Spray coating as a simple method to prepare catalyst for growth of diameter-tunable single-walled carbon nanotubes

Rong Xiang,[1]* Haiqiang Zeng,[1] Yuquan Su,[1] Xuchun Gui,[1] Tianzhun Wu,[1] Erik Einarsson,[2] Shigeo Maruyama,[2] Zikang Tang[1,3]

[1] State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-Sen University, Guangzhou 510275, China

[2] Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

[3] Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China

* Corresponding author. Tel: +86-20-39943409. Fax: +86-20-39943262. E-mail address: xiangr2@mail.sysu.edu.cn (R. Xiang).

Single-walled carbon nanotube (SWCNT) films have received much attention due to their potential for use in applications such as thin film transistors,[1] solar cells,[2] touch panels, [3] etc. Synthesis of a SWCNT film on a substrate, e.g. Si wafer, usually involves deposition of a thin metal layer, which later aggregates into nano-sized particles at high temperature. These nanoparticles serve as the nucleation sites for SWCNT growth. In most previously reported studies, this metal layer is prepared by physical deposition methods such as sputtering or evaporation[4], and SWCNTs with various morphologies have been obtained from this approach. Key parameters of the produced SWCNTs (length, average diameter, density, etc.) can be adjusted my modifying the catalyst deposition process.[5, 6] In addition to these conventional physical deposition methods, several advances in catalyst loading by wet processes – which offer clear advantages in simplicity and scalability -- have been recently reported. Dip-coating,[7] drop-casting,[8] and spin-coating[9] have been used in catalyst preparation for synthesis of SWCNTs and multi-walled CNTs (MWCNTs), but are limited to flat substrates with appropriately wettable surfaces. Here, we report the synthesis of high quality SWCNTs from catalyst prepared by a spray coating technique, which had previously only been able to generate MWNTs.[10] The obtained SWCNTs are shown to be comparable to those grown from dip-coated catalyst by alcohol

catalytic chemical vapor deposition (ACCVD),[7] and the nanotube diameter can be modulated by modifying the deposition recipe.

Figures 1a and b present schematics of spray coating and our conventional dip-coating process. [7, 11, 12] Spray coating is an efficient method for coating a thin liquid film on a solid surface, and is widely used in industry. Spray coating has also recently been used to produce ZnO and ITO films. However, in all these cases the particles produced are on the order of hundreds of nanometers or even micrometers in diameter. The growth of SWCNTs requires particles with much smaller diameter, typically below 5 nm. Figure 1c shows a characteristic scanning electron microscope (SEM) image of the material grown from catalyst prepared by spray coating. A random mat of SWCNTs is formed on the substrate after CVD. The thickness of the mat can be adjusted from a few tens of nanometers up to several micrometers by changing the CVD time. Transmission electron microscope (TEM) images in Figure 1f confirm that the SWCNTs are well crystallized, with little amorphous carbon or other impurities. Since the SWCNT films were detached from the substrate using HF etching, the catalyst particles are also transferred onto the TEM grid together with the SWCNT film. This allows us to confirm that catalyst particles deposited by spray coating have a mean diameter of approximately 2 nm. In general, the SWCNTs obtained on spray-coated

catalyst are comparable to those grown from dip-coated catalyst (Figures 1d and 1f) in terms of key structural parameters such as diameter, purity and yield.

Figure 2 shows typical Raman spectra of the SWCNTs grown from spray-coated catalyst with various catalyst recipes. In this series of experiments, we adjusted the catalyst ratio by simply prolonging the deposition time of Mo acetate solution from 1 s to 128 s. A strong G peak at 1592 cm^{-1} and a very weak D peak centered near 1350 cm^{-1} are observed in all cases, confirming the high degree of crystallization despite changing the relative Mo concentration over two orders of magnitude. Clear fingerprints in the RBM region from 100–300 cm^{-1} always exist. The trend in both the RBM region (slight intensity increase at higher wavenumbers) and the G- peak (clear shift to lower wavenumbers) suggests that SWCNT diameter decreases with increasing amount of Mo.

