

# REPORT

## Controlling Structural Characteristics of Single-Walled Carbon Nanotubes (SWNT) by Tailoring Catalyst Composition and Synthesis Conditions

(GRANT NUMBER DE-FG02-02ER15345)

PERIOD OF EXECUTION:  
May 2006 – May 2009

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### 1. OVERALL RESEARCH GOAL:

The main goal of this proposal is to advance the knowledge of the mechanism responsible for the formation of single-walled carbon nanotubes (SWNT) in order to get control over their structural parameters (diameter and chirality). Only through a detailed knowledge of the growth mechanism it will be possible to produce SWNT with tailored properties since they are directly related to the structural parameters.

### 2. SPECIFIC OBJECTIVES FOR THE CURRENT FUNDING PERIOD

- Understand the mechanism of nanotube formation to optimize the control of structural growth of carbon nanostructures
- Produce nanotube structures of specific arrays:
  - Vertical forests
  - Nanotube pillars
  - Hybrid nanotube/fullerenes
- Develop kinetic models to quantify the different steps in the growth process

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## ***Solid Nanoparticles that Catalyze Biofuel Upgrade Reactions at the Water/Oil Interface***

Published in: *Science* **2010**, 327, 68-72 (Steven Crossley, Jimmy Faria, Min Shen, Daniel E. Resasco)

A recoverable catalyst that simultaneously stabilizes emulsions would be highly advantageous in streamlining processes such as biomass refining, in which the immiscibility and thermal instability of crude products greatly complicates purification procedures. Here, we report a family of solid catalysts that can stabilize water-oil emulsions and catalyze reactions at the liquid/liquid interface.

By depositing palladium onto carbon nanotube-inorganic oxide hybrid nanoparticles, we demonstrate biphasic hydrodeoxygenation and condensation catalysis in three substrate classes of interest in biomass refining. Microscopic characterization of the emulsions supports localization of the hybrid particles at the interface.

In phase-transfer catalysis, reactions are carried out in a biphasic mixture of two immiscible solvents, often water and a hydrophobic organic liquid; added surfactants such as quaternary ammonium salts enhance interfacial surface area (through emulsification) and facilitate transfers between the phases (1). The technique is especially useful in cases in which a product might otherwise be unstable under the reaction conditions in one phase but can partition into the other phase after rapid formation. Such process improvements could have a major impact in the field of biomass conversion to fuels. In cases such as the refining of bio-oils in which the system is biphasic and contains up to 30% water, the most efficient way of catalyzing reactions is to place the solid catalyst at the liquid/liquid interface and to maximize the extent of interface by creating an emulsion. Otherwise, the catalyst particles will preferentially remain in the heavier phase, such as water. Therefore, the concept of solid particles that can simultaneously stabilize an emulsion and catalyze reactions in both phases becomes an attractive proposition.

Carbon nanotubes have also been shown to produce emulsions, but of the water-in-oil variety because they are hydrophobic. We recently prepared hybrid nanoparticles by fusing carbon nanotubes to silica. By tuning their composition, we could modify the hydrophilic-hydrophobic balance and assemble water-in-oil or oil-in-water emulsions systematically and reproducibly.

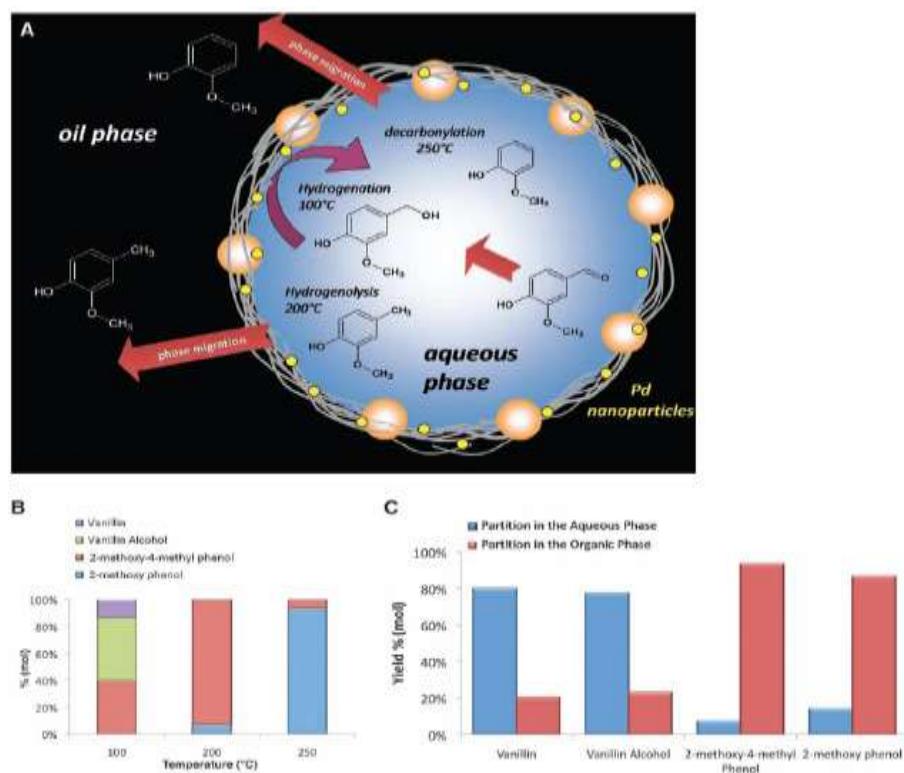
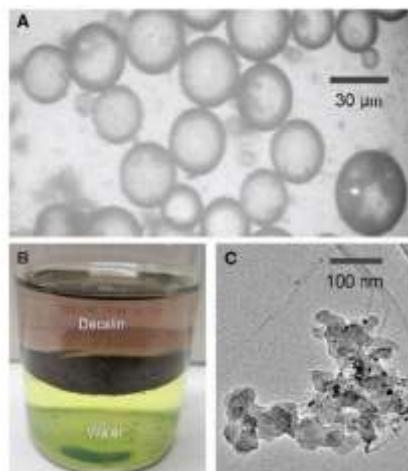
One of the main objectives of the present study was to extend the utility of these nanohybrids by incorporating a transition metal, rendering them catalytically active for hydrogenation.

