Spray-Coated Carbon-Nanotubes for Crack-Tolerant Metal Matrix Composites as Photovoltaic Gridlines

Omar K. Abudayyeh[1], Nathan D. Gapp[2], Geoffrey K. Bradshaw[2], David M. Wilt[2], Sang M. Han[1]

[1]Univesity of New Mexico, Albuquerque, NM 87131, USA

[2]Air Force Research Laboratories, Kirtland AFB, NM

Abstract — **In this work, we present the use of a simple, cost-effective, and manufacturable method of depositing carbon nanotubes onto metal films to create metal matrix composite gridlines for photovoltaic cells. Carbon nanotubes are deposited using a spray coating method to create layer-by-layer microstructure composites. Initial strain failure tests show the ability of composite lines to remain electrically connected with fractures up to 35-μm-wide, where carbon-nanotubes electrically bridge the gap. The metal-carbon-nanotube composites are electrically characterized though I-V sweeps. The composite lines can carry current densities ranging from 500 to 2500 A/cm^2.**

Index Terms — **carbon nanotubes, coatings, composite materials, photovoltaic cells, silver**

I. INTRODUCTION

Carbon nanotubes (CNTs) are promising nanostructure materials [1], which have been actively studied in recent years due to their unique mix of structural, electronic, thermal, and mechanical properties [2]–[5]. The conductivity and high aspect ratio of CNTs are attractive characteristics for producing conductive composites using only minute amounts of CNTs. This feature can be used in coatings to get conductive and transparent networks [6]–[13]. In addition, individual CNTs can tolerate mechanical treatment, such as bending, buckling, or even certain degree of defect creation without loss of conductivity [14]–[16].

Possessing such a unique mixture of properties, CNTs demonstrate their potential in different scientific and technological areas, including transistors [17]–[20], diodes [21], sensors [22]–[24], and conductive pathways for electrochemical polymers coatings [25]. Recently, we have developed and investigated metal matrix composites (MMC) consisting of silver and CNTs as replacement gridlines for standard photovoltaic (PV) cell metallization, which typically consists of pure Ag metal. These MMC gridlines are capable of maintaining electrical connection in the event of semiconductor mechanical fracture [26]. PV cells suffer performance degradation due to microcracks generated in the semiconductor material [27,28]. These cracks can propagate to metal contacts on the cell, resulting in electrically isolated areas that lead to substantial power loss [28]. More recently, microcracks have been correlated with snail trails, a type of dislocation defect on PV modules, in which the maximum power production was reduced by about 40% [29].

The high mechanical strength and good electrical/thermal conductivities of CNTs [4,5] make them a suitable component in the MMC to reinforce the metal gridlines. As we have shown in our previous work [26], CNTs provide a secondary conduction pathway when cracks are generated in the gridlines, conducting approximately 30 mA in total current once a crack is generated. In the work presented here, we further investigate the current carrying capability of CNTs through the cracked MMC gridlines.

Several methods exist today to obtain thin CNT networks, such as filtration [30,31], spin coating [32], or Langmuir–Blodgett [33] method. We have explored previously [26] a variety of other CNT deposition techniques, including electrochemical deposition [34,35], nanospreading [36], and drop casting. However, all the aforementioned methods were limited in either the speed of deposition or the surface uniformity or in some cases both. For this work, we make use of an air brush technique [13], [24,25], [37,38] which is a simple and fast method that results in homogenously continuous and thin layers of CNTs.

CNTs are spray-coated on a 3-μm-thick plated Ag followed by a final 3-μm-thick Ag plating step obtaining a layer-by-layer (LBL) microstructure of Ag-CNT. We are able to manipulate the surface coverage of CNTs by altering certain spray coating parameters. As determined previously [26], the surface coverage of CNTs is an important variable that directly affects the CNT packing fraction and metal intercalation through the CNT network. We quantify the CNT surface coverage as a function of different deposition variables by digitally analyzing scanning electron microscopy (SEM) images. 1-mm-wide MMC gridlines are prepared and electromechanically characterized. Initial pull tests show that MMC gridlines are capable of maintaining electrical connection across a 35-μm-wide gap. The pull test is repeated 8 additional times upon complete failure of gridlines: i.e., when electrical connection is completely lost past ~35-μm-wide displacement. The gridlines are able to reestablish electrical connection and sustain the connection across the gap with additional pull tests.

