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Langmuir–Blodgett Films of Single-Wall Carbon Nanotubes: Layer-by-layer Deposition and In-plane Orientation of Tubes

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The Langmuir–Blodgett technique has been applied to build optically homogeneous thin films of chemically solubilized single-wall carbon nanotubes (s-SWNTs) which possess good surface spreading properties at the air/water interface. Deposition can be performed in a layer-by-layer fashion up to 100 or more layers either by horizontal lifting or vertical dipping, allowing to readily control the film thickness. Their visible to near-infrared absorption spectra showing the characteristic features of semiconducting and metallic SWNTs prove the intactness of their one-dimensional electronic states during the preparation process. Polarized absorption spectroscopy and atomic force microscope (AFM) observation demonstrate that the tubes are oriented in the direction of the trough barrier (horizontal lifting) or in the dipping direction (vertical dipping). These are attributed to compression-induced or flow-induced orientation, respectively, the latter found to be much stronger than the former. The realization of homogeneous thin films of SWNTs with a controllable thickness and tube orientation should be an important basis for the future development of their scientific understanding and technological applications. [DOI: 10.1143/JJAP.42.7629]

KEYWORDS: carbon nanotube, LB film, layer-by-layer deposition, orientation, polarized absorption spectrum, dichroism, atomic force microscopy

1. Introduction

Development of thin film fabrication techniques constitutes an indispensable part of materials science and technology. In particular, for investigating their optical, optoelectronic, and electrical properties in a macroscopic scale, the availability of high quality, homogeneous thin films is a fundamental prerequisite. Furthermore, techniques pertaining to thin film fabrication form an important basis for the construction of various types of optical, electrical and chemical devices. The importance of thin films is best illustrated by the research on polyacetylenes thin films by Shirakawa *et al.*^{1,2)} Realizing homogenous thin films of polyacetylenes, their work triggered and enabled comprehensive studies of their optical and electrical properties, eventually establishing the concept of conductive polymers and pioneering the vast field of related basic and applied research.

For single-wall carbon nanotubes (SWNTs), in contrast, no such development in thin film research has been achieved yet despite an exploding amount of work on this new, unique form of carbon. This is an unjustifiable situation in view of their great potential as well as of the necessity for the basic understanding of their properties as an essential basis for industrial applications. There have been a number of reports that mentioned preparation of SWNT thin films in various contexts of research: spraying ethanol dispersion of SWNTs onto substrates,^{3,4)} stretching polymer films dispersed with SWNTs,⁵⁾ monolayer deposition by horizontally transferring surfactant-dispersed or chemically derivatized SWNTs spread on the water,^{6,7)} electrophoretic deposition,^{8,9)} and self-assembly.^{10–12)} With these fabrication techniques, however, it has been difficult to realize optically homogeneous SWNT thin films with a controlled thickness and nanostructures. As a result basic understanding about the optical and electronic properties of SWNTs to be macroscopically measured using such samples has long remained at a

primitive stage despite its primary importance. These include optical absorption, luminescence excitation and emission, photoconductivity, optical pump-probe techniques, and non-linear optics, to mention just a few of them. These are the properties that need to be understood for any optoelectronic applications of SWNTs. What is more, without a thin film form, the fabrication of many useful devices would be difficult, such as chemical sensors, pressure sensors, switches, linear and nonlinear optical devices, and even nano-electronic devices.

In a previous work, we fabricated homogeneous thin films of chemically solubilized SWNTs (s-SWNTs) dispersed in an amphiphilic polymer, poly(N-dodecylacrylamide) (PDDA), by using the Langmuir–Blodgett (LB) technique.¹³⁾ By the assistance of the good film-forming properties of PDDA,^{14–16)} a stable monolayer of polymer-dispersed s-SWNTs can be formed on the water surface. They can be transferred to substrates in a layer-by-layer fashion, forming homogenous mono- or multi-layer thin films. In the present work, after re-examining the conditions for the pre-treatments and chemical solubilization of SWNTs, we have succeeded in fabricating homogeneous LB films of SWNTs even without using the matrix polymer. More important, s-SWNTs in these films are found to be considerably oriented in a specific direction as demonstrated by polarized visible to near infrared absorption spectroscopy and atomic force microscopy (AFM). We employed both horizontal lifting and vertical dipping as methods for LB film deposition and examined their effects on tube orientation, on the basis of which the orientation mechanisms are discussed. The realization of optically homogeneous films of SWNTs with controlled thickness and tube-orientation should have a strong impact on the future progress in the science and technology of SWNTs.