The second objective was to add a solid base function to catalyze condensation reactions. After the addition of Pd metal particles these particles still straddle the organic/aqueous interface, and the appearance and stability of the emulsions formed are unaffected. We envisioned that their selective metal functionalization would be a powerful strategy for directing reactivity in a specific phase: Depositing a metal such as Pd on the hydrophilic face would catalyze aqueous reactions, whereas deposition on the hydrophobic face would favor chemistry in the organic solvent

The schematic illustration shows the reactions taking place at the water/oil interface in the solid-stabilized emulsions. Depending on the reaction temperature, the prevailing reactions are hydrogenation, hydrogenolysis, or decarbonylation, and depending on the relative solubilities, the products remain in the aqueous phase or migrate to the oil phase. Total weight fraction of the various products as a function of temperature after 30-min reaction in a batch reactor, from gas chromatographic analysis of each phase (combined). Partition of the various products as in (B) between the individual aqueous and organic phases.

With solid-stabilized emulsions, a continuous process could be designed in which the two homogeneous phases coexist with the emulsion in a layered configuration: oil/emulsion/water. One can achieve full conversion on both sides of the emulsion followed by constant removal of oil-soluble products from the top layer and water-soluble products from the bottom layer while the reaction keeps occurring in the emulsion.

Our results highlight the preliminary applications of solid catalysts localized at the interface between two liquid phases. We anticipate that tailoring such emulsion-stabilizing solids with additional catalytic functional groups will facilitate a broad range of reactions.



**Quantifying the Semiconducting Fraction in Single-Walled Carbon Nanotube Samples through Comparative Atomic Force and Photoluminescence Microscopies**

Published in: *Nano Letters* **2009**, 9, 3203-3208 (Anton V. Naumov, Oleg A. Kuznetsov, Avetik R. Harutyunyan, Alexander A. Green, Mark C. Hersam, Daniel E. Resasco, Pavel N. Nikolaev, and R. Bruce Weisman)

A new method was used to measure the fraction of semiconducting nanotubes in various as-grown or processed single-walled carbon nanotube (SWCNT) samples. SWCNT number densities were compared in images from near-IR photoluminescence (semiconducting species) and AFM (all species) to compute the semiconducting fraction. The results show large variations among growth methods and effective sorting by density gradient ultracentrifugation. This counting-based method provides important information about SWCNT sample compositions that can guide controlled growth methods and help calibrate bulk characterization techniques.

Reliable characterization is a key step in the preparation of pure semiconducting or metallic SWCNT samples. At the level of individual nanotubes, the two types can be distinguished and counted by specific  $(n,m)$  determination through highly resolved scanning tunneling microscopy (STM)<sup>25</sup> or electron nanodiffraction.<sup>26,27</sup> However, these precise microscopic methods are too tedious for routine use. The metallic/semiconducting composition of a sample can also in principle be determined by counting individual nanotubes using voltage-contrast SEM, which distinguishes metallic from semiconducting SWCNTs. We note that this approach involves the complexity of size exclusion chromatography followed by electrophoretic SWCNT deposition. In addition, systematic errors may arise from nonuniform sampling or the presence of small bundles of mixed electronic type. Photoluminescence (PL) spectroscopy offers an incisive probe of bulk or individual semiconducting SWCNTs but does not detect metallic species. Raman spectroscopy also provides a relatively rapid tool for studying SWCNTs as individuals or bulk ensembles.<sup>35,36</sup> However, it has the disadvantage of requiring a wide variety of incident laser wavelengths to detect nanotubes spanning a range of structures. Raman has been used to estimate the relative semiconducting and metallic contents in processed SWCNT samples but the calibration factors needed to extract reliable values of these ratios are not known. Visible-near-IR absorption spectroscopy of SWCNT samples reveals distinct optical transitions of semiconducting and metallic species and appears more promising for quantitative determination of metallic/semiconducting ratios if adequate and consistent calibration methods become available.

