at 1400 - 1600 nm, while no distinct peak was found for the aligned SWNTs. However, when the substrate was placed at a certain angle with respect to the incident light, the E_s^{11} peak emerged in the broader range of 1300 - 1700 nm. This broadening was ascribed to the wider diameter distribution observed in Fig. 2d. The angular dependence of the absorbance, shown in Fig. 4a, is a manifestation of specimen anisotropy.

We further observed the characteristic optical transmittance using linearly polarized laser light of 488 nm. The laser beam was expanded to a spot size of ≈ 5 mm using a collimator before incidence on the substrate, which was held at a specified tilt angle. The transmitted light was then re-focused onto a laser power sensor using a convex lens. Figure 4b compares the angular dependences of the normalized transmittances for the substrates with (i) oxidized catalyst only, (ii) an unaligned SWNT film, (iii) an aligned SWNT film, and (iv) a dried film of HiPco [4] SWNTs prepared by coating a Gum Arabic (GA)-dispersed HiPco aqueous solution [17] on a quartz substrate. The absolute transmittances at $\theta = 0^\circ$ are (i) 0.93, (ii) 0.76, (iii) 0.61, and (iv) 0.23, respectively.

For unaligned SWNTs, the transmittances in s- and p-polarization closely resembled that of Fig. 4b(i). Here, "s-polarization" denotes the case where the plane constructed by the direction of propagation of the light and that normal to the substrate is perpendicular to that of the light polarization, and "p-polarization" denotes the case where that the plane is parallel to the direction of the polarization (See a schematic in the inset of Fig. 4b). In contrast, aligned SWNTs (Fig. 4b(iii)) exhibited quite different behavior in the p-polarization case, where the optical cross-section (i.e. the length component of the SWNTs in the direction of polarization) increases according to $\sin\theta$. Note that transmittance was only 15 % lower than that of the unaligned specimen at $\theta = 0^\circ$. The HiPco film with random orientation (Fig. 4b(iv)), which had the lowest transmittance at $\theta = 0^\circ$ among all the cases, showed similar transmittance for both polarizations, indicating the dominance of isotropic

absorption and scattering of light. From the above comparison, the clear optical abnormality in Fig. 4b(iii) evidences that this substrate indeed works as a polarizing plate.

In the inset in Fig. 4b are shown pictures of substrate pieces with unaligned SWNTs (left, not seen due to brightness) and aligned SWNTs (right) are placed in front of a linearly polarized backlight at an angle of 60° with respect to the normal of the page. The change of the backlight polarization from p (right) to s (left) diminishes the visibility of the quartz piece with aligned SWNTs, which simply behaves as an SWNT polarizer. This polarizer effect helps one to quickly discern whether or not the film is successfully aligned, because the film of vertically aligned SWNTs, when seen from a shallow angle, looks perfectly opaque whereas an unaligned SWNT film retains some transparency until the total reflection of the quartz surface occurs.

4. Discussion

As evidenced by the foregoing observations, dense mono-dispersion of catalyst particles supported by the present liquid-based dip-coat process and enhanced activation of the catalyst by the continuous reduction with H_2 during CVD lead to the alignment of SWNTs. We attribute the fine dispersion of the catalyst to the use of the metal *acetate* solution as well as the dip-coat process itself. As demonstrated by Sun et al. [18], the interaction of Co-acetate with SiO_2 (silica gel) support is expected to be stronger and results in finer dispersion (one order of magnitude smaller diameter) of Co particles than Co-*nitrate*. This interaction should help the catalyst to prevent sintering during the heat up in the CVD apparatus. In fact, when Co-*nitrate* was combined with Mo-acetate keeping each metallic concentration in the solution unchanged (i.e. 0.01 wt %), the amount of SWNTs was found to decrease by a factor of ≈ 5 from the usual Co-Mo acetates case [19].

The dense and mono-dispersed catalyst particles prepared by the present process with small diameters of 1.0 ~ 2.0 nm, as fully characterized with XPS and TEM by our group [15], account for the high-density growth of SWNTs needed for the vertical growth shown in Fig. 1. The vertical alignment is likely to arise from such high density of SWNTs, by which the bundles are allowed to grow only upright from the substrate due to the interference with neighboring bundles. Therefore, the continuous reduction with H_2 during CVD is essential for the alignment to enhance the catalyst activity and, hence, the density and amount of SWNTs. The increase in the diameter distribution of SWNTs observed from the unaligned case of Fig. 3(b) to the aligned case of Fig. 2(d) agrees with this argument.