We replaced the conventional Si wafer substrate by Al_2O_3 fiber and quartz wool, and deposited catalyst by spray coating. This is motivated by the fact that unlike dip-coating or spinning coating, where substrates need to be either submerged into a solution or placed on a spin-coating stage, spray coating has far less stringent requirements regarding size, shape, and porosity of a substrate, and hence can be applied to more systems. In principle, this protocol may be also applied to material with

other shapes or rough surfaces. Figure 3 shows typical SEM images of Al_2O_3 fibers before (a, c) and after (b, d) spray coating and SWCNT growth. From these SEM images it is clear that SWCNTs were successfully grown on the surface of a fiber with a diameter of several micrometers. A typical Raman spectrum of fiber-supported SWCNTs is shown in Figure 3e (red line), along with a spectrum of a pristine Al_2O_3 fiber (black line) for reference. The appearance of clear G and RBM peaks confirms the synthesis of SWCNTs. We measured the electrical conductance of the fiber before and after SWCNT coating. The quartz wool changed from an insulator to a conductor with a surface resistivity of 10^4 Ω•cm, which is a typical value of ACCVD-produced SWCNTs. The wetability of the fibers also changed significantly, exhibiting a water contact angle of 140° after SWCNT growth (Figure 3f).

Unlike in dip-coating, where the amount of catalyst deposited onto the substrate is determined by the concentration of the precursor solution and finally limited by the solubility of the precursor salt, the amount of catalyst that can be deposited by spray-coating can be increased (in principle infinitely) by prolonging the deposition time. This facilitates an investigation of the catalyst window and its relationship to the grown SWCNTs across a broader concentration regime. Figure 4 shows characteristic TEM images and diameter distribution histograms of SWCNTs synthesized from

different amounts of deposited catalyst. The mean diameter of SWCNTs (determined by measuring more than 100 tubes for each sample) changed from 1.55 nm to 1.75 nm after a 128-fold increase in Co deposition time, but decreased from 1.85 nm to 1.35 nm when the Mo deposition time was increased by the same amount. This trend (both decreasing Co and increasing Mo yields smaller diameter SWCNTs) is consistent with previous findings using the dip-coating approach.[11] Though the detailed catalytic mechanism in this bimetallic system is not fully clarified, it is generally accepted that Mo can inhibit aggregation or ripening of catalyst nanoparticles. For example, Zhao et al. performed a carful element mapping Fe/Mo catalyst loaded on layered double oxides and confirmed that Mo pinned between Fe particles prevented sintering of Fe at high temperature.[13] Hu et al. proposed that Mo existed as oxide and molybdates that can improve dispersion and stability of metallic Co.[14] However, in this experiment increasing the amount of deposited Mo did not yield SWCNTs thinner than 1.2 nm, which was the limit obtained in our previous work.[11] Nonetheless, the ability to prepare catalyst with an unlimited catalyst amount/ratio (like physical deposition) by using a simple wet process may extend the feasibility of wet catalyst preparation methods and provide better chance for structural control in the future studies.

To conclude, we propose spray coating as an optional liquid-based method that can prepare nano-sized particles suitable for the growth of SWCNTs with tunable diameter. The obtained SWCNT films are comparable to those produced by conventional ACCVD in terms of crystallization, tube diameter and carbon yield. Beside its potential advantage in scalability and large area deposition, spray coating is more feasible than dip-coating or spin-coating in controlling the amount and composition of catalyst deposited onto a substrate, resulting in an efficient modulation of the mean diameter (from 1.85 to 1.35 nm) of the obtained SWCNTs. In addition, spray coating allows catalyst preparation on supports other than flat wafer. High quality SWCNTs are synthesized on quartz and Al_2O_3 wool.

Acknowledgments

Part of this work was financially supported by National Science Foundation of China (51002190), Guangdong Provincial Natural Science Foundation of China (2011040004714) and the open funds of State Key Laboratory of Optoelectronic Materials and Technologies.

