

5-19-2008

Electrodeposition study of ODN : SWCNT hybrids on gold substrates

Roya R. Lahiji

Birck Nanotechnology Center, Purdue University, rlahiji@purdue.edu

Bridget D. Dolash

Birck Nanotechnology Center, Purdue University, bdolash@purdue.edu

Jennifer McDonald

Purdue University - Calumet Campus

Dmitry Zemlyanov

Birck Nanotechnology Center, Purdue University, dimazemlyanov@purdue.edu

Donald E. Bergstrom

Birck Nanotechnology Center and Bindley Bioscience Center, Purdue University, bergstrom@purdue.edu

See next page for additional authors

Follow this and additional works at: <http://docs.lib.purdue.edu/nanopub>



Part of the [Nanoscience and Nanotechnology Commons](#)

Lahiji, Roya R.; Dolash, Bridget D.; McDonald, Jennifer; Zemlyanov, Dmitry; Bergstrom, Donald E.; and Reifenberger, R., "Electrodeposition study of ODN : SWCNT hybrids on gold substrates" (2008). *Birck and NCN Publications*. Paper 322. <http://docs.lib.purdue.edu/nanopub/322>

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact epubs@purdue.edu for additional information.

Authors

Roya R. Lahiji, Bridget D. Dolash, Jennifer McDonald, Dmitry Zemlyanov, Donald E. Bergstrom, and R. Reifenberger

Electrodeposition study of ODN:SWCNT hybrids on gold substrates

Roya R. Lahiji^{*,1,2}, Bridget D. Dolash^{2,3,4}, Jennifer McDonald⁵, Dmitry Zemlyanov², Donald E. Bergstrom^{2,3,4}, and R. Reifenberger^{1,2}

¹ Department of Physics, Purdue University, West Lafayette, IN 47907, USA

² Birck Nanotechnology Center, West Lafayette, IN 47907, USA

³ Department of Medicinal Chemistry and Molecular Pharmacology, Purdue University, West Lafayette, IN 47907, USA

⁴ The Walther Cancer Institute, Indianapolis, IN 46208, USA

⁵ Department of Chemistry, Purdue Calumet University, IN 46323, USA

Received 1 October 2007, accepted 15 February 2008

Published online 19 May 2008

PACS 68.37.–d, 68.55.am, 81.05.Lg, 81.07.Pr, 81.15.Pq, 82.80.Pv

* Corresponding author: e-mail rlahiji@purdue.edu, Phone: +00 765 496 3238, Fax: +00 765 494 0706

Sonication of short single-stranded DNA (oligodeoxyribonucleotide; ODN) with Single-Walled Carbon Nanotubes (SWCNTs) greatly facilitates the dispersion of SWCNTs from entangled ropes in an aqueous solution, creating ODN:SWCNT hybrids. Electrodeposition has been investigated to determine if well-dispersed ODN:SWCNT hybrids on a metal substrate can be created. Preliminary studies indicate that electrodeposition using an Au substrate held at

+0.5 V produces ODN:SWCNT hybrids that are uniformly deposited across the Au substrate. This result can be compared to samples produced by drop casting and evaporation techniques which yield a thick tangled mat of ODN:SWCNT hybrids across the substrate. The resulting electrodeposited samples were characterized using Scanning Probe Microscope (SPM) and X-ray Photoemission Spectroscopy (XPS) techniques.

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction With the recent reports that the dispersion of Single-Walled Carbon Nanotubes (SWCNTs) [1, 2] in an aqueous solution is facilitated by single-stranded DNA (oligodeoxyribonucleotide; ODN), the production of ODN:SWCNT hybrids [3, 4] for biological and medical applications has become more promising. Hughes et al. [5] suggested that ODN binding to SWCNT results from π stacking interactions and hydrophobic forces. Although there are theoretical calculations to describe the nature of the ODN:SWCNT association [4–6], confirming experimental evidence is generally scarce. Recently, we have studied ODN:SWCNT hybrids on insulating mica substrates using Scanning Probe Microscopy (SPM). This work focused on a thorough characterization of T30 ODN:SWCNTs [7]. Our results suggested that the association of ODNs to SWCNTs is facilitated by defects along the walls of the SWCNTs.