Finally, we estimated the area densities of the catalyst particles and SWNTs. The catalyst density can be derived directly from the TEM image (Fig. 2c) to be $\approx 1.3 \times 10^{17} \text{ m}^{-2}$. The density of SWNTs is roughly calculated as a product of [the density of SWNT bundles read from a SEM

micrograph (Fig. 1)] times [the number of SWNTs in a bundle counted from a TEM image (Fig. 2b)], to be $(1.0 \sim 2.0) \times 10^{17} \text{m}^{-2}$. This is comparable with the catalyst density and suggests an efficient use of supported catalyst for the synthesis of SWNT.

5. Summary

We have developed a simple and reproducible technique for synthesizing a vertically aligned SWNT film on a quartz surface by CVD. The high selectivity and quality of synthesized SWNTs has been confirmed by TEM and Raman analyses.

This SWNT-material will find various applications and augment the possibility of SWNT-based devices proposed so far based on randomly oriented SWNTs deposited on a substrate. The method presented in the present article may also bring forth SWNTs with nearly constant lengths defined by the thickness of the height of aligned SWNTs.

Acknowledgements

The authors thank Prof. R. E. Smalley for his supply of HiPco sample, Mr. T. Sugawara and Mr. H. Tsunakawa for assistances in FE-SEM and TEM observations. Part of this work was financially supported by KAKENHI #13555050 from JSPS, and #13GS0019 from MEXT.

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] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tománek, J.E. Fischer, R.E. Smalley, *Science* 273 (1996) 483.
- [4] M.J. Bronikowski, P.A. Willis, D.T. Colbert, K.A. Smith, R.E. Smalley, *J. Vac. Sci. Technol. A* 19 (2001) 1800.
- [5] P. Avouris, *Chem. Phys.* 281 (2002) 429.
- [6] A. Modi, N. Koratkar, E. Lass, B. Wei, P.M. Ajayan, *Nature* 424 (2003) 171.
- [7] Y.-C. Chen, N.R. Raravikar, L.S. Schadler, P.M. Ajayan, Y.-P. Zhao, T.-M. Lu, G.-C. Wang, X.-C. Zhang, *Appl. Phys. Lett.* 81 (2002) 975.
- [8] S. Fan, M.G. Chapline, N.R. Franklin, T.W. Tombler, A.M. Cassell, H. Dai, *Science* 283 (1999) 512.

- [9] B.Q. Wei, R. Vajtai, Y. Jung, J. Ward, R. Zhang, G. Ramanath, P.M. Ajayan, *Nature* 416 (2002) 495.
- [10] Y. Zhang, A. Chang, J. Cao, Q. Wang, W. Kim, Y. Li, N. Morris, E. Yenilmez, J. Kong, H. Dai, *Appl. Phys. Lett.* 79 (2001) 3155.
- [11] E. Joselevich, C.M. Lieber, *Nano Lett.* 2 (2002) 1137.
- [12] J.E. Fischer, W. Zhou, J. Vavro, M.C. Llaguno, C. Guthy, R. Haggenueller, M.J. Casavant, D.E. Walters, R.E. Smalley, *J. Appl. Phys.* 93 (2003) 2157.
- [13] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, M. Kohno, *Chem. Phys. Lett.* 360 (2002) 229.
- [14] Y. Murakami, Y. Miyauchi, S. Chiashi, S. Maruyama, *Chem. Phys. Lett.* 377 (2003) 49.
- [15] M. Hu, Y. Murakami, M. Ogura, S. Maruyama, T. Okubo, *J. Phys. Chem. B*, submitted.
- [16] A. Jorio, R. Saito, J.H. Hafner, C.M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, M.S. Dresselhaus, *Phys. Rev. Lett.* 86 (2001) 1118.
- [17] R. Bandyopadhyaya, E. Nativ-Roth, O. Regev, R. Yerushalmi-Rozen, *Nano Lett.* 2 (2002) 25.
- [18] S. Sun, N. Tsubaki, K. Fujimoto, *Appl. Catal. A* 202 (2000) 121.
- [19] Y. Murakami, S. Chiashi, Y. Miyauchi, S. Maruyama, *Jpn. J. Appl. Phys.*, in press.
- [20] Y. Homma, Y. Kobayashi, T. Ogino, D. Takagi, R. Ito, Y. J. Jung, P.M. Ajayan, *J. Phys. Chem. B* 107 (2003) 12161.