We report here a new counting-based method for the absolute measurement of semiconducting fractions in SWCNT samples. In this approach, we capture AFM and near-IR photoluminescence images of dried dilute SWCNT dispersions. Both semiconducting and metallic species are visible in the AFM images, while only semiconducting nanotubes are visible in photoluminescence. The ratio of observed nanotube densities therefore gives the semiconducting fraction in the sample. We have performed this analysis on SWCNTs prepared by a variety of growth and/or

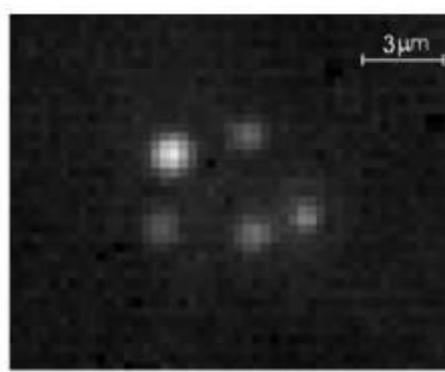
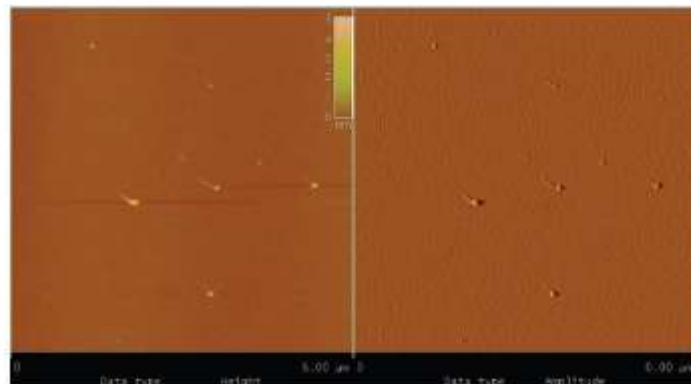
postprocessing methods. The results provide compositional reference data that should be useful to researchers working with such samples or attempting to calibrate bulk analysis techniques.

Several SWCNT batches produced by different methods were analyzed in this work. After the slides were coated with aqueous surfactant suspensions of SWCNTs, the total number of SWCNTs per unit area was determined from AFM images, and the number of semiconducting SWCNTs per unit area was found from near-IR photoluminescence images. A Veeco AFM (Multimode 3A) was used to study up to 40 regions, each  $10 \times 10 \mu\text{m}$  or  $6 \times 6 \mu\text{m}$ , within a  $\sim 100 \times 100 \mu\text{m}$  area of the sample. The number of SWCNTs in each image was counted. Photoluminescence of individual semiconducting SWCNTs in the sample was observed using a custom built near-IR fluorescence microscope.<sup>34</sup> In this setup, semiconducting SWCNTs were excited in their E22 transitions with 660 and 780 nm diode lasers. Our experience in photoluminescence analysis indicates that this combination of excitation wavelengths will induce detectable emission from essentially all semiconducting  $(n,m)$  species in the studied samples. This occurs because of the high detection sensitivity and the large effective resonance windows arising from long Lorentzian tails of the principal E22 peaks, plus many weaker spectral features from E22 vibronic sidebands, E11 vibronic sidebands, higher excitonic bands associated with E22, and underlying continuum-like transitions.

In summary, we have demonstrated a new counting-based method for measuring the semiconducting fraction in SWCNT samples. This method was applied to analyze a variety of SWCNT batches produced by different growth techniques or purified by DGU. Our results, based on measurements of hundreds of nanotubes per sample, show good precision and appear consistent with prior expectations for the sample compositions. The findings can serve as a useful reference for researchers growing or using SWCNTs prepared by these methods. They may also assist in the absolute calibration of bulk spectroscopic characterization methods.

