Hydrophobic Carbon Nanotube AFM Probes for High Resolution Imaging of Biological Materials

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ABSTRACT

Carbon nanotube (CNT) tipped atomic force microscope (AFM) probes have shown a significant potential for obtaining high resolution imaging of nanostructure and biological materials. In this work, we report a simple method to fabricate single-walled carbon nanotube (SWNT) nano-probes for atomic force microscopy (AFM) using the Langmuir-Blodgett (LB) technique. Moreover, to obtain hydrophobic property of SWNT-AFM probes with a capability of high resolution imaging in atmospheric and high relative humidity conditions, the SWNT-AFM probe was modified through vapor deposition of trichloro[1H, 1H, 2H, 2H,-perfluorotyl]silane (FTOS). Using this FTOS-modified SWNT-AFM probe, a high resolution image of plasmid DNA standard sample was acquired at 80~90 % RH condition. The measured dimension of plasmid DNA had a middle width of 4~5 nm (true width 2nm). We demonstrate that the FTOS-modified SWNT-AFM probes have extremely high resolution imaging capability, which allows to measure higher resolution images compared with conventional AFM probe.

Keywords: Atomic force microscope, Carbon nanotube, Surface modification, High resolution images.

1 INTRODUCTION

Since their discovery in 1991, carbon nanotubes [1] have attracted much attention because of their unique properties and wide variety of applications, for examples, probe tips for scanning probe microscopy [2-4], nanoelectronic devices [5], field emission displays [6], hydrogen storage [7], and batteries [8-9]. Among these applications, the SWNT-AFM probes offer important advantages of high resolution imaging over conventional silicon probes due to their small tube diameter, high aspect ratio, stiffness, reversible elastic buckling and chemical stability. Since the first report of SWNT-AFM probe by Dai et al., [10] various fabrication methods of SWNT-AFM probe have been developed; for example, mechanical assembly of nanotube tips, applying an electric or magnetic field attraction [11] and direct growth of nanotubes onto AFM tip by catalytic Chemical Vapor Deposition (CVD) [12]. In our previous work [13], we reported that the SWNT-AFM probe was well formed by the Langmuir-Blodgett technique. The purpose of this paper is to investigate the effect of hydrophobic property of SWNT-AFM probe for high resolution AFM imaging at high humidity conditions. In this work, to induced hydrophobicity, we modified the SWNT-AFM probe through vapor deposition of a trichloro[1H, 1H, 2H, 2H,-perfluorotyl]silane (FTOS). We assume that if SWNT-AFM probe modified with hydrophobic materials it would reduce the water meniscus effect between the tip and sample. Moreover, we evaluated image resolution using the FTOS-modified SWNT-AFM probes and compared with a conventional high resolution AFM probe by utilizing the standard samples of a deoxyribonucleic acid (DNA). The FTOS-modified SWNT AFM probe showed excellent imaging capability and stability, allowing higher-resolution images compared with conventional AFM probes.

2 EXPERIMENTAL

2.1 Materials and Methods

SWNTs synthesized by the arc discharge method were purchased from Iljin Nanotech Co. (Seoul, Korea). Here, we used thiophenyl (-SH)-modified SWNTs (SWNT-SHs) solution for fabricating SWNT-AFM probes. In a typical experiment, purified SWNTs were shortened and carboxylated, by chemical oxidation, in a mixture of concentrated sulfuric and nitric acids (3:1, v/v, 98 % and 70 %) under ultrasonication (Cole-Palmer, 55 kHz) at 70 ℃ for 4h. The reaction mixture was filtered through an alumina filter (Whatman, England, pore size = 0.2 μm). The remains left on the filter were then washed by deionized water until the filtrate pH became nearly neutral. The resulting filtrate was dispersed by sonic agitation for 1 h in 100 ml of aqueous Triton X-100 surfactant solution (3 wt %). Immediately after sonication, the sample was centrifuged at 6000 rpm for 4 h. The supernatant was then carefully decanted. The resulting carboxylated SWNT were then reacted with 4-aminothiophenol in the presence of 1-[2-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochlorid and N-hydroxysuccin-imide SWNTs to obtain

SWNT-SHs. The SWNTs obtained were dissolved in chloroform.

2.2 Manufacture of SWNT-AFM Probes

Commercially available AFM probes (M2N, Inc., Korea) were immerged into the water surface. The SWNTs solution (~3 ml) was spread by carefully casting minute droplets on the air/water interface of the LB trough (KSV 10002, KSV instruments). After the solvent evaporated, the hydrophobic SWNTs bundles remained on the air/water interface. The bundles were then compressed by moving the barriers at a speed of 4 mm/min until the surface pressure isotherm recorded 50mN/m. A vertical dipping method was employed to transfer the SWNTs onto the commercial AFM probes surface with a deposition rate 1 mm/min at a surface pressure of 50 mN/m. The SWNT modified probes were dried under the air atmosphere for 30 min. Figure 1. is schematic diagrams of the fabrication of individual SWNTs onto the tip of a conventional AFM probe using LB technique.

