

Langmuir–Blodgett Films of Matrix-Diluted Single-Walled Carbon Nanotubes

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Since the discovery of single-walled carbon nanotubes (SWNTs) by Iijima¹ in 1991, a strong interest in the properties of these remarkable molecular objects is recognized. The unique mechanical, electrical, and optical properties of the nanotubes (NTs) have been predicted theoretically.²

Composites of NTs incorporated in different (polymer) matrixes are of considerable interest for the development of materials with increased mechanical strength or for optical applications. NTs embedded in Langmuir–Blodgett (LB) films are a suitable model system to study the phase behavior of such materials.

One crucial problem in the controlled manipulation of SWNTs is their damage-free purification, which up to now could only be achieved by methods using surfactant solution.^{3,4} Purification techniques in organic solvents, however, give much less satisfactory results or require prolonged ultrasonic agitation, which introduces tube defects.⁵ On the other hand, purification techniques using detergents in an aqueous medium do not lead to tube dispersions in an organic solvent, which is required in the standard LB technique. How this problem can be overcome if the water soluble tube/surfactant complex is stabilized at the air/water interface through a suitable subphase composition is described in this paper. This allows preparation of LB films consisting of chemically unmodified, isolated carbon SWNTs embedded in a surfactant matrix. To achieve this goal, SWNTs were dispersed in water with the aid of a surfactant, followed by a centrifugation-based purification step. The resulting aqueous dispersions were then spread onto a subphase containing a positively charged polyelectrolyte.

First, 0.2 mg of SWNT soot produced by the catalytic arc-discharge method⁶ was added to 275 μL of an aqueous 1 wt % lithium dodecyl sulfate (LDS, from Fluka) solution. Then the sample was subjected to ultrasonic agitation for 2 min (KLN-Ultraschall-Generator 281/101). During this treatment, the entangled SWNT network is disintegrated into SWNT

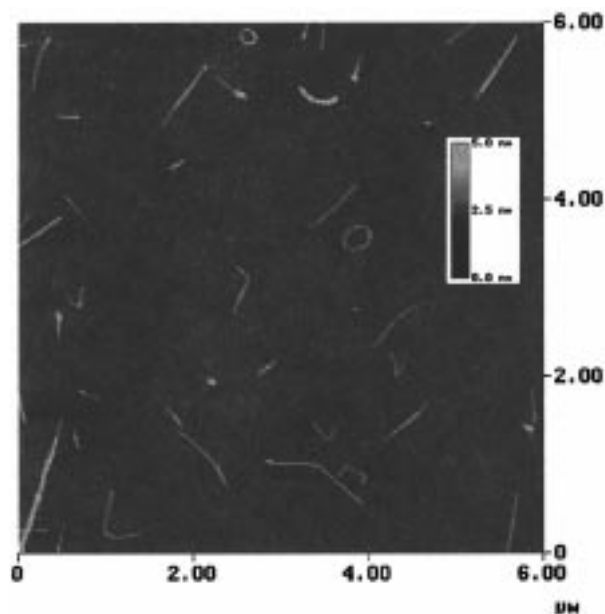


Figure 1. AFM image of SWNTs adsorbed from surfactant-stabilized supernatant on a 3-aminopropyltriethoxysilane-modified SiO_2 wafer.

bundles and individual SWNTs, which are surrounded by a surfactant shell.³ Thus-prepared dispersions are stable for several days.

Centrifugation of the dispersions for 30 min at 8000 rpm (Eppendorf, centrifuge 5417 C) was performed in order to collect larger aggregates in the sediment. The number of tubes in the supernatant varies considerably, mainly because of the inhomogeneity of the raw material. AFM investigations of the particles adsorbed from the supernatant on 3-aminopropyltriethoxysilane (Aldrich) modified Si/SiO_2 wafers³ revealed predominantly SWNTs and SWNT bundles. This is demonstrated by Figure 1, which displays a representative AFM image (Nanoscope IIIa, Digital Instruments, tapping mode). Only individual SWNTs, SWNT bundles, and a small number of catalytic particles are observed.