**Table 1.** Compositions Determined for As-Produced or Processed SWCNT Samples

sample	source	% semiconducting	% metallic	% standard error
HiPco	Rice Univ.	62.9	37.1	0.5
CoMoCAT, standard grade	SWeNT Inc.	92.1	7.9	1.1
CoMoCAT, commercial grade	SWeNT Inc.	51.9	48.1	3.5
laser ablation, low temperature method	ERC Inc./NASA-JSC	54.7	45.3	1.4
CVD preferential growth	Honda Res. Inst. USA Inc.	15.4	84.6	2.6
HiPco, starting material	Northwestern Univ.	60.5	39.5	3.8
HiPco, semiconducting-enriched by DGU	Northwestern Univ.	96.0	4.0	0.6
HiPco, metallic-enriched by DGU	Northwestern Univ.	3.1	96.9	0.6



## **Adsorption of Glucose Oxidase onto Single-Walled Carbon Nanotubes and Its Application in Layer-By-Layer Biosensors**

Published in: *Analytical Chemistry* 2009, 81, 7917-7925 (Ta-Wei Tsai, Gustavo Heckert, Lui's F. Neves, Yongqiang Tan, Der-You Kao, Roger G. Harrison, Daniel E. Resasco, and David W. Schmidtke)

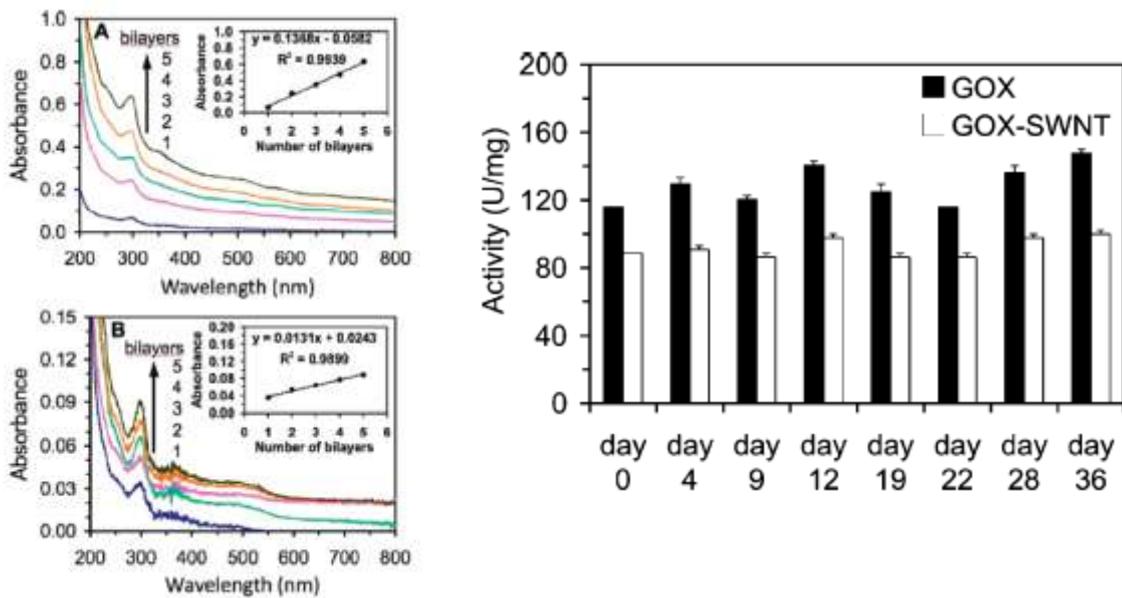
In this study, we describe the use of a sodium cholate suspension-dialysis method to adsorb the redox enzyme glucose oxidase (GOX) onto single-walled carbon nanotubes (SWNT). By this method, solutions of dispersed and debundled SWNTs were prepared that remained stable for 30 days and which retained 75% of the native enzymatic activity. We also demonstrate that GOX-SWNT conjugates can be assembled into amperometric biosensors with a poly[(vinylpyridine)Os(bipyridyl)<sub>2</sub>Cl<sub>2+3+</sub>] redox polymer (PVP-Os) through a layer-by-layer (LBL) self-assembly process. Incorporation of SWNT-enzyme conjugates into the LBL films resulted in current densities as high as 440  $\mu$ A/cm<sup>2</sup>, which were a 2-fold increase over the response of films without SWNTs. We also demonstrate that the adsorption pH of the redox polymer solution and the dispersion quality of SWNTs were important parameters in controlling the electrochemical and enzymatic properties of the LBL films.

The attachment of biological molecules (e.g., enzymes, antibodies, DNA) to single-walled carbon nanotubes (SWNTs) has gained considerable attention due to the high surface areas of SWNTs and their exceptional mechanical, electrical, and fluorescent properties. Protein-SWNT conjugates are being developed for a wide range of biomedical devices and therapies, including drug delivery, cancer therapy, and biosensing applications. To achieve these applications it is desired that the protein-SWNT conjugates have the following characteristics: (i) they form stable and homogeneous dispersions of individual SWNTs; (ii) the unique structure and properties of SWNTs are retained; and (iii) the native structure and activity of the protein is retained.

In this study we investigate whether this method of protein attachment is applicable to other enzymes as well. To test this we used the enzyme glucose oxidase (GOX), which is commonly used in the development of biosensors for glucose Detection as well as in miniaturized biofuel cells. Enzymatic activity measurements and UV-vis spectroscopy demonstrated that dispersions of the GOX-SWNTs conjugates were highly stable and biocatalytic. Based on these results we investigated the potential benefits of the GOX-SWNT conjugates in fabricating glucose biosensors.