References

[1] Cao Q, Kim HS, Pimparkar N, Kulkarni JP, Wang CJ, Shim M, et al. Medium-scale carbon nanotube thin-film integrated circuits on flexible plastic substrates. Nature 2008; 454(7203): 495-U494.

[2] Pasquier AD, Unalan HE, Kanwal A, Miller S, Chhowalla M. Conducting and transparent single-wall carbon nanotube electrodes for polymer-fullerene solar cells. Appl Phys Lett 2005; 87(20).

[3] Gruner G. Carbon nanotube films for transparent and plastic electronics. J Mater Chem 2006; 16(35): 3533-3539.

[4] Noda S, Sugime H, Osawa T, Tsuji Y, Chiashi S, Murakami Y, et al. A simple combinatorial method to discover Co-Mo binary catalysts that grow vertically aligned single-walled carbon nanotubes. Carbon 2006; 44(8): 1414-1419.

[5] Yamada T, Namai T, Hata K, Futaba DN, Mizuno K, Fan J, et al. Size-selective growth of double-walled carbon nanotube forests from engineered iron catalysts. Nat Nanotechnol 2006; 1(2): 131-136.

[6] Zhong GF, Warner JH, Fouquet M, Robertson AW, Chen BA, Robertson J. Growth of Ultrahigh Density Single-Walled Carbon Nanotube Forests by Improved Catalyst Design. Acs Nano 2012; 6(4): 2893-2903.

[7] Murakami Y, Miyauchi Y, Chiashi S, Maruyama S. Direct synthesis of high-quality single-walled carbon nanotubes on silicon and quartz substrates. Chem Phys Lett 2003; 377(1-2): 49-54.

[8] Zhang L, Tan YQ, Resasco DE. Controlling the growth of vertically oriented single-walled carbon nanotubes by varying the density of Co-Mo catalyst particles. Chem Phys Lett 2006; 422(1-3): 198-203.

[9] Alvarez NT, Hamilton CE, Pint CL, Orbaek A, Yao J, Frosinini AL, et al. Wet Catalyst-Support Films for Production of Vertically Aligned Carbon Nanotubes. ACS Appl Mater Inter 2010; 2(7): 1851-1856.

[10] Terrado E, Redrado M, Munoz E, Maser WK, Benito AM, Martinez MT. Carbon nanotube growth on cobalt-sprayed substrates by then-nal CVD. Mat Sci Eng C-Bio S 2006; 26(5-7): 1185-1188.

[11] Xiang R, Einarsson E, Murakami Y, Shiomi J, Chiashi S, Tang ZK, et al. Diameter Modulation of Vertically Aligned Single-Walled Carbon Nanotubes. ACS Nano 2012; 6(8): 7472.

[12] Xiang R, Wu TZ, Einarsson E, Suzuki Y, Murakami Y, Shiomi J, et al. High-Precision Selective Deposition of Catalyst for Facile Localized Growth of Single-Walled Carbon Nanotubes. J Am Chem Soc 2009; 131(30): 10344-10345

[13] Zhao MQ, Zhang Q, Zhang W, Huang JQ, Zhang YH, Su DS, et al. Embedded High Density Metal Nanoparticles with Extraordinary Thermal Stability Derived from Guest-Host Mediated Layered Double Hydroxides. J Am Chem Soc 2010; 132(42): 14739-14741.
[14] Hu MH, Murakami Y, Ogura M, Maruyama S, Okubo T. Morphology and chemical state of Co-Mo catalysts for growth of single-walled carbon nanotubes vertically aligned on quartz substrates. J Catal 2004; 225(1): 230-239.

