

Self-Assembly of DNA-Wrapped Carbon Nanotubes for Sensing Applications

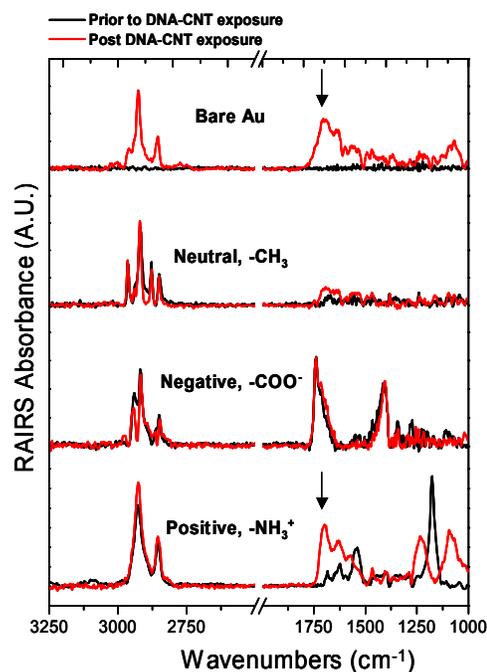
Carbon nanotubes (CNTs) are promising materials for chemical and biological sensing applications. Several studies have shown that the electrical conductivity of CNTs is extremely sensitive to changes in the local chemical environment, a property most likely resulting from the fact that all carbon atoms of CNTs reside at the surface. Some researchers have reported near single-molecule detection capabilities with CNT-derived conductivity sensors. In contrast, other groups have reported much more modest sensitivities. These discrepancies along with other irreproducible behaviors that have plagued CNT sensing studies are most likely due to the inherent polydispersity (i.e., metallic and semiconducting) of CNT samples and the difficulty in precisely assembling CNTs in sensing devices. One promising approach to these major challenges is to use single-stranded DNA (ssDNA) to disperse the CNTs as pioneered by Zheng and coworkers at Dupont. The ssDNA wraps around the CNTs and imparts a negative charge on the DNA/CNT hybrid material that allows for rudimentary purification of metallic vs. semiconducting CNTs by anion-exchange chromatography. We postulate that the ssDNA moieties will also allow for controlled placement of CNTs onto nanodevice test structures based on ssDNA-surface interactions.

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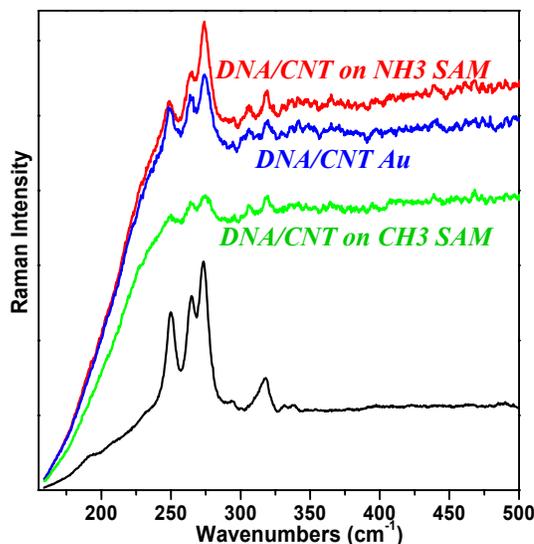
The NIST research team is studying the adsorption of DNA/CNT hybrid materials on model self-assembled monolayer (SAM) to determine which chemical functional groups can be used to anchor DNA/CNTs to surfaces. The long-term goal is to use organic monolayers to direct the placement of CNTs with nanometer resolution to fabricate conductometric-based sensing devices. Reflection absorption FT-IR (RAIRS), x-ray photoelectron spectroscopy (XPS), and Raman spectroscopy are used to study the interactions of the hybrid material with model surfaces terminated with various chemical end groups. This project is part of a larger effort within CSTL to examine this hybrid bio-nanomaterial; the separation and purification of DNA/CNT hybrid materials by capillary and temperature gradient focusing are also being investigated in CSTL's Analytical Chemistry Division.

The adsorption of the DNA/CNT hybrid materials on SAM model surfaces were examined using RAIRS, XPS, and Raman spectroscopy. The addition of characteristic DNA absorbance bands was observed on bare gold, positively charged, and on neutral (to a small extent) model surfaces as indicated by the arrows in the figure after exposure to a

solution of DNA/CNTs. The figure illustrates the DNA/CNT adsorption by RAIRS.



Raman microscopy confirmed the presence of the DNA/CNT complex on these surfaces.



The attraction between the DNA/CNT hybrid material and these surfaces was anticipated based on prior knowledge of the interactions of ssDNA on model surfaces. The negative charge associated with the ssDNA causes the

DNA/CNT material to adsorb to positively charged amine-terminated surfaces due to electrostatic interactions. Similarly, the adsorption of the hybrid material on bare gold surfaces is likely due to the strong chemisorption of DNA bases on gold surfaces. The minimal attraction of the DNA/CNT hybrid material to neutral surfaces is attributable to weaker hydrophobic interactions.

***Future studies* will exploit the specific adsorption of the DNA/CNT materials in conjunction with chemically patterned model surfaces to gain control over the deposition of these materials on patterned surfaces with micrometer- and nanometer-scale lateral resolution.**

These studies indicate that organic monolayers can be used to selectively deposit DNA-wrapped CNTs on surfaces. The ssDNA of the DNA/CNT hybrid appears to be in a chemical environment similar to that of free DNA such that it can adsorb predictably to model SAM surfaces.