A key issue in developing glucose biosensors based on GOXSWNT conjugates is the detection method. We chose amperometry as the basis for our detection method due to its simplicity, low cost, and fast response. A second important issue in GOX-SWNT based biosensors is the method of immobilization Since the LBL assembly process can be performed in aqueous solutions under conditions that minimize protein denaturation, allows for precise control of the composition and film thickness, and is compatible with a variety of substrates and geometries, we opted for this technique. Furthermore recent studies have reported that incorporation of SWNTs<sup>43</sup> or MWNTs<sup>41</sup> into LBL films containing GOX have the added benefit of increasing sensor response by enhancing the electron diffusion through the films and/or the electrochemical surface area.

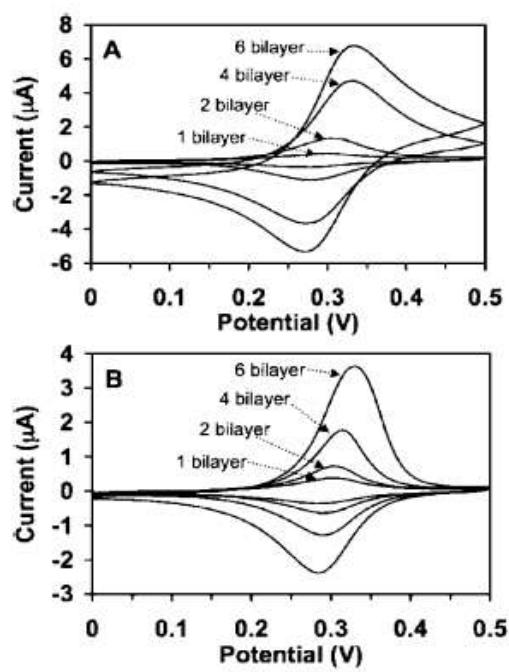
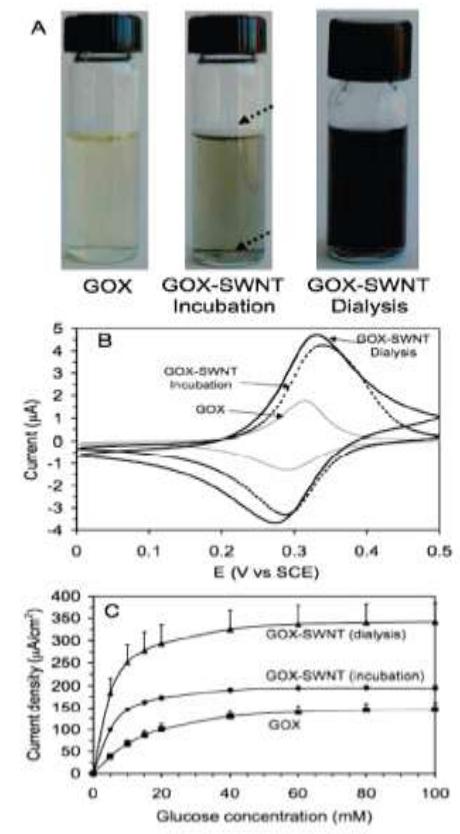
**Layer-by-Layer Assembly of the PVP-Os/GOX-SWNT Films.** Thin films composed of GOX-SWNTs conjugates and redox polymer PVP-Os were fabricated on gold electrodes by the layer-by-layer (LBL) technique the strong adsorption band at 300 nm increases linearly with the number of PVP-Os/GOX-SWNT bilayers deposited and suggests that the amount of material deposited can be easily controlled. As a control, films without SWNTs were also fabricated to determine the effect of SWNTs on the self-assembly process. Similar to the films with SWNTs, a strong absorbance band at 300 nm was observed, and there was a linear increase in the absorbance intensity with the number of bilayers. It should be noted that for films made with the same number of bilayers, films with SWNTs had higher absorbance readings than those without SWNTs. These results suggest that the presence of SWNTs caused more material to be deposited.



**Electrochemical Characterization of Multilayer Films.** There were however a couple of differences in the electrochemical behavior between films made with and without SWNTs. The first difference is in the magnitude of the peak current densities. LBL films made with GOX-SWNT conjugates had peak currents that were 2-3 times greater than films made with GOX alone. This increase in the electrochemical response with SWNTs is similar to our previous report. The other noticeable difference is that, in the CVs for the four- and six-bilayer films made with GOX-SWNTs, the current never returns to zero at the limits of the potential scans. This nonzero current (i.e., “diffusional tail”) and not all of the redox centers in the film are completely oxidized or reduced. The presence of the diffusional tail is characteristic of “thick” films and suggests semi-infinite linear diffusion. In contrast, the current of films made without SWNTs returned to zero at both potential limits indicating that all of the redox centers were exhaustively oxidized and reduced.