2. Experimental

SWNTs used in the present study were commercially obtained from Carbon Nanotechnologies Inc. (HiPco SWNTs) which are synthesized by chemical vapor deposi-

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tion from carbon mono-oxide using iron as a catalyst.^{17–19} HiPco SWNTs were purified by oxidation in wet air at 220°C for 24 h and then by stirring in concentrated hydrochloric acid at room temperature for 16 h to remove any catalyst iron.¹⁸ Analysis by TGA and ICP plasma emission indicated the purity of SWNTs to be higher than 96%. Next, we performed acid-mixture etching to shorten SWNTs for 0.5–1.5 h at 30–40°C using a 40 KHz sonicator.²⁰ To introduce carboxylic groups, these shortened tubes were further oxidized with H₂O₂/H₂SO₄ for 1 h at 20–30°C.²¹ The products were reacted with thionyl chloride to introduce acyl chloride groups into the SWNTs, and then reacted with octadecylamine (ODA).²²

These procedures were performed in large part following the reported methods. However, appropriate conditions for these treatments were found to depend greatly on the nature of the starting material. Accordingly, the reaction condition for each step needed to be carefully examined. In our previous experiences, for example, acid etching for more than 20 h on SWNTs prepared by arc discharge resulted in total destruction of SWNTs and no tubular materials remained. Even for shorter etching time of 4 h, the SWNTs became too short, due to which no clear images of tubes could be obtained within the resolution of our AFM observation. Furthermore, it was difficult to sufficiently remove carbonaceous impurities from these arc discharged SWNTs, resulting in AFM images consisting mostly of irregular aggregation of particulate materials. This enhanced the difficulty in observing clear images of s-SWNTs and their orientation in a specific direction. For HiPco SWNTs, which were used as the starting material in this study, the procedures described above are the ones chosen after several trials.

The products thus prepared possess substantial solubility in chloroform, CS₂, and various aromatic solvents. The solution was visually non-scattering and no precipitation occurred for months. The optical absorption and Raman spectra of these s-SWNTs are essentially the same as those reported for non-functionalized HiPco SWNTs,^{18,19} showing that the one-dimensional electronic states particular to SWNTs mostly remained intact during the pre-treatments and chemical functionalization.

Measurements of surface pressure-area isotherms and thin film deposition were performed at 19°C using a Langmuir trough (Lauda Filmwaage). A chloroform solution of s-SWNT (1 mg/50 ml) was spread on the surface of the water, which was purified by a Millipore Milli-Q system. Quartz and glass substrates used for film deposition were cleaned in a KOH/ethanol solution and washed by pure water, resulting in hydrophilic surfaces. To prepare hydrophobic surfaces, substrates were dipped in 1,1,1,3,3,3-hexamethyldisilazane. While we found that s-SWNTs can be deposited on either hydrophilic or hydrophobic substrates, the latter were mainly used because they tended to retain a better transfer ratio up to a larger number of deposited layers. For thin film deposition, two methods, horizontal lifting and vertical dipping were employed (Fig. 1). For the former, a Teflon lattice consisting of 21 rectangular cells (size: 14.4 × 20.5 mm) was placed on the trough and the s-SWNT Langmuir film was divided into 21 sections. The Langmuir film thus confined in each rectangular cell was horizontally

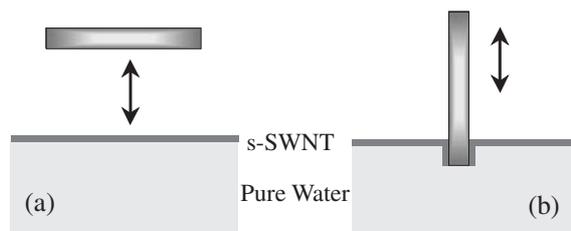


Fig. 1. Scheme of the preparation of Langmuir-Blodgett films by the horizontal lifting (a) and vertical dipping (b) methods.

transferred to a substrate one by one. For the vertical dipping, the velocity of the substrates motion was normally 10 and 15 mm/min for upward and downward strokes, respectively. During the deposition, the surface pressure of the spread film was controlled at 20 mN/m.