978-1-5090-5605-7/17/$31.00

II. EXPERIMENTAL METHODS AND RESULTS

Low-Cost, multi-walled CNTs purchased from SWeNT (SMW200, purity 99% by TGA) are first functionalized with COOH for negative surface charge, following a standard acid reflux method [39,40]. Carboxylated-CNTs are filtered and thoroughly washed to remove any residual acid. A 1.3g/L CNT suspension is prepared through sonicating functionalized CNTs in de-ionized water without any additives. The suspension is directly spray-coated with an air brush pistol (Badger, USA) onto the substrate. Spray deposition is performed with the aid of a heated movable stage to assist in the drying of the fine droplets on the surface. The stage temperature and speed are controlled up to 150˚C and 3.6 mm/s, respectively.

The spray process involves a number of parameters such as stage-scan speed (s), airbrush height (h), flow rate (v_o), nozzle outlet pressure (p_o), and substrate temperature (T_s) [41]–[44]. Substrate temperature is critical for the drying dynamics of droplets, in which higher substrate temperatures allow for faster drying of the droplets and prevent coalescence into a larger droplet before drying [45]. In our case, our stage operating temperature is ~130˚C. This temperature is high enough to allow for faster evaporation rates, yet low enough to be compatible with PV devices.

Nozzle outlet pressure and height are other critical parameters in the deposition process. High pressure results in a higher pressure drop across the nozzle resulting in high fluid velocity through the air brush nozzle. Consequently, liquid dispersion breaks into smaller/finer ligaments and droplets [42,43]. Although nozzle pressure affects the mass flow rate of CNTs, the nozzle height controls the mass of CNTs being deposited per unit area of substrate. In our depositions, we found a nozzle pressure and height of 20 psi and 10 cm respectively to be the optimum conditions allowing for fast droplet drying and uniform coats of CNTs. Under these conditions, we are able to spray continuous multiple layer of CNTs that are coalescence-free to the naked eye.

While substrate temperature, nozzle pressure and height, and flow rate all affect the spray deposition, the scan speed is the most critical parameter in our process. Under the operating conditions mentioned earlier, we are able to deposit CNTs at different surface coverages through altering the substrate scan speeds. The surface coverage is quantified through a digital image analysis (imageJ processing) [26]. Fig. 1 shows the percentage surface coverage of CNTs at three scan speeds with corresponding SEM images (Fig.1 insets). Higher scan speeds result in shorter dwell times under the liquid flow. At a fast scan speed (s = 3.57 mm/s), 95% CNT surface coverage is achieved after 5 cycles (Fig. 1), while slower scan speeds required a less number of cycles to achieve close-to-complete coverage.

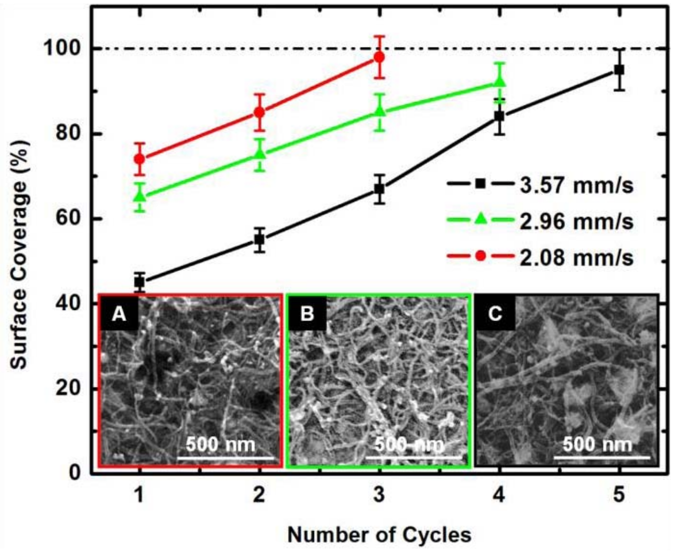

Fig. 1. CNTs surface coverage as a function of number of cycles of depositions at three scan speeds. Operating nozzle pressure and height are 20 psi and 10 cm respectively. Image insets A, B, C are SEM images after three cycles of depositions at 2.08, 2.96, and 3.57 mm/s scan speeds respectively.