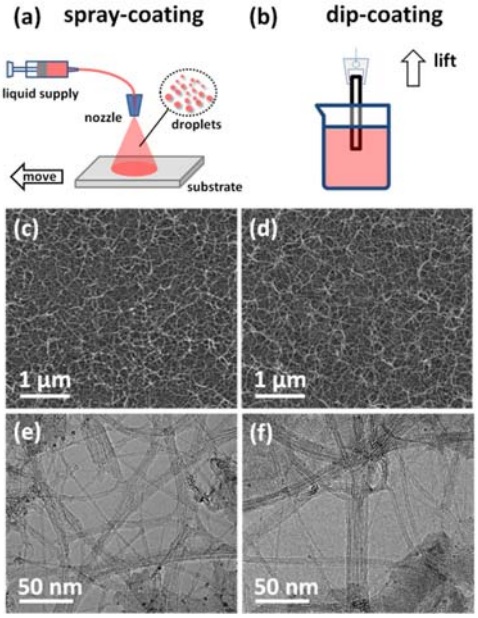

Figure 1. A comparison between spray-coating and conventional dip-coating: (a)(b) schematics of the two processes, (c)(d) characteristic SEM images and (e)(f) TEM micrographs the SWCNTs grown from catalysts prepared by these two methods.

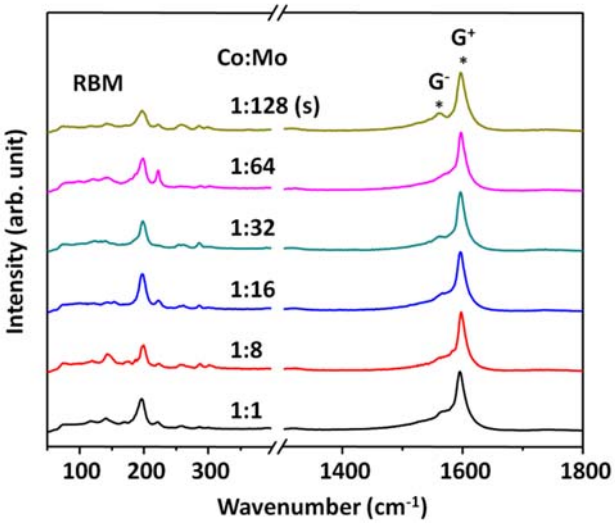

Figure 2. Raman spectra of SWCNTs grown from catalyst with fixed a fixed amount of Co (1 s deposition) but increasing amount of Mo. A strong G band and clear RBM peaks are observed in all samples.

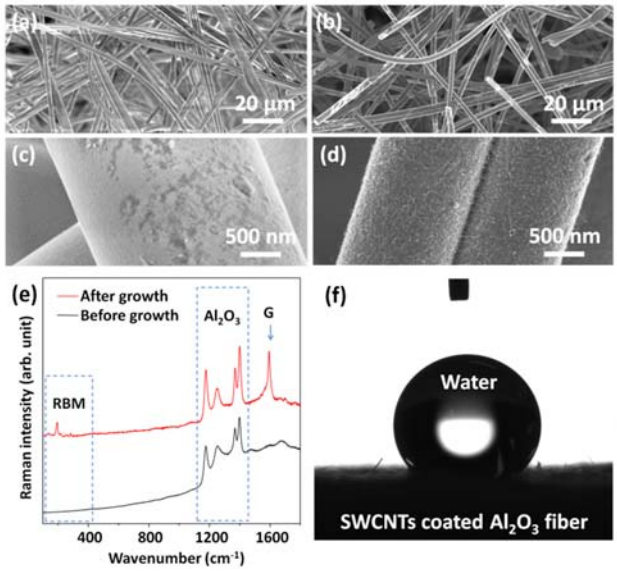

Figure 3. Characteristic SEM micrographs of Al_2O_3 wool (a)(c) before and (b)(d) after catalyst deposition and CVD; (e) Raman spectra of Al_2O_3 fibers before and after CVD growth; (f) water contact angle of SWCNT-coated Al_2O_3 fibers.