The film deposition process was followed by UV-Vis-NIR absorption spectroscopy (Cary 500). To study the in-plane anisotropy of these films, polarized absorption spectroscopy was used, and the dichroic ratio was taken as a measure of the average degree of the tube orientation. An atomic force microscope (Seiko SPA 300HV with an SPI 3800 probe station) was used to nanoscopically image the film surface; Si cantilevers with a resonance frequency of 25 kHz and a force constant of 1.5 N/m were used in the non-contact mode. For AFM measurements, mica, which presents a hydrophilic surface, was used as a substrate because of its flatness.

3. Results and Discussion

Figure 2 shows a surface pressure-area isotherm at 19°C, which is characterized by a steep rise in pressure as well as by a high collapse pressure (up to 50 mN/m). This indicates that a stable and condensed layer of s-SWNT was formed on the water surface. It should be noted here that the actual trough area was used as the abscissa instead of area per molecule because these s-SWNTs are a mixture of tubes with different diameters and lengths. The reversibility of the surface pressure-area isotherm was checked by repeating the compression/expansion cycle several times (Fig. 3). As long as the pressure was kept below 30 mN/m, they followed essentially the same trace, showing the good surface

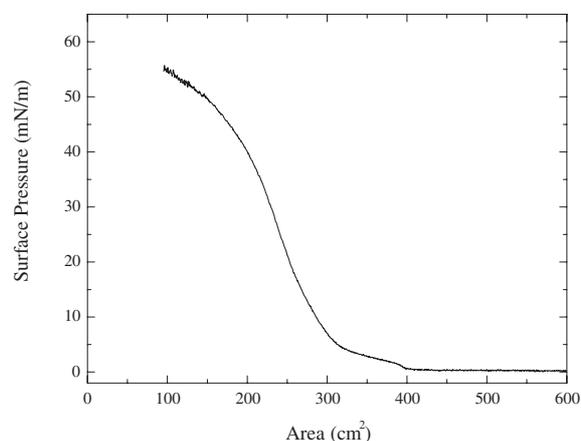


Fig. 2. Surface pressure-area isotherm of the monolayer of s-SWNT on pure water at 19°C.

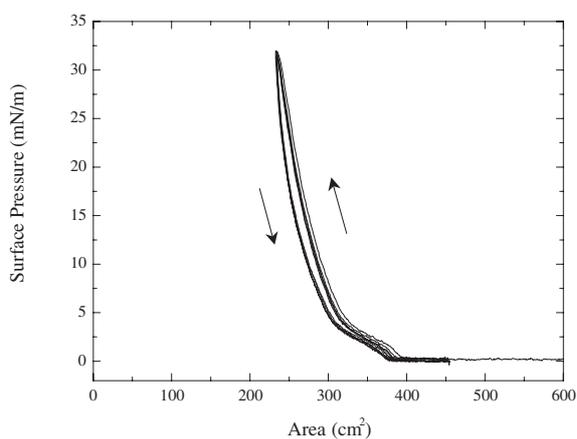


Fig. 3. Compression/expansion cycle of the isotherm of s-SWNT.

spreading properties of s-SWNT. Combined with the results of AFM observations, as will be shown later, this also excludes the possibility of an irreversible three-dimensional aggregation upon compression. While these s-SWNTs are different from traditional amphiphilic molecules like fatty acids commonly used for LB film preparations, the carboxylic and amide groups introduced by the chemical treatments probably play an important role in these processes. While these groups should be mostly located at the end of each shortened tube, some of them may be also introduced on the tube side-walls as suggested by titration experiments.^{23,24)} These introduced groups should help to introduce hydrophilicity into the tube wall, which is originally very hydrophobic before the chemical treatments, thus making it possible for s-SWNTs to spread uniformly on the water surface. This situation is similar to a monolayer of α -helical copolyglutamates with long side chains,²⁵⁾ in that rigid rod-shaped molecules can spread on the water surface with an appropriate chemical modification.