Electromechanical characterization of the MMC gridlines is carried out using a strain failure test [26], in which the voltage drop across the lines and the current flowing through them are monitored as the MMC gridlines are pulled apart at micron increments. Consequently, we are able to record the change in resistance in each gridline as the micro-cracks grow. We deposit 1-mm-wide and 6-µm-thick MMC gridlines in a LBL structure. First, a 3-µm-thick Ag layer is plated on the substrate followed by spray-coating 15 layers of CNTs (p_o = 20 psi, h = 10 cm, s = 3.6 mm/s). A final 3-µm-thick Ag layer is plated on top of the CNT network. Pull tests are first performed at 6 V and 30 mA. When the first complete failure of all gridlines occurs, and the electrical connection is completely lost, the stage is reset, and the pull test is repeated.

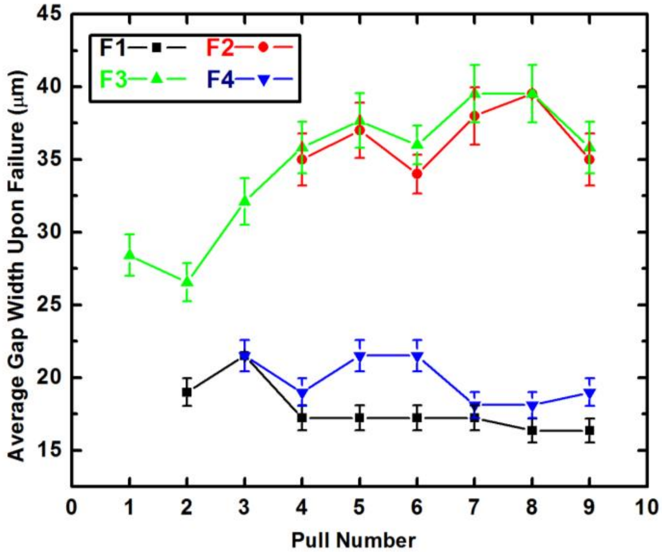

Fig. 2. Strain failure test of MMC gridlines. Fingers 1, 4 sustained an electrical connection across ~20-µm-wide gaps while fingers 2, 3 maintained connection up to ~35-µm-wide gaps.

A total of 9 pull tests and 8 resets are performed. Fig. 2 shows the average gap width, at which each of the gridlines maintains electrical connection with successively additional pulls. This clearly shows that the incorporation of CNTs within the Ag matrix enhances the electrical conductivity of metal lines upon fracture. These results are consistent with our strain failure data of other MMC lines prepared using drop casting method [26], indicating that spray-coating is a viable high-throughput, high-uniformity CNT deposition method.

In order to evaluate the current carrying capability of MMCs, the gridlines are pulled apart at three gap widths (5, 10, and 15 µm), and a current-voltage sweep is performed up to 30 V. We observe a linear behavior between current measured and voltage applied independent of the gap width (see Fig. 3), which further highlights the excellent electrical properties of CNTs [11,15]. MMC gridlines (1-mm-wide and 6-µm-thick) are capable of maintaining current densities ranging from 500 to 2500 A/cm^2, even after the microcracks form. Due to the voltage and current limits of our power supply, we are able to perform I-V sweeps up to 30 V and 150 mA only; therefore, we expect the maximum achievable current density to be much greater than 2500 A/cm^2. These current densities well exceed the requirements for PV cells; Boeing-Spectrolab recorded a current density of 52.7 mA/cm^2 for a 1 cm^2 inverted metamorphic triple junction (IMM3J) cell under AM1.5D [46,47].