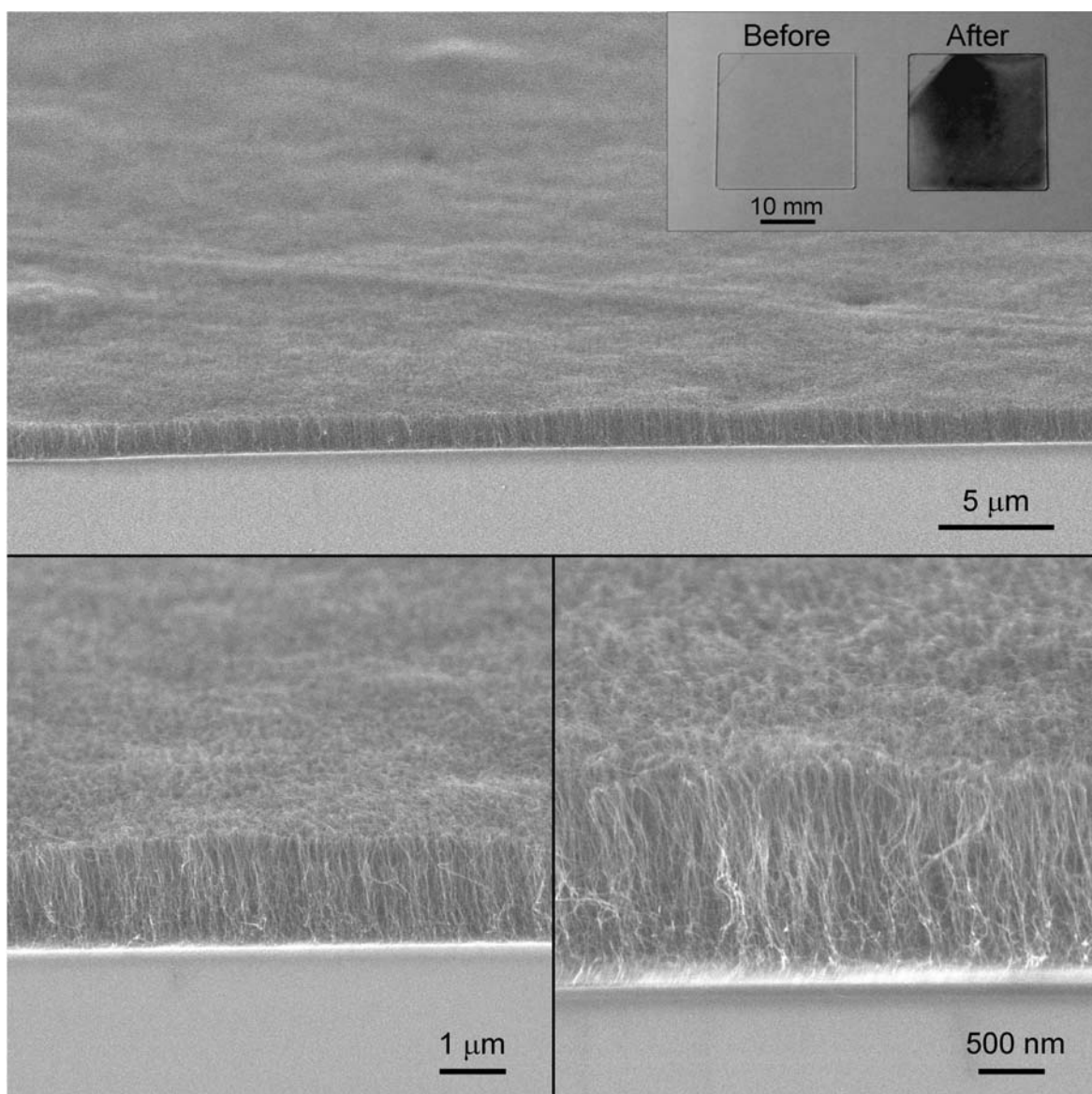


Fig. 1. SEM micrographs of vertically aligned SWNT bundles grown on quartz surface with different magnifications, taken at 20° from the horizon. Fractured substrate edges were observed to study cross-sectional morphology. The inset shows the substrate without CVD (left) and that with CVD used for synthesis of vertically aligned SWNT film (right); its upper left corner is blank because it was covered during the dip-coat process.