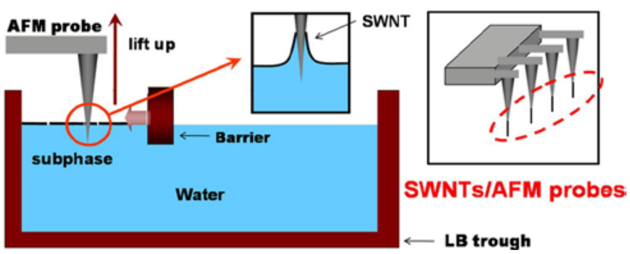

Figure 1. Schematic diagrams of the SWNT-AFM probes fabrication method using the LB technique.

2.3 Surface Modification of SWNT-AFM Probes

To obtain hydrophobic property of SWNT-AFM with capability of high resolution imaging in high RH (80~90%) condition, we modified the SWNT-AFM probe through vapor deposition of FTOS (trichloro[1H, 1H, 2H, 2H,-perfluorotyl]silane). First, the SWNT-AFM probes were cleaned and hydroxylated simultaneously by a UV/ozone cleaning for 5 minute. The light source was an excimer lamp with $\lambda = 172$ and 10 mWcm^2 (Ushio Electric, UER20-172V). After UV/ozon cleaning the SWNT-AFM probes were functionalized by FTOS. The vapor deposition procedure involves placing a SWNT-AFM probe in a reaction vessel saturated with FTOS vapor for 30 second.

2.4 Characterization and Instrumentation

The attachment of SWNTs onto the end of the tip was confirmed by scanning electron microscopy (SEM, LEO SUPRA 55, Carl Zeiss NTS GmgH) operated at 10 kV. All AFM images were recorded in non-contact mode on a XE-100 AFM system (PSIA, Inc., Korea) in air and in high RH (80~90%) condition. SWNTs-AFM probes were vibrated with a resonance frequency at approximately 310 kHz. SWNT Langmuir-films and DNA plasmid pGem7zf+ (3000 b. p. linearized with the SmaI endonuclease deposited on freshly cleaved mica, NT-MDT, Rusia) were used as standard samples.

3 RESULTS AND DISCUSSION

3.1 Evaluation of Hydrophobic SWNTs LB Films and SWNTs-AFM Probes

In our previous report, we have demonstrated a simple and effective method for transferring SWNT on AFM tip for high resolution imaging using the LB technique. To study the effect on the wettability of the SWNT LB film by FTOS functionalization, dynamic contact angles were measured by using contact angle analyzer. The contact angles of the FTOS modified SWNT LB film was compared with that of the bare silicon wafer and the thiophenyl-modified SWNTs LB film. Figure 2. shows that the typical contact angle measurements with a series of bare silicon wafer and thiophenyl-modified SWNTs LB film after FTOS coating. The contact angles were measured with a water droplet of 3 μL. The substrate was silicon wafer. Figure 2. shows a consistent increase of contact angle from 31° (bare silicon wafer) to 66° (SWNT LB film) and then to 109°, when SWNT LB film was functionalized. This clearly suggests that FTOS can be used as a suitable reagent for modifying the hydrophobic behavior of SWNT LB film. It was shown that such approach results in smooth and stable monolayer silane film with hydrophobicity. The mechanism of interaction between the FTOS and SWNT LB film can be attributed to the lowering of interfacial free energy which is evident from the change in the contact angles of the functionalized SWNT LB film.

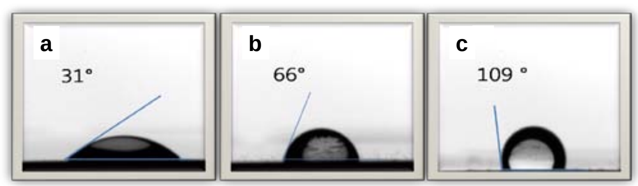

Figure 2. Contact angle measurements with a series of (a) bare silicon wafer (b) SWNT LB film (c) after FTOS coating on SWNT LB film. The contact angles were measured with a water droplet of 3 μL.

We also employed the same method of functionalization in SWNT-AFM probe mentioned above. To obtain hydrophobic property of SWNT-AFM with capability of high resolution imaging in atmospheric and high humidity environments, we modified the SWNT-AFM probe through vapor deposition of FTOS. Figure 3. demonstrate the SEM images of SWNT-AFM probes assembled by the LB technique. Figure 3. (a) represent SEM image of the bare silicon AFM probe. Figure 3. (b) shows SEM image of

SWNT-AFM probe obtained from a single LB process as shown in Figure 1. and Figure 3. (C) indicates the SWNT-AFM probe modified with FTOS through vapor deposition method. From this data, it is observed that the surface morphology of FTOS-modified SWNT-AFM probe was similar in comparison with non treated SWNT-AFM probe.