A limitation of depositing ODN:SWCNT hybrids on insulating substrates is that the hybrids cannot be patterned

in an easy way. Such patterning might be facilitated by conducting substrates, where an electric field can be used to guide the assembly of the ODN:SWCNT hybrids. As examples, Lindsay et al. used electrodeposition to drive DNA onto a crystalline Au surface for study by STM [8] and, more recently, Keller et al. [9] have reported the electrodeposition of coli RNA directly onto a gold substrate. Another alternative approach to patterning is to immobilize DNA or DNA-based nano-particles onto a gold substrate using chemical functionalization [10–12].

To further explore the deposition of ODN:SWCNT hybrids onto conducting substrates, we report on our initial efforts to deposit ODN:SWCNT hybrids onto a gold substrate using electrodeposition techniques.

2 Experimental

2.1 Sample preparation Single-walled carbon nanotubes (SWCNT) grown by a high-pressure carbon monoxide process (HiPco) were used as-received from

Carbon Nanotechnologies Inc. (Houston, TX). The oligodeoxyribonucleotide (ODN) used in this study was 5'-TTT TTT TTT TTT TTT TTT TTT TTT TTT-3' (T30) obtained from Integrated DNA Technologies, Inc. (Coralville, IA). All other chemicals were purchased from Sigma–Aldrich.

The ODN:SWCNT hybrids were prepared in a way similar to that described previously [7]. Briefly, the as-received SWCNTs (4 mg) were placed in piperazine-1,4-bis(2-ethanesulfonic acid) (PIPES) buffer (8 ml, 1 mM, pH = 7) in a 15 ml polypropylene centrifuge tube; then T30 ODN (4 mg) was added to the mixture. The tube was placed on ice and sonicated (Sonics Model VC 130) at 20 kHz for 120 minutes using a 6 mm diam. probe tip vibrating at 80% amplitude. Typically 8–9 Watts of power were required to maintain a probe tip amplitude of ~98 microns.

After sonication, the samples were centrifuged for 90 minutes at 16,000 g and the supernatant was carefully collected. Samples were each placed in a Millipore Amicon® Ultra-4 centrifugal filter device (Molecular Weight cut off 100 kDa) and desalted according to the manufacturer's protocol, using Birk Nanotechnology Grade (BNG) [13] water as the solvent. The concentrated, desalted samples (~50 µl) were collected and stored at 4 °C. The concentrated ODN:SWCNT solution was typically diluted by ~80 fold before imaging by SPM or characterization by XPS.

2.2 Scanning probe microscope A Nanotec Electronica scanning probe microscope operating under ambient conditions was used to study ODN:SWCNT hybrids deposited on both mica and gold substrates. WSxM software (version 8.7) was used to process the SPM images [14]. Ambient humidity in the room was kept near ~40%. Mikromasch ultrasharp CSC37/NoAl cantilevers having a nominal spring constant of 0.35 N/m and a nominal resonant frequency of 28 kHz were used throughout. Imaging was performed under ambient conditions at constant amplitude in the non-contact mode.

2.3 X-ray photoemission spectrometer The X-ray Photoemission Spectroscopy (XPS) data were obtained with a Kratos Ultra DLD spectrometer using monochromatic Al K_α radiation ($h\nu = 1486.58$ eV). Survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively. The spectra were collected at 0° with respect to the surface normal. All binding energy (BE) values refer to the Fermi level, and were referenced to Au 4f_{7/2} at 84.0 eV. The standard deviation of the peak position associated with the calibration procedure was ±0.05 eV. The data were analyzed with commercially available software, CasaXPS (version 2313Dev64). The individual peaks were fitted by a Gaussian/Lorentzian function after linear or Shirley type background subtraction.