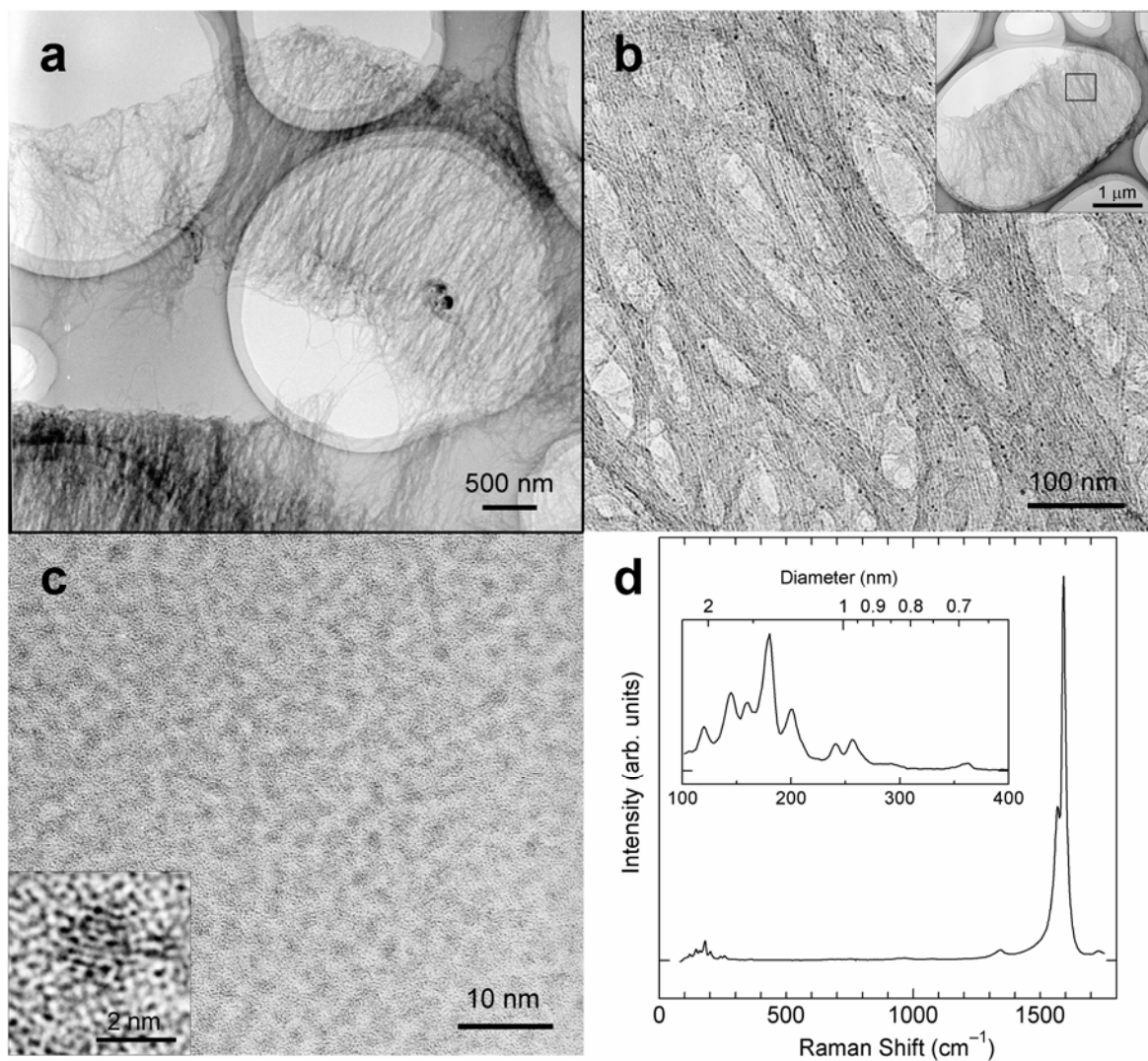


Fig. 2. Characterization of vertically aligned SWNTs by TEM and Raman scattering analyses. (a) A typical TEM image of SWNT flakes retaining their alignment. (b) Image of the flake with higher magnification made up of bundles of SWNTs. Dots among SWNTs are carbides of catalyst with ≈ 3 nm diameter. The inset shows the entire image of the observed flake in which the location of the enlarged area is indicated with a solid square. (c) A TEM image of catalyst particles (black circles) finely mono-dispersed on the quartz surface just before the CVD reaction. The inset is a typical magnified image of the catalyst particle. (d) Raman spectra of aligned SWNTs, indicating a wide diameter distribution of 1.0 - 2.0 nm.