III. CONCLUSION

In this work presented here, we demonstrate the use of a fast, cost-effective, and easily scalable method of depositing CNTs using a spray coating technique. We develop MMC gridlines in a LBL microstructure that are capable of withstanding fractures up to 35-µm-wide. MMC lines are able to reestablish and maintain electrical connection once gridlines are reset to their starting position. Therefore, spray-coated CNTs provide an electrical bridge support, should the microcracks propagate through the metal gridlines, preserving the power generation of the cell. In addition, MMC gridlines have measured current densities ranging from 500 to 2500 A/cm^2, which far exceeds the typical current densities of PV cells.

IV. FUTURE WORK

We recognize the importance of demonstrating our material on active solar cells, and we are currently in the process of integrating MMCs onto commercial space PV cells. The active solar cells with MMC gridlines will be subjected to external stress in order to induce the formation of microcracks. The spectral response of PV cells after cracking will be analyzed using electroluminescence (EL) and current-voltage (I-V) measurements. We expect the cracked solar cells with MMC gridlines to have similar EL and I-V responses to healthy/un-cracked cells, while solar cells with the standard metallization will suffer performance degradation due to microcrack formation that extends through the metal gridlines.

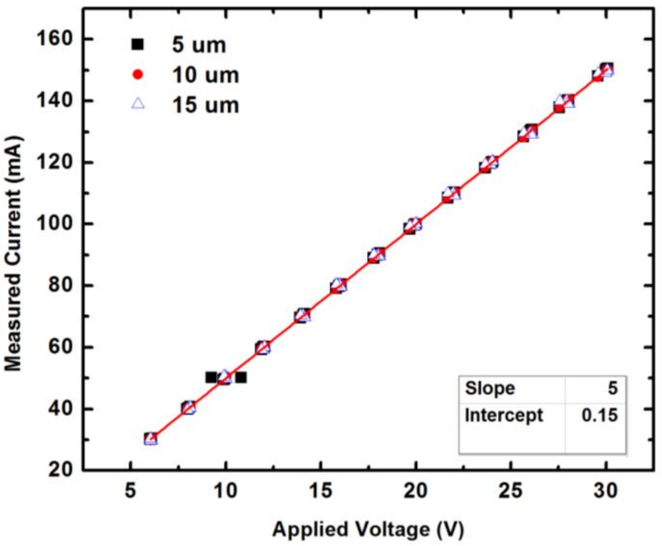

Fig. 3. Voltage current sweeps of fractured MMC gridlines at 5, 10 and 15 µm displacements.

V. ACKNOWLEDGMENTS

This work is supported in part by the Air Force Research Laboratory under Grant FA9453-14-1-0242.

REFERENCES

[1] Iijima, S. "Helical Microtubules of Graphitic Carbon." *Nature* 354, no. 6348 (Nov 1991): 56-58.
[2] Thostenson, E. T., Z. F. Ren, and T. W. Chou. "Advances in the Science and Technology of Carbon Nanotubes and Their Composites: A Review." *Composites Science and Technology* 61, no. 13 (2001): 1899-912.
[3] Dai, H. J. "Carbon Nanotubes: Synthesis, Integration, and Properties." *Accounts of Chemical Research* 35, no. 12 (Dec 2002): 1035-44.
[4] Dresselhaus, M. S., G. Dresselhaus, P. C. Eklund. *Science of fullerenes and carbon nanotubes*. Academic Press, New York,1996.
[5] Saito, R., M. S. Dresselhaus, G. Dresselhaus. *Physical properties of carbon nanotubes*. Imperial College Press, London, 1998.
[6] Kataura, H., Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, and Y. Achiba. "Optical Properties of Single-Wall Carbon Nanotubes." *Synthetic Metals* 103, no. 1-3 (Jun 1999): 2555-58.
[7] Jost, O., A. A. Gorbunov, W. Pompe, T. Pichler, R. Friedlein, M. Knupfer, M. Reibold*, et al.* "Diameter Grouping in Bulk Samples of Single-Walled Carbon Nanotubes from Optical Absorption Spectroscopy." *Applied Physics Letters* 75, no. 15 (Oct 1999): 2217-19.
[8] Kavan, L., P. Rapta, L. Dunsch, M. J. Bronikowski, P. Willis, and R. E. Smalley. "Electrochemical Tuning of Electronic

Structure of Single-Walled Carbon Nanotubes: In-Situ Raman and Vis-Nir Study." *Journal of Physical Chemistry B* 105, no. 44 (Nov 2001): 10764-71.