3 Results and discussion

3.1 SPM results Previous work from our labs reported a deposition technique for ODN:SWCNTs on an insulating substrate, mica [7]. The procedure for the deposition on mica requires a freshly cleaved mica substrate treated by 1 M magnesium sulphate (MgSO₄) for five minutes. After treatment, the substrate was rinsed thoroughly with BNG deionized water and blown dry with a stream of high purity nitrogen gas. After drying the mica substrate, approximately 0.1 ml of diluted solution was dripped across the treated mica surface, causing individual drops to form and roll off the substrate. Following this procedure, the mica substrate was rinsed with a stream of BNG deionized water and blown dry with a stream of high purity nitrogen gas.

Figure 1 shows a typical SPM image of T30 ODN:SWCNT hybrids on mica. As obvious from this figure the SWCNTs are well dispersed on the mica substrate.

The above technique might not be useful for other substrates. For example, SPM studies have been attempted on ODN:SWCNT hybrid samples deposited on annealed Au substrates using the above method for deposition. A few drops of the diluted ODN:SWCNT solution was dropped onto a clean Au substrate. The sample was washed with BNG deionized water, blown dry with nitrogen and then immediately SPM scans were taken. The images revealed no sign of ODN:SWCNTs on the gold substrate. We conclude that the hybrids do not strongly adhere to the Au substrate. These results suggest the deposition techniques developed for mica are not appropriate for a gold substrate.

As a result, an evaporation technique for the deposition of these hybrids onto a gold substrate was attempted. First, a gold substrate cut from a Au foil was washed with a piranha solution (a 1:3 ratio of H₂SO₄ to H₂O₂) and then hydrogen flame annealed. The Au substrate was immersed in Piranha solution for couple of minutes and then rinsed thoroughly with BNG water before blow drying under a nitrogen stream. In parallel studies, STM images of the substrate revealed evidence of step edges and atomically flat plateaus.

A drop of the ODN:SWCNT solution was placed on the gold substrate and the substrate was placed in covered

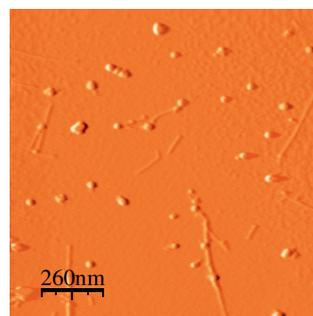


Figure 1 (online colour at: www.pss-a.com) SPM image of ODN:SWCNT hybrids on mica substrate. The sample preparation is from Ref. [7]. The globular features in the background represent amorphous carbon and particulates that are in the solution and have been deposited onto substrate.

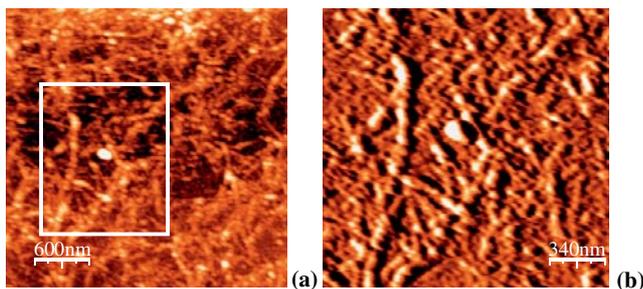


Figure 2 (online colour at: www.pss-a.com) (a) SPM image of ODN:SWCNT hybrids on an annealed gold substrate using the evaporation technique. This method created a dense mat of ODN:SWCNT hybrids. (b) shows a zoomed in image of the area shown in (a).

Petri dish overnight, allowing complete evaporation of the liquid. An SPM scan was taken of the substrate and reveal a crowded mat of ODN:SWCNTs as shown in Fig. 2.

Although this method was successful in producing a mat of ODN:SWCNT hybrids, it is difficult to produce a uniform deposition across the Au substrate. Therefore an electrodeposition technique was developed to produce a better dispersion of the hybrids across a gold substrate.