In this study, we demonstrated that GOX-SWNT conjugates produced by the sodium cholate suspension-dialysis method were highly dispersed, remained stable for 30 days, and retained a significant amount (75%) of native enzymatic activity. We also demonstrate that these GOX-SWNT conjugates can be combined with a cationic redox polymer (PVP-Os) by the LBL self-assembly technique to fabricate highly sensitive sensors to glucose. The electrochemical and enzymatic properties of these films were dependent upon the adsorption pH of the redox polymer solution and the dispersion quality of SWNTs. These results are significant and noteworthy for a variety of reasons. First, several recent studies have highlighted the fact that retention of protein structure and activity upon attachment to SWNTs is dependent upon the type of protein,<sup>56,57</sup> the amount of protein adsorbed,<sup>58</sup> and the method of attachment.

Thus demonstrating that the sodium cholate suspension- dialysis method could be applied to GOX and produce highly active GOX-SWNT conjugates is novel. In addition the enzyme loadings obtained are ~4 times higher than the loadings (~5.3 mg GOX/SWNT) achieved by an ultrasonic processing method.<sup>60</sup> A second important aspect of this work is that we report the resonance ratio, which is related to the fraction of individual SWNTs,<sup>48</sup> of our GOX-SWNT dispersions. A persistent challenge in the SWNT field is quantitatively comparing the quality of SWNT dispersions produced by different methods. Our measurements of the resonance ratio provide useful information for comparison as new methods of SWNT solubilization are developed. Moreover the resonance ratio of 0.129 compares favorably with values measured for surfactant dispersed SWNTs. A final significant aspect of this work is the high biocatalytic response of the sensors (limiting current density of 440  $\mu\text{A}/\text{cm}^2$  and sensitivity of 56  $\mu\text{A}/\text{mM}$  biosensors based on GOX, and should allow for miniaturization in biosensor development and for increased power output in biofuel cell applications.



A- PVP-Os/GOX-SWNT  
B- PVP-Os/GOX

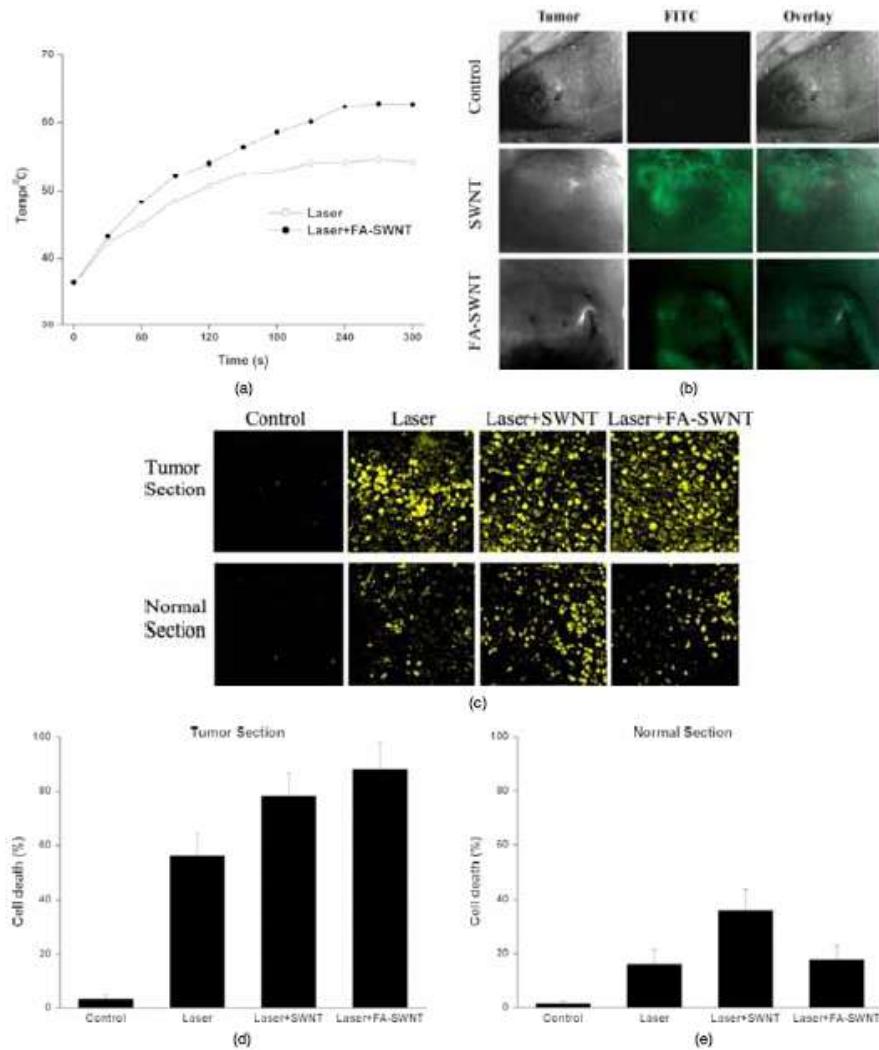
## **Cancer photothermal therapy in the near-infrared region by using single-walled carbon nanotubes**