[9] Minami, N., S. Kazaoui, R. Jacquemin, H. Yamawaki, K. Aoki, H. Kataura, and Y. Achiba. "Optical Properties of Semiconducting and Metallic Single Wall Carbon Nanotubes: Effects of Doping and High Pressure." *Synthetic Metals* 116, no. 1-3 (Jan 2001): 405-09.

[10] Hennrich, F., S. Lebedkin, S. Malik, and M. M. Kappes. "Free-Standing Single-Wall Carbon Nanotube Thin Films." In *Structural and Electronic Properties of Molecular Nanostructures*, edited by H. Kuzmany, J. Fink, M. Mehring and S. Roth. Aip Conference Proceedings, 619-23. Melville: Amer Inst Physics, 2002.

[11] Hu, L., D. S. Hecht, and G. Gruner. "Percolation in Transparent and Conducting Carbon Nanotube Networks." *Nano Letters* 4, no. 12 (Dec 2004): 2513-17.

[12] Kouklin, N., M. Tzolov, D. Straus, A. Yin, and J. M. Xu. "Infrared Absorption Properties of Carbon Nanotubes Synthesized by Chemical Vapor Deposition." *Applied Physics Letters* 85, no. 19 (Nov 2004): 4463-65.

[13] Kaempgen, M., G. S. Duesberg, and S. Roth. "Transparent Carbon Nanotube Coatings." *Applied Surface Science* 252, no. 2 (Oct 2005): 425-29.

[14] Hirsch, A. "Functionalization of Single-Walled Carbon Nanotubes." *Angewandte Chemie-International Edition* 41, no. 11 (2002): 1853-59.

[15] de Pablo, P. J., C. Gomez-Navarro, M. T. Martinez, A. M. Benito, W. K. Maser, J. Colchero, J. Gomez-Herrero, and A. M. Baro. "Performing Current Versus Voltage Measurements of Single-Walled Carbon Nanotubes Using Scanning Force Microscopy." *Applied Physics Letters* 80, no. 8 (Feb 2002): 1462-64.

[16] Minot, E. D., Y. Yaish, V. Sazonova, J. Y. Park, M. Brink, and P. L. McEuen. "Tuning Carbon Nanotube Band Gaps with Strain." *Physical Review Letters* 90, no. 15 (Apr 2003): 4.

[17] Snow, E. S., J. P. Novak, M. D. Lay, E. H. Houser, F. K. Perkins, and P. M. Campbell. "Carbon Nanotube Networks: Nanomaterial for Macroelectronic Applications." *Journal of Vacuum Science & Technology B* 22, no. 4 (Jul-Aug 2004): 1990-94.

[18] Lay, M. D., J. P. Novak, and E. S. Snow. "Simple Route to Large-Scale Ordered Arrays of Liquid-Deposited Carbon Nanotubes." *Nano Letters* 4, no. 4 (Apr 2004): 603-06.

[19] Shiraishi, M., T. Takenobu, T. Iwai, Y. Iwasa, H. Kataura, and M. Ata. "Single-Walled Carbon Nanotube Aggregates for Solution-Processed Field Effect Transistors." *Chemical Physics Letters* 394, no. 1-3 (Aug 2004): 110-13.

[20] Meitl, M. A., Y. X. Zhou, A. Gaur, S. Jeon, M. L. Usrey, M. S. Strano, and J. A. Rogers. "Solution Casting and Transfer Printing Single-Walled Carbon Nanotube Films." *Nano Letters* 4, no. 9 (Sep 2004): 1643-47.