A gold substrate was prepared in a way similar to that described above. Immediately after cleaning, the gold substrate was immersed in a dilute ODN:SWCNT solution containing as received HiPco SWCNTs sonicated with T30 ODN for 120 minutes. Since ODN has a negative phosphate backbone, it might be expected that an electrodeposition technique might work. A Pt wire was used as a cathode electrode and a DC voltage of +0.5 volts was applied to the Au anode overnight before removing the Au substrate for further study.

After the electrodeposition, the sample was studied using SPM and a typical scan is presented in Fig. 3. The electrodeposition technique produced ODN:SWCNT hybrids that are uniformly deposited across the Au substrate.

3.2 XPS results The ODN:SWCNT samples prepared on Au substrates were also studied using XPS. Of particular interest is the C 1s core level emission as shown

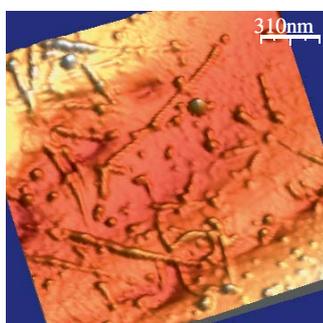


Figure 3 (online colour at: www.pss-a.com) A typical SPM image of ODN:SWCNT hybrids deposited on a gold substrate using the electrodeposition technique. A DC voltage of +0.5 volts was applied to the Au substrate.

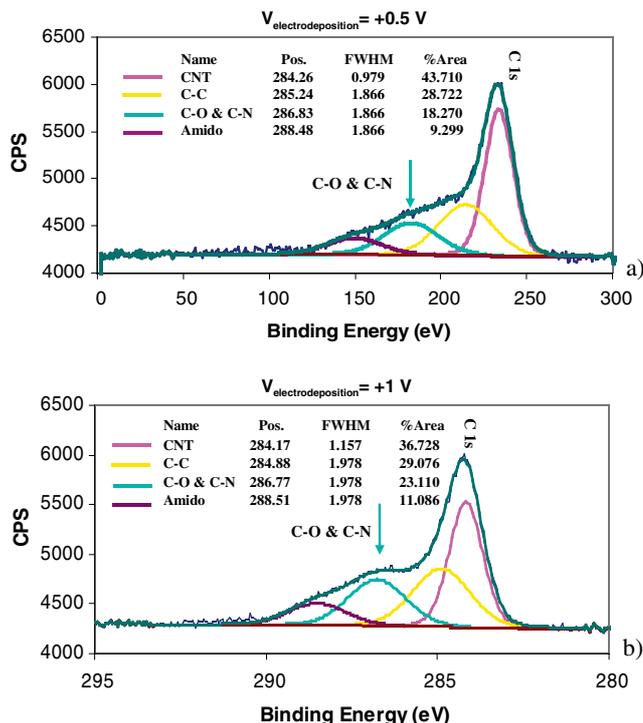


Figure 4 (online colour at: www.pss-a.com) XPS spectra obtained from ODN:SWCNT electrodeposited onto Au substrate. The observed C 1s peak can be explained by combining the contributions of electrons photoemitted from C in SWCNTs, from C-C and C-O complexes in ODN, and from C-amido complexes. In (a), the XPS data of ODN:SWCNT hybrids electrodeposited on Au substrate at potential of +0.5 V is shown. In (b), the XPS data of ODN:SWCNT hybrids electrodeposited on Au substrate at potential of +1.0 V is shown. An increase in C-O and C-N signal is seen at this potential compared to sample prepared at +0.5 V.

in Fig. 4. The N 1s and P 2p core level spectra was collected as well (not shown here) to provide evidence for T30 ODN presence.