Figure 4 shows the absorption spectra of s-SWNT LB films deposited by horizontal lifting with a surface pressure kept at 20 mN/m. The measurements were performed successively on the same sample, using a hydrophobic quartz plate as the substrate. The spectra consist of two main

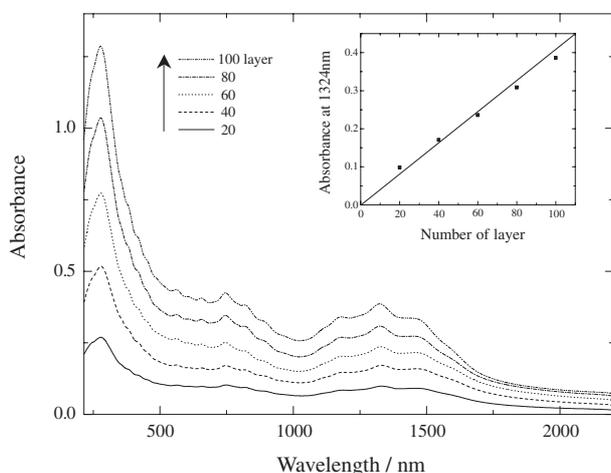


Fig. 4. UV-Vis-NIR absorption spectra of s-SWNT LB films deposited on hydrophobic quartz by the horizontal lifting method. Inset: Relationship between the absorbance at 1324 nm and the number of layers.

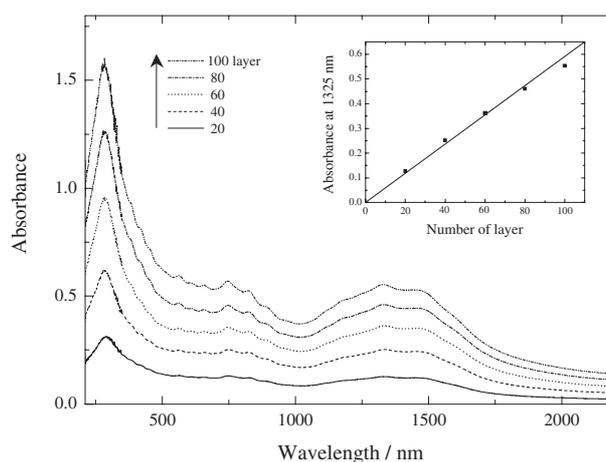


Fig. 5. UV-Vis-NIR absorption spectra of s-SWNT LB films deposited on hydrophobic quartz by the vertical dipping method. Inset: Relationship between the absorbance at 1325 nm and the number of layers.

features at 1200–1500 nm and at 600–800 nm, corresponding to the optical transition due to the first and second energy gap of semiconducting SWNTs, respectively. The latter shorter wavelength overlaps with other spectral features originating from optical transitions in metallic SWNTs and by π -plasmons. The observation of many absorption peaks over a range of wavelength reflects the broad distribution of the tube diameter of HiPco SWNTs. The overall spectral shape resembling those of starting HiPco SWNTs¹⁸⁾ certifies that electronic structures characteristic of SWNTs are essentially preserved throughout the chemical functionalization and film deposition. The absorbance at 1324 nm plotted as a function of the number of layers gives a straight line up to at least 100 layers. Similar results were obtained for LB films prepared by vertical dipping (Fig. 5). Here the film was deposited on hydrophobic quartz with a surface pressure of 20 mN/m. The transfer ratio was about 0.8 for both downward and upward strokes. Again, the absorbance at 1325 nm versus the number of layers gives a straight line up to 100 layers (50 layers on each side), thereafter showing saturation. These results demonstrate that homogeneous LB films can be formed in a layer-by-layer fashion by either horizontal lifting or vertical dipping without using an amphiphilic polymer matrix. The films appear optically homogeneous and no light scattering can be seen (Fig. 6). For a thicker film (140 layers), a greenish tint caused by interference is visible when light is obliquely incident on the film surface, indicative of its optical quality.