[21] Zhou, Y. X., A. Gaur, S. H. Hur, C. Kocabas, M. A. Meitl, M. Shim, and J. A. Rogers. "P-Channel, N-Channel Thin Film Transistors and P-N Diodes Based on Single Wall Carbon Nanotube Networks." *Nano Letters* 4, no. 10 (Oct 2004): 2031-35.

[22] Li, Z. L., P. Dharap, S. Nagarajaiah, E. V. Barrera, and J. D. Kim. "Carbon Nanotube Film Sensors." *Advanced Materials* 16, no. 7 (Apr 2004): 640–3.

[23] Abraham, J. K., B. Philip, A. Witchurch, V. K. Varadan, and C. C. Reddy. "A Compact Wireless Gas Sensor Using a Carbon Nanotube/Pmma Thin Film Chemiresistor." *Smart Materials & Structures* 13, no. 5 (Oct 2004): 1045-49.

[24] Penza, M., F. Antolini, and M. V. Antisari. "Carbon Nanotubes as Saw Chemical Sensors Materials." *Sensors and Actuators B-Chemical* 100, no. 1-2 (Jun 2004): 47-59.

[25] Ferrer-Anglada, N., M. Kaempgen, V. Skakalova, U. Dettlaf-Weglikowska, and S. Roth. "Synthesis and Characterization of Carbon Nanotube-Conducting Polymer Thin Films." *Diamond and Related Materials* 13, no. 2 (Feb 2004): 256-60.

[26] Abudayyeh, O. K., N. D. Gapp, C. Nelson, D. M. Wilt, and S. M. Han. "Silver-Carbon-Nanotube Metal Matrix Composites for Metal Contacts on Space Photovoltaic Cells." *Ieee Journal of Photovoltaics* 6, no. 1 (Jan 2016): 337-42.

[27] Kontges M., I. Kunze, S. Kajari-Schröder, X. Breitenmoser, and B. Bjørneklett, “Quantifying the risk of power losses in PV modules due to micro-cracks,” in Proc. 25th Eur. Photovoltaic Solar Energy Conf. Exhib., 2010, pp. 3745–52.

[28] Kontges, M., I. Kunze, S. Kajari-Schroder, X. Breitenmoser, and B. Bjorneklett. "The Risk of Power Loss in Crystalline Silicon Based Photovoltaic Modules Due to Micro-Cracks." *Solar Energy Materials and Solar Cells* 95, no. 4 (Apr 2011): 1131-37.

[29] Dolara, A., S. Leva, G. Manzolini, and E. Ogliari. "Investigation on Performance Decay on Photovoltaic Modules: Snail Trails and Cell Microcracks." *Ieee Journal of Photovoltaics* 4, no. 5 (Sep 2014): 1204-11.

[30] Kouklin, N., M. Tzolov, D. Straus, A. Yin, and J. M. Xu. "Infrared Absorption Properties of Carbon Nanotubes Synthesized by Chemical Vapor Deposition." *Applied Physics Letters* 85, no. 19 (Nov 2004): 4463-65.

[31] Wu, Z. C., Z. H. Chen, X. Du, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras*, et al.* "Transparent, Conductive Carbon Nanotube Films." *Science* 305, no. 5688 (Aug 2004): 1273-76.

[32] Meitl, M. A., Y. X. Zhou, A. Gaur, S. Jeon, M. L. Usrey, M. S. Strano, and J. A. Rogers. "Solution Casting and Transfer Printing Single-Walled Carbon Nanotube Films." *Nano Letters* 4, no. 9 (Sep 2004): 1643-47.

[33] Kim, Y., N. Minami, W. H. Zhu, S. Kazaoui, R. Azumi, and M. Matsumoto. "Langmuir-Blodgett Films of Single-Wall Carbon Nanotubes: Layer-by-Layer Deposition and in-Plane Orientation of Tubes." *Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers* 42, no. 12 (Dec 2003): 7629-34.