The effect of the DC voltage applied during the electrodeposition was also studied. Thus, Fig. 4(a) and (b) show the C 1s spectra obtained after controlled emersion at +0.5 V and +1.0 V respectively. After emersion, the samples were immediately transferred to the UHV chamber of XPS spectrometer. The curve fitting procedure allows us to distinguish four carbon chemical states: graphite-like carbon (CNT), carbon bond with carbon and hydrogen (C-C), carbon bond with oxygen or nitrogen (C-O & C-N) and amido carbon (N-C=O). The C-O & C-N contribution increases as the voltage changes from +0.5 V to +1.0 V as shown in Fig. 4(b). The increase in the amount of oxidized carbon might be tentatively attributed to oxidation of the ODN or to the increased deposition of oxidized C at the higher deposition voltages. We hypothesize there is an optimum voltage for the electrodeposition of the ODNs onto the Au substrate, which is the adsorption potential. Above the adsorption potential of ODN:SWCNT hybrids, oxida-

tion of ODN occurs and/or more amorphous carbon particulates adsorb on the Au surface.

4 Conclusion We have investigated an electrodeposition technique to deposit ODN:SWCNT hybrids on a Au substrate. The technique does not require the prior functionalizing of either ODN or the substrate. As judged by our preliminary results, a potential of +0.5 volts applied to the Au substrate overnight produced a uniform deposit of ODN:SWCNT hybrids. The electrodeposited ODN:SWCNTs were further studied using SPM and XPS techniques.

Acknowledgements R.L. acknowledges support from a Summer Research Grant from Purdue University. J.M. would like to thank the 2007 Summer Undergraduate Research Internship (SURI) Program sponsored by the NASA funded Institute for Nanoelectronics and Computing (INAC) at Purdue for support during the course of this work. The authors acknowledge the helpful support of Nanotec Electronica for the WSxM software that was used to acquire and analyze the SPM data. We also thank D. K. Pandey for his STM study of the flame annealed Au substrate and Tim Miller from the Birck Nanotechnology Center at Purdue University kindly provided the Nanotechnology grade water used in these experiments.

References

- [1] S. Iijima, *Nature* **354**, 56 (1991).
- [2] D. S. Bethune, C. H. Kiang, M. S. Devries, G. Gorman, R. Savoy, J. Vazquez, and R. Beyers, *Nature* **363**, 605 (1993).
- [3] M. Zheng, A. Jagota, E. D. Semke, B. A. Diner, R. S. McLean, S. R. Lustig, R. E. Richardson, and N. G. Tassi, *Nature Mater.* **2**, 338 (2003).
- [4] M. Zheng, A. Jagota, M. S. Strano, A. P. Santos, P. Barone, S. G. Chou, B. A. Diner, M. S. Dresselhaus, R. S. McLean, G. B. Onoa, G. G. Samsonidze, E. D. Semke, M. Usrey, and D. J. Walls, *Science* **302**, 1545 (2003).
- [5] M. E. Hughes, E. Brandin, and J. A. Golovchenko, *Nano Lett.* **7**, 1191 (2007).
- [6] J. Rajendra, M. Baxendale, L. G. Dit Rap, and A. Rodger, *J. Am. Chem. Soc.* **126**, 11182 (2004).
- [7] R. R. Lahiji, B. D. Hines, D. E. Bergstrom, and R. Reifenberger, *Small* **3**, 1912 (2007).
- [8] S. M. Lindsay, T. Thundat, L. Nagahara, U. Knipping, and R. L. Rill, *Science* **244**, 1063 (1989).
- [9] R. W. Keller, D. J. Keller, D. Bear, J. Vasenka, and C. Bustamante, *Ultramicroscopy* **42**, 1173 (1992).
- [10] K. S. Chen, S. C. Chen, H. R. Lin, T. R. Yan, and C. C. Tseng, *Mater. Sci. Eng. C* **27**, 716 (2007).
- [11] C. N. Kirchner, S. Szunerits, and G. Wittstock, *Electroanalysis* **19**, 1258 (2007).
- [12] U. Plutowski, S. S. Jester, S. Lenhart, M. M. Kappes, and C. Richert, *Adv. Mater.* **19**, 1951 (2007).
- [13] The Nanotechnology grade water used in this study has been passed through an ultra filter with a molecular cut off of 6000 Daltons. The boron content is below the detection limits of 15 parts per trillion. The total organic carbon is less than 200 parts per trillion.
- [14] I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, and A. M. Baro, *Rev. Sci. Instrum.* **78**, 013705 (2007).