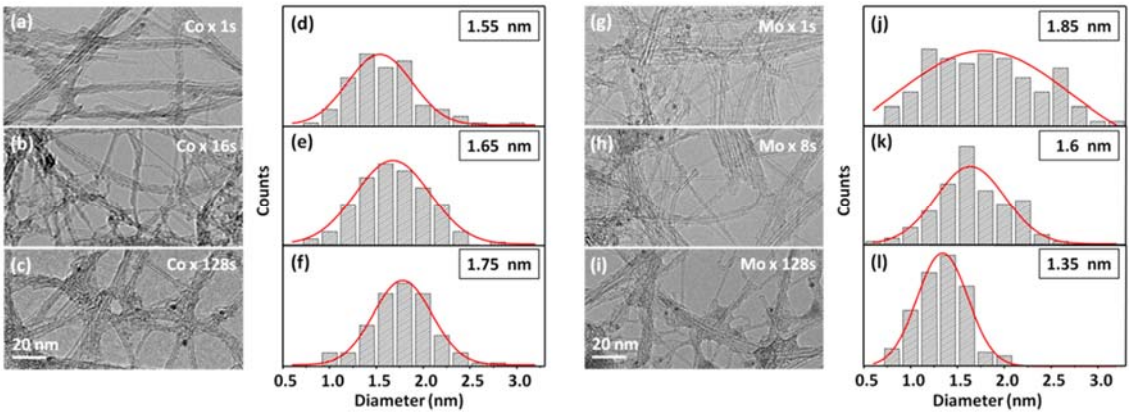

Figure 4. Representative TEM images and diameter histograms of SWCNTs grown using different catalyst recipes, suggesting the SWCNT diameter can be tuned simply by changing the deposition time of the catalyst precursor solution. The diameter is more sensitive to the amount of Mo than to the amount of Co.

Spray coating as a simple method to prepare catalyst for growth of diameter-tunable single-walled carbon nanotubes

Rong Xiang,[1]* Haiqiang Zeng,[1] Yuquan Su,[1] Xuchun Gui,[1] Tianzhun Wu,[1] Erik Einarsson,[2] Shigeo Maruyama,[2] Zikang Tang[1,3]

[1] State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-Sen University, Guangzhou 510275, China

[2] Department of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

[3] Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China

* Corresponding author. Tel: +86-20-39943409. Fax: +86-20-39943262. E-mail address: xiangr2@mail.sysu.edu.cn (R. Xiang).

Details of Catalyst Preparation, Carbon Nanotube Growth and Characterization

The catalyst is prepared by an ultra-sonic spray generator operating at 1000W. Two solutions, cobalt acetate dissolved in ethanol (0.01 mol/L) and molybdenum acetate dissolved in ethanol (0.01 mol/L), are used separately as the catalyst precursor. The precursor solution forms droplets (200 nm to 2 μm in diameter) before depositing onto the substrate (silicon wafer with 500 nm oxide layer), which is placed 2 cm lower to the spray nozzle. After deposition, the substrate is annealed at 400 °C to decompose the acetate. Single-walled carbon nanotubes are synthesized by a chemical vapor deposition (CVD) using ethanol as the carbon source at a CVD temperature of 800 °C and an ethanol pressure of 1.3 kPa. More details of the dip-coating and CVD process may be found in our previous reports.[1-3] The obtained material is characterized by scanning electron microscope (SEM, S-4800), Raman spectrometer (Horiba HR800). The diameter information is collected by transmission electron microscope (TEM, FEI Tecnai F12). The conductivity of SWCNT coated Al_2O_3 fiber is measure by a four probe stage connecting to a semiconductor analyzer (Agilent B1505A). The wetability is measured by a contact angle tester (Kruss DSA100).

REFERENCES

[1] Xiang R, Einarsson E, Murakami Y, Shiomi J, Chiashi S, Tang ZK, et al. Diameter Modulation of Vertically Aligned Single-Walled Carbon Nanotubes. ACS Nano 2012; 6(8): 7472.

[2] Xiang R, Wu TZ, Einarsson E, Suzuki Y, Murakami Y, Shiomi J, et al. High-Precision Selective Deposition of Catalyst for Facile Localized Growth of Single-Walled Carbon Nanotubes. J Am Chem Soc 2009; 131(30): 10344.

[3] Murakami Y, Miyauchi Y, Chiashi S, Maruyama S. Direct synthesis of high-quality single-walled carbon nanotubes on silicon and quartz substrates. Chem Phys Lett 2003; 377(1-2): 49.