[34] Kang, X. H., Z. B. Mai, X. Y. Zou, P. X. Cai, and J. Y. Mo. "A Sensitive Nonenzymatic Glucose Sensor in Alkaline Media with a Copper Nanocluster/Multiwall Carbon Nano Tube-Modified Glassy Carbon Electrode." *Analytical Biochemistry* 363, no. 1 (Apr 2007): 143-50.

[35] Ferrer-Anglada, N., V. Gomis, Z. Ei-Hachemi, U. D. Weglikovska, M. Kaempgen, and S. Roth. "Carbon Nanotube Based Composites for Electronic Applications: Cnt-Conducting Polymers, Cnt-Cu." *Physica Status Solidi a-Applications and Materials Science* 203, no. 6 (May 2006): 1082-87.

[36] Prevo, B. G., and O. D. Velev. "Controlled, Rapid Deposition of Structured Coatings from Micro- and Nanoparticle Suspensions." *Langmuir* 20, no. 6 (Mar 2004): 2099-107.

[37] Kaempgen, M., U. Dettlaff, and S. Roth. "Characterization of Carbon Nanotubes by Optical Spectra." *Synthetic Metals* 135, no. 1-3 (Apr 2003): 755-56.

[38] Ramasamy, E., W. J. Lee, D. Y. Lee, and J. S. Song. "Spray Coated Multi-Wall Carbon Nanotube Counter Electrode for Tri-Iodide (I-3(-)) Reduction in Dye-Sensitized Solar Cells." *Electrochemistry Communications* 10, no. 7 (Jul 2008): 1087-89.

[39] Ramanathan, T., F. T. Fisher, R. S. Ruoff, and L. C. Brinson. "Amino-Functionalized Carbon Nanotubes for Binding to

Polymers and Biological Systems." *Chemistry of Materials* 17, no. 6 (Mar 2005): 1290-95.

[40] Osswald, S., M. Havel, and Y. Gogotsi. "Monitoring Oxidation of Multiwalled Carbon Nanotubes by Raman Spectroscopy." *Journal of Raman Spectroscopy* 38, no. 6 (Jun 2007): 728-36.

[41] Scardaci, V., R. Coull, P. E. Lyons, D. Rickard, and J. N. Coleman. "Spray Deposition of Highly Transparent, Low-Resistance Networks of Silver Nanowires over Large Areas." *Small* 7, no. 18 (Sep 2011): 2621-28.

[42] Fernando, R. H., L. L. Xing, and J. E. Glass. "Rheology Parameters Controlling Spray Atomization and Roll Misting Behavior of Waterborne Coatings." *Progress in Organic Coatings* 40, no. 1-4 (Dec 2000): 35-38.

[43] Lavernia, Enrique J., and Yue. Wu. 1996. *Spray Atomization and Deposition.* Chichester: John Wiley. 50–153 (Chapter 4).

[44] Glass, J. E., American Chemical Society, and American Chemical Society. 1997. *Technology for Waterborne Coatings*. ACS symposium series, 663; ACS symposium series, 663. Washington, DC: American Chemical Society. 265–295 (Chapter 15).

[45] Majumder, M., C. Rendall, M. Li, N. Behabtu, J. A. Eukel, R. H. Hauge, H. K. Schmidt, and M. Pasquali. "Insights into the Physics of Spray Coating of Swnt Films." *Chemical Engineering Science* 65, no. 6 (Mar 2010): 2000-08.

[46] Law, D. C., R. R. King, H. Yoon, M. J. Archer, A. Boca, C. M. Fetzer, S. Mesropian*, et al.* "Future Technology Pathways of Terrestrial III-V Multijunction Solar Cells for Concentrator Photovoltaic Systems." *Solar Energy Materials and Solar Cells* 94, no. 8 (Aug 2010): 1314-18.

[47] Yoon, H., M. Haddad, S. Mesropian, J. Yen, K. Edmondson, D. Law, R. R. King*, et al.* "Progress of Inverted Metamorphic III-V Solar Cell Development at Spectrolab." In *Pvsc: 2008 33rd Ieee Photovoltaic Specialists Conference, Vols 1-4*. Ieee Photovoltaic Specialists Conference, 82-87. New York: Ieee, 2008.