

Correlative Microscopic and Spectroscopic Characterization of Carboxylated Single-Walled Carbon Nanotubes

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The strong optical absorbance of single-walled carbon nanotubes (SWNTs) from 700 to 1,100 nm in the near-infrared makes them suitable for numerous nanodevice applications [1]. However, their intrinsic hydrophobicity presents an apparent impediment to their control and efficiency. This study presents a temporal analysis and optimization of SWNT carboxylation by nitric acid treatment. Our chemical modification process creates carboxyl functional groups at SWNT defect sites that provide the necessary and sufficient chemical anchor to facilitate nanoscale applications, while retaining their desirable physical, chemical, and optoelectronic properties.

Raw HiPco SWNTs were dispersed via sonication in an aqueous Triton X-100 solution prior to chemical oxidation with aqueous nitric acid for reflux times ranging from 30 min to 48 h. Subsequently, gold nanoparticles were covalently attached to the carboxyl sites using thiol chemistry. The SWNT samples were imaged by atomic force microscopy (AFM) (Digital Instruments, Inc. Nanoscope III Multimode Scanning Probe Microscope) operated in the Tapping Mode™ and characterized by UV-Vis-NIR (Perkin-Elmer Lambda 900 UV-Vis-NIR spectrophotometer), Raman (Jobin Yvon Horiba T 64000 high-resolution LabRam), FTIR (Nicolet AVATAR Omni), and X-ray photoelectron spectroscopy (XPS) (Kratos Axis Ultra spectrometer, Al K α monochromatic X-ray source) spectroscopies.

AFM images reveal that carboxylation occurs first at the end caps (Fig. 1a) and subsequently at the sidewalls (Fig. 1b,c) [2]. The AFM image of the control sample (Fig. 1d) indicates that no gold labeling occurred at the end caps or sidewalls in the absence of the thiol linker. Following 12 h of acid reflux, quantitative XPS studies revealed the presence of functional groups (-OH, -CHO, etc) as well as 11% absolute carboxylation of the SWNTs (Fig. 2) and UV-Vis-NIR spectra showed that these SWNTs maintained their optical properties (Fig. 3). FTIR characterization demonstrates the increase in the carboxylation (Fig. 4). Raman spectroscopy revealed shifts in G-band intensities due to charge transfer effects as shown in Fig. 5.

In summary, we have devised a route to control and optimize the carboxylation of SWNTs. Functionalization of SWNTs enhances their dispersion and processability. It also provides a mechanism to tether application specific chemical and biological moieties to SWNTs.

References

1. P. W. Barone et al., *Nat. Mater.* 4, (2005), 86.
2. Liu, J. et al., *Science* 280 (1998) 1253.
3. This work was supported by the Department of Defense (IHM).

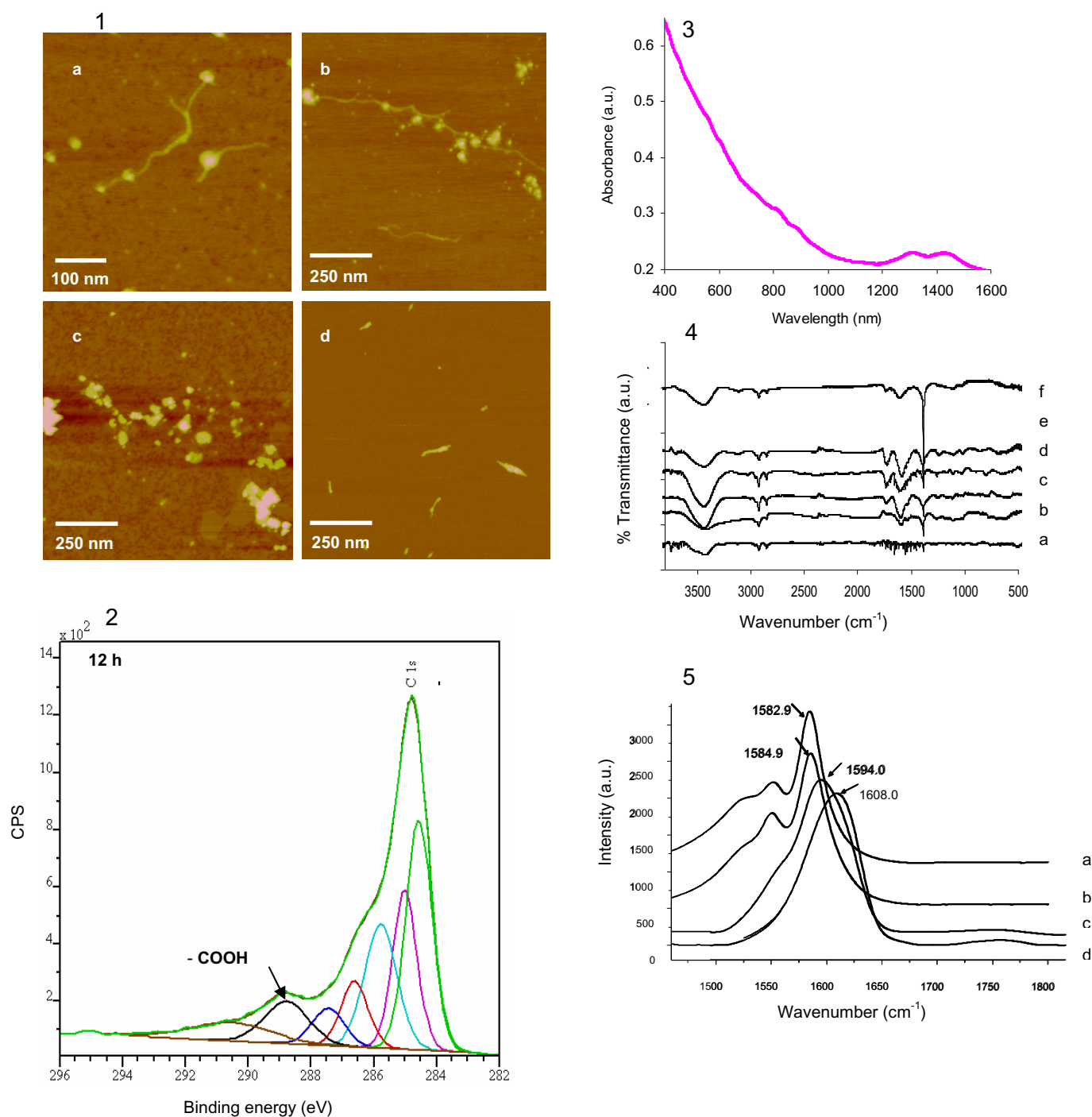


Fig. 1. AFM images of SWNTs refluxed in nitric acid for (a) 12, (b) 24, and (c) 48 h and then coupled chemically to gold nanoparticles. SWNTs refluxed in nitric acid for 24 h and then treated with gold nanoparticles in the absence of the linker to serve as the control (d).

Fig. 2. XPS curve-fitted high resolution C 1s spectrum of SWNTs refluxed in nitric acid for 12 h.

Fig. 3. UV-Vis-NIR spectrum of SWNTs refluxed for 12 h and dispersed in DMF.

Fig. 4. Raman spectra showing an upshift in the tangential mode of SWNTs refluxed for (a) 8, (b) 12, (c) 24, and (d) 48 h.

Fig. 5. FTIR spectra of SWNT samples refluxed for time intervals of (a) 2, (b) 5, (c) 8, (d) 12, (e) 24, and (f) 48 h.