For LB films of s-SWNTs, two mechanisms are expected to influence their orientation: compression and flow. When compressed, molecules with large aspect ratios floating on water surface are expected to be oriented with their axis in parallel to the barrier of a Langmuir trough [Fig. 7(a)]. For horizontally deposited films, this is the only orientation mechanism expected to occur [Fig. 7(b)]. For vertically deposited films, an additional mechanism, flow-induced orientation, comes into effect due to tube flow induced by the disappearance of the materials from the water surface caused by the upward and downward motion of the substrate [Fig. 7(c)]. Such an effect is known for elongated J-aggregates of a merocyanine dye diluted with a fatty acid and interpreted using a model based on flow orientation of

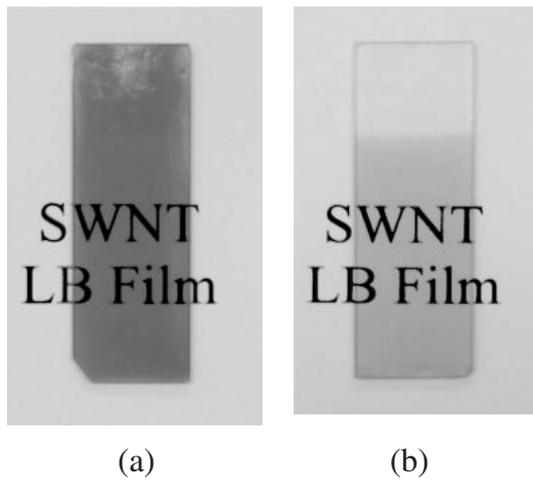


Fig. 6. Photographs of s-SWNT LB films prepared by the horizontal lifting (140 layers) (a) and vertical dipping (58 layers) (b) methods.

molecules caused by two-dimensional fluid dynamics.²⁶⁾

To investigate the occurrence and the interplay of these orientation mechanisms for s-SWNT LB films, we measured the linear dichroism of their absorption spectra. According to a calculation by Ajiki and Ando,²⁷⁾ the optical transitions in SWNTs depend strongly on the light polarization direction. If the electric vector of the incident light is perpendicular to the tube axis, the optical absorption almost disappears due to the depolarization effect, reflecting the huge aspect ratio of SWNT. As a result, the linear dichroism can give a good measure of the orientation of SWNTs. In fact, a strong linear dichroism is observed for SWNTs that were grown inside

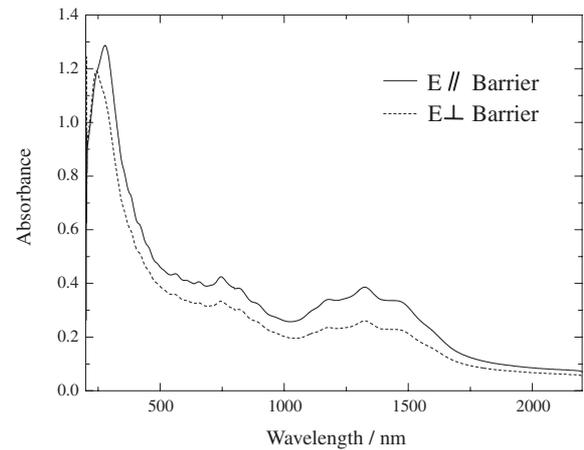


Fig. 8. Polarized UV-Vis-NIR absorption spectra of a 100-layer LB film of s-SWNT deposited by the horizontal lifting method: with the electric vector of the incident light parallel (—) and perpendicular (---) to the direction of the barrier.

one-dimensional channels of a zeolite crystal and thus were nearly perfectly oriented in the direction of the channels.²⁸⁾

Figure 8 shows polarized absorption spectra of a 100 layer LB film prepared by horizontal lifting. Stronger absorption was observed for light polarized parallel to the direction of barrier than for light polarized perpendicular. A dichroic ratio [defined by Abs (parallel to barrier)/Abs (perpendicular to barrier)] of 1.48 was found for the 1325 nm peak. This means that s-SWNTs in this film are oriented to a certain extent along the barrier direction as illustrated in Fig. 7. To see the effect of the surface pressure, higher

