Optical characterization of vertically aligned single-walled carbon nanotube arrays

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Here we discuss spectroscopic investigation and characterization of vertically aligned single-walled carbon nanotube (VA-SWNT) arrays, which were synthesized using the alcohol catalytic CVD method [1]. Growth of the VA-SWNTs was monitored using an *in situ* absorbance measurement [2], which provides information about the growth process. Primary methods employed were Resonance Raman and UV-Vis-NIR optical absorbance spectroscopy.

Polarization-dependent resonance Raman scattering (RRS) spectra were obtained from VA-SWNTs. A previous study [3] had employed two incident polarizations (parallel and perpendicular to the SWNT alignment direction) and found some anisotropy in the radial breathing mode (RBM) peak behaviors. This anisotropy was attributed to resonances with different transition energies, $E_{\mu,\mu}$ for parallel polarized excitation and $E_{\mu,\mu\pm1}$ for perpendicularly polarized excitation (where μ denotes a cutting line index in the one-dimensional Brillouin zone). In order to test this hypothesis, we performed more comprehensive measurements in which both the incident and scattered light was polarized. Our results indicate that contribution from perpendicularly excited SWNTs is not significant, and the anisotropic features arise from the sample morphology.

RRS measurements at various locations along the cross-section of the VA-SWNT array also yielded different spectra, which indicate larger diameters near the root of the array. This suggests the diameter distribution changes during synthesis. However, RRS is only suitable to evaluate diameter distribution in an ensemble if many laser energies are used to obtain a comprehensive Raman map [4], thus a less selective method was necessary.

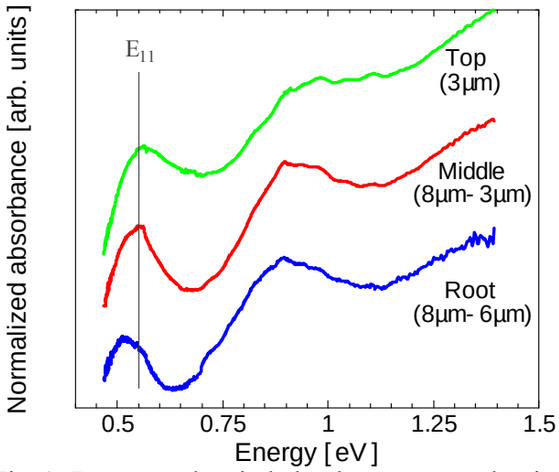

Fig. 1: Decomposed optical absorbance spectra showing contribution from different regions of a VA-SWNT array.

To obtain a more reliable estimate of the average SWNT diameter, UV-Vis-NIR optical absorbance spectra were measured for arrays of increasing height, and the spectra were decomposed to reveal contributions from different regions of the array (Fig. 1). This was accomplished by synthesizing three VA-SWNT arrays under identical conditions, but allowing them to growth to 3, 6, and 8 μm. Since all three arrays exhibited essentially the same growth behavior, one can assume the only difference among them is their height. It is known that these VA-SWNT arrays form by a root-growth mechanism [5], thus the spectrum of the 3 μm array should be identical to the upper portion of the 6 μm array. Similarly, the root portion of the thickest (8 μm) array should be the difference between its overall absorbance spectrum and that of the 6 μm array (Fig. 1).

Lastly, we show that the average diameter of these VA-SWNTs can be adjusted by changing the concentration of the catalyst in the dip-coat solution. Increasing both the relative and absolute amounts of molybdenum with respect to cobalt resulted in SWNTs with smaller average diameters. The average diameter could be adjusted between 1.4 and 2.5 nm by changing the amount of molybdenum over just one order of magnitude (Fig. 2). These results give a better understanding of and improved control over the synthesis process. Furthermore, this shows the array height as well as the SWNT diameter can now be controlled, allowing for the synthesis of VA-SWNTs tailored to different applications.

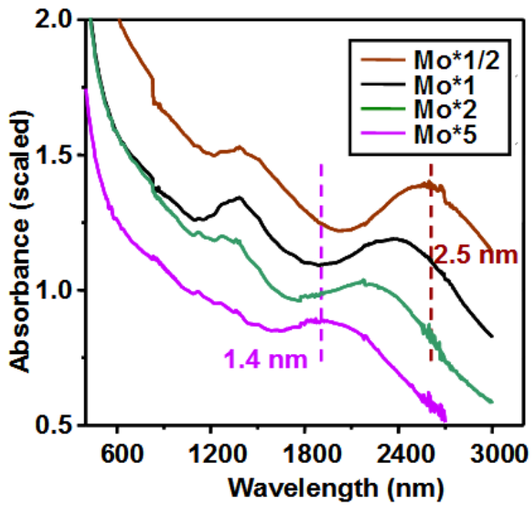

Fig. 2: Optical absorption spectra showing the average diameter can be adjusted by changing the relative catalyst concentration.

References:

[1] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, M. Kohno, *Chem. Phys. Lett.* **260** (2002) 229.
[2] S. Maruyama, E. Einarsson, Y. Murakami, T. Edamura, *Chem. Phys. Lett.* **403** (2005) 320.
[3] Y. Murakami, S. Chiashi, E. Einarsson, S. Maruyama, *Phys. Rev. B* **71** (2005) 085403.
[4] P.T. Araujo, S.K. Doorn, S. Kilina, S. Tretiak, **E. Einarsson**, S. Maruyama, H. Chacham, M.A. Pimenta, A. Jorio, *Phys. Rev. Lett.* **98** (2007) 067401.
[5] R. Xiang, Z. Zhang, K. Ogura, J. Okawa, **E. Einarsson**, Y. Miyauchi, J. Shiomi, S. Maruyama *Jpn. J. Appl. Phys.* **47** (2008) 1971.