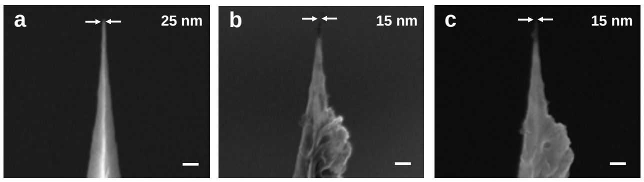

Figure 3. SEM images of SWNT-AFM probes assembled by the LB technique. (a) SEM image of the bare silicon AFM probe. (b) SEM image of SWNT-AFM probe obtained from a single LB process. (C) The SWNT-AFM probe modified with FTOS through vapor deposition method (scale bar : 50 nm)

3.2 High Resolution Images of DNA

To acquire FTOS-modified SWNT-AFM probe with the capability of high resolution imaging in air, we evaluated the FTOS-modified SWNT-AFM probe and compared to conventional high resolution AFM probe by utilizing the standard sample of a plasmid DNA. Figure 4. represent AFM images and cross-section profiles of a plasmid DNA deposited on a freshly cleaved mica surface, which was obtained by using a conventional AFM probe (Fig. 4 (a)) and an FTOS modified SWNT-AFM probe (Fig. 4 (b)). Figure 4 (a) shows the radius of curvatures of the DNA was 29~30 nm.

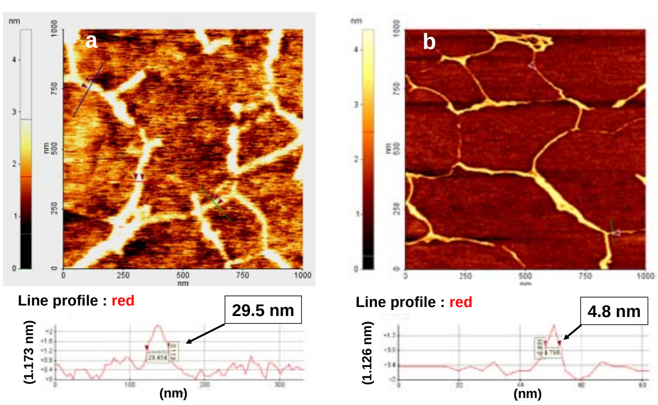

Figure 4. AFM images and cross-section profiles of a plasmid DNA obtained by using a conventional AFM probe (a) and an FTOS modified SWNT-AFM probe (b). (a) The radius of curvatures of the DNA was 29~30 nm. The result suggests that the radius of a conventional AFM probe is 27~28 nm and (b) the radii of curvatures of the DNA was measured to be 4~5 nm, indicating the radius of an FTOS modified SWNT-AFM probe is 2~3 nm.

The result suggests that the radius of a conventional AFM probe is 27~28 nm and Fig. 4 (b) indicate the radii of curvatures of the DNA was measured to be 4~5 nm, indicating the radius of an FTOS modified SWNT-AFM probe is 2~3 nm. This indicated that FTOS-modified SWNT-AFM probe have extremely high resolution imaging capability, which allows to measure higher resolution images compared with conventional AFM probe. Although the non-treated SWNT-AFM probe also has a high resolution imaging property in atmospheric condition, [13] the FTOS-modified SWNT AFM probe would be more better for measurement in atmospheric as well as in 80~90 % RH condition. It is due to the fact that a continuous and homogeneous SWNT film leads to AFM probe coated with densely packed, hierarchical SWNT arrays, which are mechanically stable because of the strong interaction between SWNT bundles. Also, the FTOS-modified SWNT-AFM probe has a high hydrophobicity so it reduces the water meniscus effect between the tip and the sample.

4 CONCLUTION

We have developed an LB process which can be used to fabricate SWNT-modified nanoprobes for high-resolution AFM measurement. A simple dipping process of conventional tips into a uniaxially aligned SWNT Langmuir monolayer results in the formation of well-oriented, robust SWNT nanoprobes that maintain their shape and direction even after successive AFM measurements. Moreover, to obtain hydrophobic property of SWNT-AFM with capability of high resolution imaging in atmospheric and aqueous environments, we modified the SWNT-AFM probe through vapor deposition of FTOS. Using this FTOS modified SWNT-AFM probe, we demonstrated the high resolution imaging of a plasmid DNA standard sample with a middle width of 4~5 nm (true width 2nm). This indicated that FTOS-modified SWNT-AFM probe have extremely high resolution imaging capability, which allows to measure higher resolution images compared with conventional AFM probe.

5 ACKNOWLEDGMENT

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