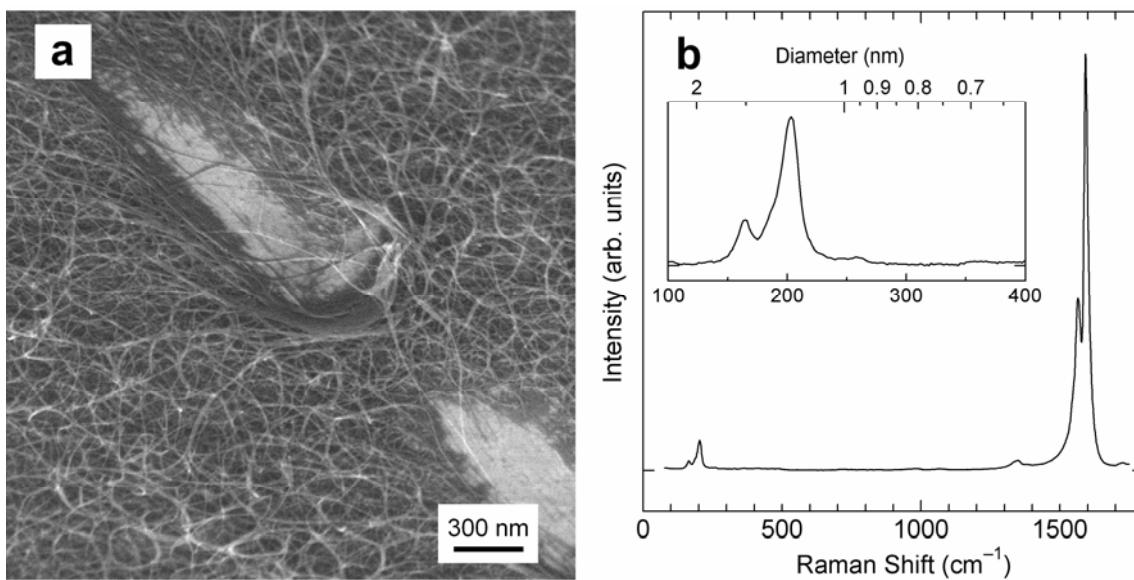


Fig. 3. Reference material in which SWNTs are randomly aligned. (a) A typical SEM image of unaligned SWNTs grown on quartz surface, where a part of the film was peeled to estimate the thickness and morphology. (b) Raman spectra of an unaligned specimen, which has a narrower diameter distribution than that of the aligned sample shown in Fig. 2d.

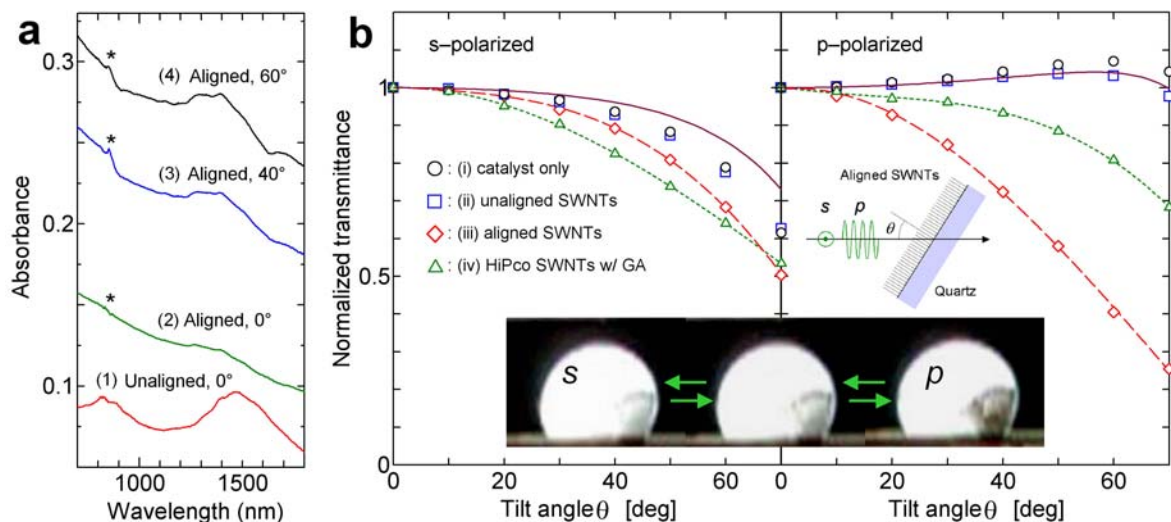


Fig. 4. Optical anisotropy of vertically aligned SWNTs grown on quartz substrate. (a) Optical absorption spectra (measured with randomly polarized incident light) of the substrates on which (1) unaligned and (2-4) aligned SWNTs were grown. The tilt angle of the substrate to the incident light is indicated. Asterisks denote peaks inherent in our instrument. (b) Angular dependences of optical transmittances normalized by those at 0° . The 488 nm s-polarized (left) and p-polarized (right) light was used. The solid curves represent theoretical transmittances for s- and p-polarizations calculated from the classical electromagnetic formula using the refractive index of glass to be 1.5. The inset demonstrates that the substrate with aligned SWNTs works as a polarizer when tilted, in which the diameter of the backlight is 25 mm.