LB films were fabricated in a flow box (particle class 1000) using a commercial trough (KSV Minitrough 5000) with two movable barriers. The subphase consisted of an aqueous solution (0.1 mg/mL) of poly-(allylamine hydrochloride) (PA) (Aldrich, average M_n 50000–65000), which was prepared from deionized water (18 $M\Omega$ cm resistivity, Milli-Q-System). In the next step, 15 μL of the dispersion was spread onto the subphase, which was kept at 21 $^\circ\text{C}$. The aim of the addition of PA to the subphase was to prevent the SWNTs from being dissolved into the subphase. This is achieved by formation of a polyionic complex between the LDS molecules and the oppositely charged PA, resulting in a stabilization of the Langmuir film. Similar effects have been reported for various surfactant/polyelectrolyte combinations.^{7,8}

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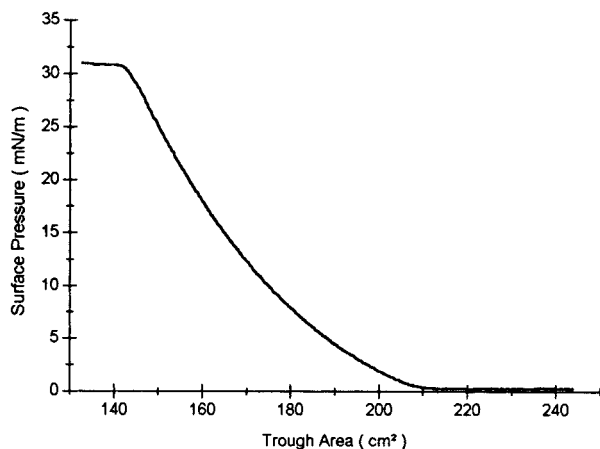


Figure 2. Surface pressure/area isotherm recorded at $T = 21\text{ }^{\circ}\text{C}$ for a SWNT/LDS supernatant spread on an aqueous poly(allylamine hydrochloride) subphase.

Figure 2 shows the surface pressure/trough area isotherm recorded after spreading of the SWNT supernatant onto a PA subphase. Since the supernatant is an aqueous SWNT dispersion, part of the LDS molecules and SWNTs dissolve into the subphase. As the fraction of dissolved molecules and tubes is not known, the abscissa of the isotherm has to be based upon the trough area instead of a mean molecular area.

If compression of spread supernatant was performed on a pure water subphase, no increase in surface pressure was observed. The isotherm obtained by spreading the same volume of the pure aqueous LDS solution (1 wt %) on PA subphase turned out to be identical to the one in Figure 2, within experimental error, indicating a small contribution of the tube particles to the total film area.

For monolayer deposition, the Langmuir film was compressed with a barrier speed of 10 mm/min, and subsequently, the surface pressure was kept constant at 14 mN/m. Stabilization of the Langmuir film was observed within 5–10 min. After this period, the Langmuir film was horizontally deposited according to the Schaefer method.⁹ In contrast, we did not succeed in a vertical transfer of the Langmuir film onto various surface-treated Si/SiO₂ substrates.

Si/SiO₂ wafers were cleaned by the RCA method¹⁰ and used as substrates. The wafers were rendered hydrophobic by immersion in a hexamethyldisilazane (Aldrich)/chloroform (1/1) solution for 12 h at room temperature. Film transfer was achieved by lowering the substrate at a speed of 1.5 mm/min onto the surface of the Langmuir film and, after a period of 1.5 min, withdrawing it with a speed of 0.5 mm/min. The transfer ratio was found to be close to 2.

In Figure 3a, an AFM image of a SWNT/LDS monolayer transferred onto a hydrophobic silicon substrate is depicted. The LDS matrix appears as being composed of dotlike islands with an average height of about 2.5 nm. The tube particles in the LB film are well-separated and no agglomeration into domains could be