Published in: *Journal of Biomedical Optics* **2009**, 14, 1-7 (Feifan Zhou, Da Xing, Zhongmin Ou, Baoyan Wu, Daniel E. Resasco, Wei R. Chen)

Single-walled carbon nanotubes (SWNTs) have a high optical absorbance in the near-infrared (NIR) region. In this special optical window, biological systems are known to be highly transparent. The optical properties of SWNTs provide an opportunity for selective photothermal therapy for cancer treatment. Specifically, CoMoCAT® nanotubes with a uniform size (about 0.81 nm) and a narrow absorption peak at 980 nm are ideal candidates for such a novel approach. Here, CoMoCAT® SWNTs are conjugated to folate, which can bind specifically to the surface of the folate receptor tumor markers. Folate-SWNT (FA-SWNT) targeted tumor cells were irradiated by a 980-nm laser. In our *in vitro* and *in vivo* experiments, FA-SWNT effectively enhanced the photothermal destruction on tumor cells and noticeably spared the photothermal destruction for nontargeted normal cells. Thus, SWNTs, combined with suitable tumor markers, can be used as novel nanomaterials for selective photothermal therapy for cancer treatment.

Photothermal therapies for cancer have been widely investigated as a minimally invasive treatment modality in comparison with other methods. However, the chromophores in healthy tissue in the light path can also absorb energy, thus reducing the effectiveness of the heat deposition within tumor cells and increasing nonspecific injury of adjacent healthy tissue. *In situ* light-absorbing dyes have been used to selectively increase the thermal destructions in the target tumors. Recently, nanotechnology has engendered a range of novel materials, such as gold nanoshells and carbon nanotubes, with unique optical properties such as a strong near-infrared absorption efficiency and photo-stability compared to the conventional dyes. Single-walled carbon nanotubes (SWNTs) have been considered for applications in various biological systems, including deliveries of biological cargoes into cells, biosensor development, bioelectrochemistry, and biomedical devices. The intrinsic property of SWNTs is their strong optical absorbance in the near-infrared (NIR) region, which could release significant heat and enhance thermal destruction of cells during NIR laser irradiation and radiofrequency irradiation. Since biological tissues exhibit a deep penetrability with very low absorption of NIR photons in the wavelength range of 700 to 1100 nm, the SWNTs, with an absorption band in the NIR region, could be the ideal candidate for photothermal therapy. The CoMoCAT® method produces SWNTs that are enriched in the (6,5) nanotube chirality with a narrow and intense absorption band at 980 nm that has a uniform size of about 0.81 nm. Its photothermal properties should be explored for selective photo-tissue interactions. Furthermore, photothermal therapy using the absorption properties of antibody-conjugated nanomaterials has demonstrated selective killing of cancer cells while leaving healthy cells unaffected. In this study, we explored the effects of irradiation by a 980-nm laser of antibody-conjugated CoMoCAT® nanotubes, that can act efficiently to convert the 980-nm laser energy into heat and to selectively destroy target cells. We used a synthetic method to enable the conjugation of the SWNTs to folate moiety, which selectively internalized SWNTs inside cells

labeled with folate receptor (FR) tumor markers. In this study, we present the results of cell death induced by the irradiation of a 980-nm laser, either *in vitro* or *in vivo* and with or without folate-SWNT(FA-SWNT).



In summary, FA-SWNT effectively enhanced the photothermal destruction of tumor cells and noticeably protected the photothermal destruction of normal cells. Thus, SWNTs combined with suitable tumor markers can be used as novel nanomaterials for targeted cancer photothermal therapy. Our study demonstrated such potential based on the folate conjugation. Further studies are needed to investigate the effectiveness of FA-SWNT and SWNTs conjugated with other biomarkers in selective photothermal therapy for cancer treatment.

