Comparative study of DNA–carbon nanotube hybrids using atomic force microscopy

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Carbon nanotubes (CNTs) are one of the promising nanomaterials that can be used in nanodevices and biosensors and for drug delivery. [1] However, the insolubility of CNTs makes the realization of such applications difficult. To solve this problem, the attachment of biomolecules on CNT surfaces is one of the effective approaches. For example, the preparation of DNA–CNT hybrids has been intensively examined by many research groups. When DNA molecules attach to and cover the CNT surface, the DNA–CNT hybrids become water soluble owing to the hydrophilic nature of DNA. Recently, it was reported that specific DNA molecules with a specific sequence tend to bind with CNTs having specific chirality. [2]

Although the preparation of DNA–CNT has become popular as a method to solubilize CNT, the detailed structures of DNA–CNT hybrids have not yet been clarified. Thus, characterization of the structures and physicochemical properties of DNA–CNT hybrids is being studied intensively these days. Spectrum analyses such as Raman spectroscopy and photoluminescence are a major approach for estimating the structures of dispersed CNTs. For example, the diameters and chirality of dispersed CNTs have been determined using spectroscopic studies. [3] Another approach is the direct observation of DNA-CNT hybrids using an atomic force microscope (AFM) or a transmission electron microscope (TEM). In this manner, the morphologies of individual DNA–CNT hybrids are visualized, and any unevenness in the structures of DNA–CNT hybrids can be discussed in detail. For instance, distributions of the diameters of individual DNA–CNT hybrids have been precisely characterized using the results of cross-section analysis of individual molecules observed with an AFM. [4]

There are several different CNT synthesis methods such as chemical vapor deposition (CVD), high-pressure Carbon monooxide (HiPco), and arc discharge. Single-walled CNTs (SWNT), double-walled CNTs (DWNT), and multi-walled CNTs (MWNT) that are synthesized via the abovementioned methods probably have various different structures and physicochemical properties. Furthermore, single-stranded DNA (ssDNA) and double-stranded DNA (dsDNA) contain various sequences. Although many papers about structures and physicochemical properties of DNA-CNT hybrids have been published recently, comparative studies of the various types of DNA–CNT hybrids are few. Researchers have employed types of various DNA molecules and CNTs without systematic comparison. Therefore, it is hard to simply summarize the knowledge about structures and properties of DNA–CNT hybrids.

In this paper, we carried out a comparative study of several types of DNA–CNT hybrids. First, hybrids of ssDNA or dsDNA with HiPco-synthesized SWNTs or CVD-synthesized SWNTs were fabricated sequentially. Four types of hybrids, ssDNA–HiPco SWNT, ssDNA–CVD SWNT, dsDNA–HiPco SWNT, and dsDNA–CVD SWNT, were comparatively characterized using AFM. For AFM observation, a certain amount of the hybrids was dropped on a 3-(Aminopropyl)triethoxysilane (APS) treated mica surface, and then, the sample was rinsed with water. After drying, AFM observations of the samples were performed in air. As a result, surfaces of ssDNA-CVD and dsDNA-CVD showed very smooth features as compared to those of ssDNA–HiPco and dsDNA–HiPco (Figure 1). Although there is only one previous report that employed CVD SWNT for hybridization with DNA [5], in most of papers, HiPco SWNT was employed to prepare DNA–CNT hybrids. Furthermore, there is no previous report on the hybridization of dsDNA molecules with CVD-synthesized CNTs. Our data clearly indicated that CVD SWNT is also suitable for preparing DNA–CNT hybrids. As for the diameters of the hybrids, when dsDNA was employed, as expected, the diameters of the hybrids were larger than when ssDNA was employed. However, the increase in the diameter with the use of dsDNA was less than twice that with the use of ssDNA. This finding suggests that the increase in diameter was not necessarily proportional to the number of DNA strands.

Second, we employed 1% sodium dodecyl sulfate (SDS) instead of DNA for comparison. It is known that SDS is an effective CNT-solubilizing compound. [6] In this case, AFM observation was difficult even after rinsing the sample with water. Without rinsing, it was not possible to obtain the AFM images. When the SWNT dispersed with the 1% SDS was dialyzed against pure water using 100x volumes to remove excess SDS, the AFM observation became much more stable. We confirmed that dialysis using 1000x and 1000000x volumes of water were also effective for stable AFM imaging. Although the dialysis treatment was effective, the dispersion with DNA was convenient for depositing the hybrids on the APS-treated mica surface. This is the first example of the direct comparison of SDS–CNT with DNA–CNT using the same CNT compound.

Finally, we examined a SWNT that was functionalized with polyethyleneglycol (PEG-SWNT). Usually, when insoluble CNT is dispersed using DNA, a mixture of DNA and CNT is sonicated to promote dispersion and the sonicated mixture is centrifuged to remove aggregates. However, in the case of PEG–SWNT, these powerful treatments can be avoided because PEG–SWNT is water soluble. We mixed ssDNA with PEG-SWNT without sonication and centrifugation, and then observed the mixture using an AFM to evaluate interaction between ssDNA and PEG–SWNT. The AFM images showed both smooth and rough filamentous structures depending on the mixing conditions. The result suggests that the AFM observation of DNA and PEG–SWNT may provide useful information to verify DNA–CNT interaction.

We compared several types of DNA–CNT hybrids using AFM sequentially. We opine that our comparative study provided useful information for understanding the DNA–CNT interaction in detail. We hope that our results will be the basis for establishing industrial applications of CNT.

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Figures

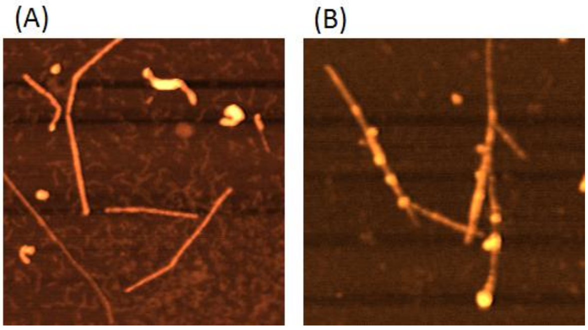

Figure 1
AFM images of ssDNA–SWNT hybrids. (A) SWNT synthesized via CVD. (B) SWNT synthesized via HiPco. Scan area was 500 nm^2.