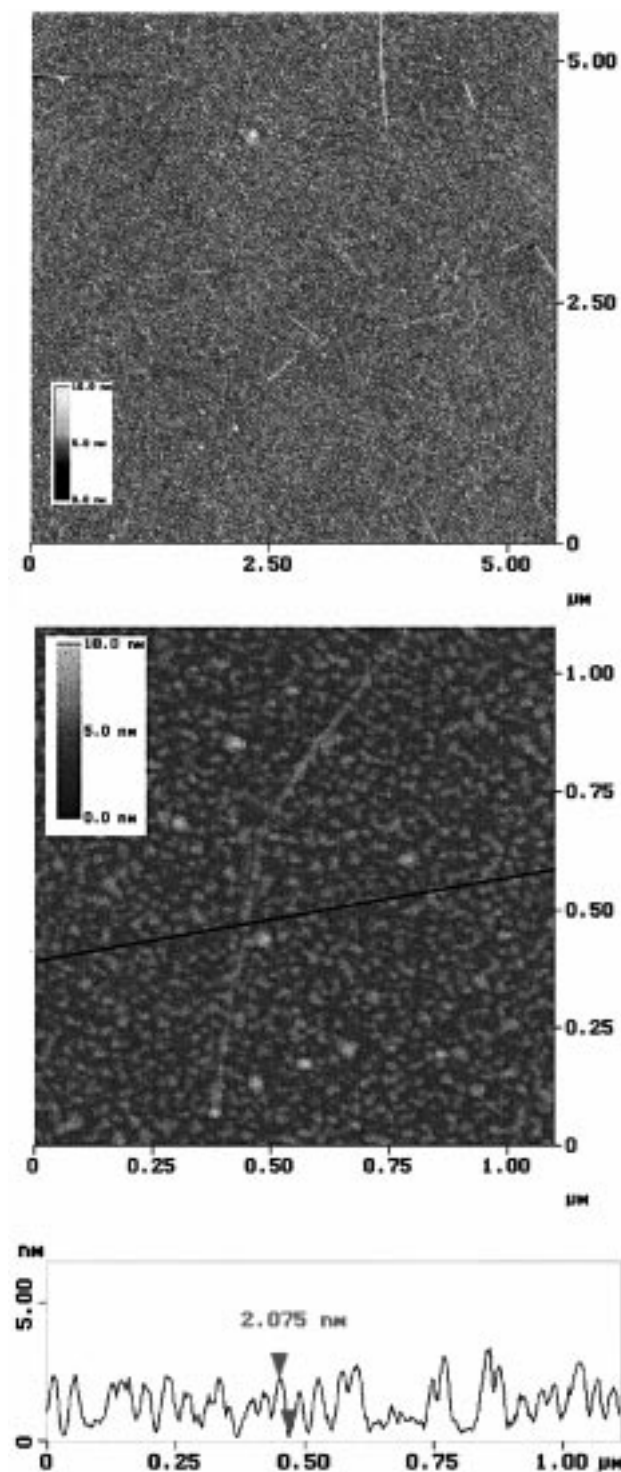


Figure 3. (a, top) AFM image of a horizontally transferred monolayer consisting of SWNTs embedded in an LDS matrix. (b, bottom) Closer AFM image of a SWNT taken from a different scan field with a section analysis.

observed. This homogeneous distribution of the tube material in the monofilm is in contrast to LB films of other matrix-embedded macromolecules.¹¹

Principally, orientation effects in LB films can be observed even if the monolayers were transferred by the Schaefer technique. This requires that the orientation occurs at the air/water interface during film compression.

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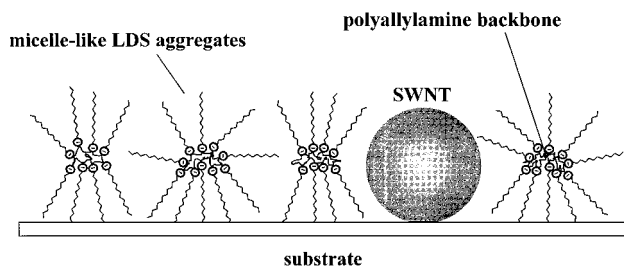
sion, which is apparently not the case in the present experiments.

Eight SWNT bundles are easily identified in Figure 3a, due to their height of more than about 3 nm. On the contrary, individual SWNTs are considerably harder to detect, especially if they are fully embedded between the LDS molecules. Nevertheless, AFM investigations performed on smaller scan sizes revealed that individual SWNTs are indeed present. This is exemplified by Figure 3b, which shows an individual SWNT together with the corresponding section analysis. The LDS matrix reveals a dotlike island structure. The relatively small content of SWNTs and SWNT bundles reflects the high ratio between the number of LDS molecules and tube particles, as it was concluded from the isotherm.

In Scheme 1, a structural model of the LB monolayer is proposed on the basis of the AFM results. The LDS/PA polyionic complex is shown to consist of micellelike aggregates with a height close to that of a LDS bilayer. It is assumed that these surfactant assemblies originate from a transferred bilayer, in accordance with the observed transfer ratio of about 2.

The presented technique should allow a broad range of modifications. Vertical transfer could be achieved by the use of different detergents, and in this way the NTs in the Langmuir film matrix may be oriented during film transfer due to flow effects. Such orientational

Scheme 1. Proposed Structural Model of a Transferred Monolayer on a Silicon Substrate^a



^a Micellelike aggregates of LDS molecules and an embedded SWNT are shown (viewed along the tube axis).

processes have been reported for a variety of different molecular systems.^{9,12} In addition, the mechanical properties of multilayered LB films could provide basic principles for the rational design of reinforced polymer systems.

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