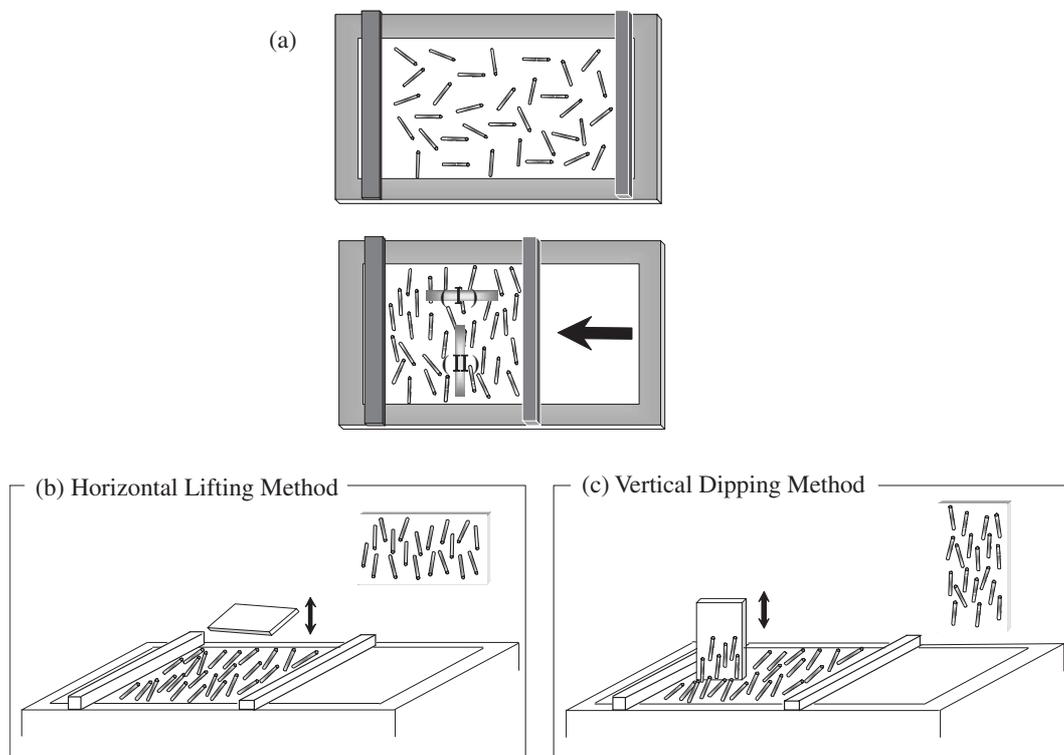


Fig. 7. Schematic illustration of the mechanism for the in-plane orientation of s-SWNT. Compression-induced orientation in the Langmuir film by barrier compression (a), in-plane tube orientation for films prepared by horizontal lifting (b), and flow orientation of tubes induced by the vertical motion of the substrate (c). (I) and (II) in Fig. 7(a) represent the placement of a substrate perpendicular and parallel to the barrier, respectively.

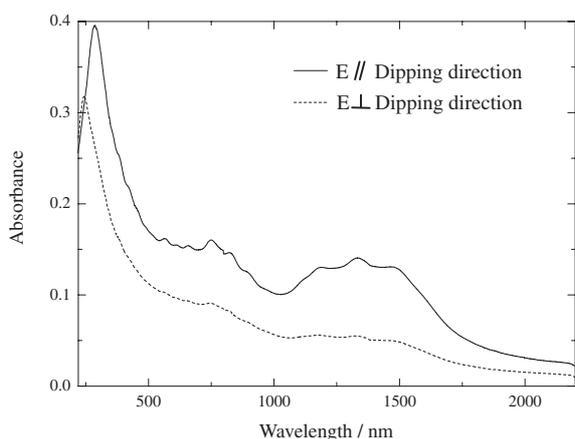


Fig. 9. Polarized UV-Vis-NIR absorption spectra of a 20-layer LB film of s-SWNT deposited by the vertical dipping method: with the electric vector of the incident light parallel (—) and perpendicular (---) to the direction of dipping.

compression was applied to a layer of s-SWNT on the water surface. The resultant dichroic ratio increased slightly, the maximum value attained being 1.63 for a film partially collapsed due to over-compression (>50 mN/m). This suggests that while the extent of the compression-induced orientation of s-SWNTs does depend on the surface pressure, the actual relation may be complicated by the involvement of other factors such as the distribution in length, aggregation and possible entanglement of the tubes.

Figure 9 displays the polarized absorption spectra of a vertically deposited 20-layer LB film, showing a dichroic ratio of 2.5, much larger than that of the horizontally deposited film. In this case, the tubes are found to be preferentially oriented in the dipping direction. To see the interplay between compression-induced and flow-induced orientation, we studied how the placement of the substrate in different directions affects the dichroic ratio. For case (I) [Fig. 7(a)], where the substrate was placed perpendicular to the barrier, the flow-induced orientation should enhance the compression-induced orientation. For case (II) [Fig. 7(a)],

where the substrate was placed in parallel to the barrier, the former should work against the latter, possibly diminishing the final degree of the tube orientation. The difference in the dichroic ratio between cases (I) and (II) turned out, however, to be only a few percent. This result indicates that, in the case of vertical deposition, flow-induced orientation dominates the overall process, mostly overriding the effect of the preceding compression-induced orientation. We also studied the effect of the deposition velocity on tube orientation for vertical dipping. With an increase in the velocity applied (from 15 to 300 mm/min), the dichroic ratio increased slightly (from 2.2 to 2.5).

Figure 10(a) shows a non-contact-mode AFM image of an s-SWNT monolayer on mica prepared by vertical dipping, the arrow corresponding to the dipping direction. Compared with a drop-and-dry film prepared from the same solution [Fig. 10(b)], it is clear that many tubes are preferentially oriented in the dipping direction. According to the surface profile of the image, the tube height distribution ranges mostly from 5 to 10 nm, indicating that most tubes are in small bundles whose length ranges from a few hundred nanometer to 1 μ m. Since the surface profile of the drop-and-dry film shows similar height distribution, the tubes should be already aggregated in the solution. We suspect that this aggregation takes place during the chemical treatment of SWNTs: additional aggregation caused by compression on the surface should be a minor factor here.

4. Conclusions

We have succeeded in the fabrication of optically homogeneous thin films of s-SWNTs using the LB method. Chemically solubilized SWNTs are found to possess good surface spreading properties that contribute to the formation of stable Langmuir monolayers on a water surface. The deposition can be performed in a layer-by-layer fashion either by the horizontal lifting or vertical dipping method, the latter giving a higher degree of tube orientation. For vertical dipping, orientation induced by compression during the Langmuir film preparation was found to be overridden by a much stronger flow-induced orientation during depo-

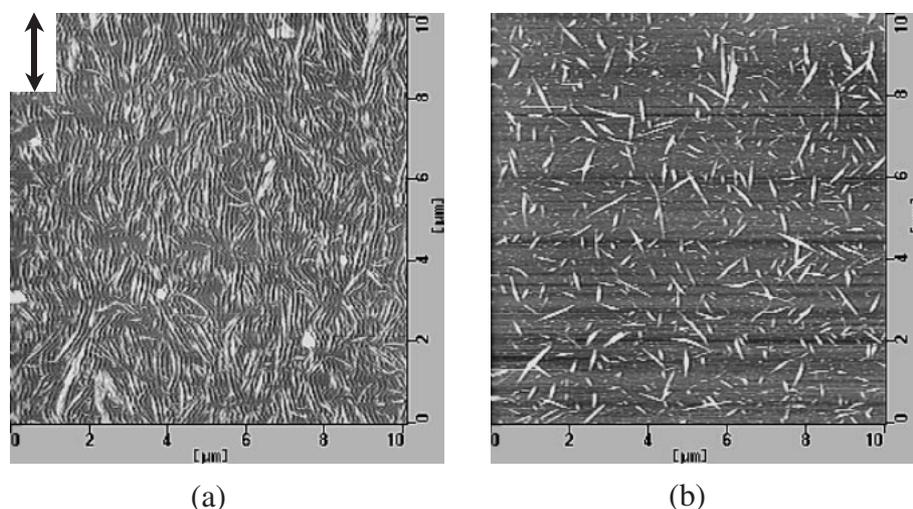


Fig. 10. Non-contact-mode AFM images of an s-SWNT single layer on mica prepared by vertical dipping (a) and a drop-and-dry film prepared from the same solution (b). The arrow indicates the dipping direction.

sition. The present results should have a considerable impact on the future development of the science and technology of SWNTs. In a basic aspect, the availability of such films should accelerate the understanding of the electronic and optoelectronic properties of SWNTs in their aggregated forms, as various optical and electrical characterization techniques can now be applied. In terms of applications, these SWNT thin films may contribute to developments in the design and construction of chemical sensors, optical devices, and other molecular and nanoscopic structures.

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