## ***Emulsions Stabilized by Carbon Nanotube-Silica Nanohybrids***

Published in: *Langmuir* **2009**, 25, 10843-10851 (Min Shen and Daniel E. Resasco)

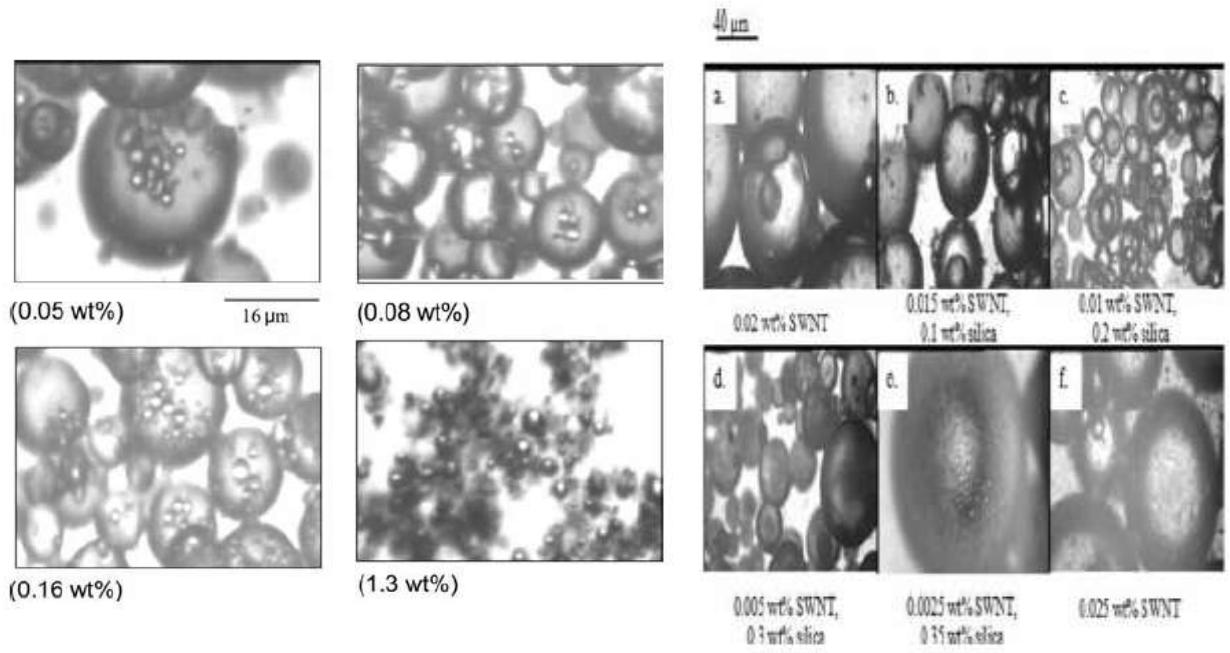
Emulsions have been stabilized by carbon nanotube-silica nanohybrids. The as-prepared nanotube-silica particles generate water-in-oil (w/o) emulsions, regardless of the water/oil volume ratio used. The emulsion volume fraction was much higher than that obtained with nanotubes only, and it was found to increase with water/oil ratio due to an increasing amount of water retained in the emulsion droplets. However, beyond a certain water/oil ratio, the emulsion fraction rapidly decreased. This point of collapse is a strong function of the amount of carbon nanotube-silica particles in the system. Oxidation of the nanohybrids by nitric acid can effectively modify the particle surfaces and change the resulting emulsion properties. The treatment in nitric acid increases the density of functional groups on the carbon nanotubes. Depending on the extent of functionalization, the effect of oxidation can vary from increasing the volume of emulsion stabilized to reversing the type of emulsion to oil-in-water (o/w). The emulsions are remarkably stable against coalescence and sedimentation and can be easily separated by filtration or centrifugation, which make them suitable for applications in interfacial catalytic processes in which the catalyst can be easily recovered after reaction.

In this contribution we describe the behavior of emulsions stabilized by carbon nanotube-silica hybrids. Surface wettability and particle size are two important parameters for controlling emulsion properties, but they are not easily controlled in pristine SWNTs. The SWNT-silica hybrids discussed in this contribution allows us to control these properties. Therefore, we anticipate that the SWNT-silica combination offers a unique structure that can offer great flexibility in controlling the surface wettability by adjusting the carbon/silica ratio, silica particle size, nanotube length, and surface functionalities, which in turn can be varied by varying reaction conditions and surface treatments. Thus, it is possible to modify the distributions of partitioning coefficients between oil and water.

We report the preparation of water-in-oil and oil-in-water emulsions with variable fractions of emulsion volume by using the carbon nanotube-silica nanohybrids as stabilizers. For a given water/oil ratio, the volume fraction of emulsion obtained with the nanotube-silica nanohybrids is much higher than the fractions obtained under the same conditions with either nanotubes or silica particles alone. The effects of varying the water/oil volume ratios, the concentration of added solids, and the functionalization of the nanotube surface on the type of emulsion formed, emulsion droplet size, and total emulsion volume, have been investigated. Potential applications of these solid emulsifiers as interfacial catalysts and for emulsion polymerization are proposed.

We have shown that particle-stabilized w/o and o/w emulsions can be prepared by SWNT-silica nanohybrids. Water/oil volume ratio, particle concentration, and nitric acid oxidation pretreatment greatly affect the emulsion type, emulsion volume fractions, and average droplet diameters, in a reproducible and controllable way. The resulting emulsions exhibit good resistance to coalescence and sedimentation. This novel way to

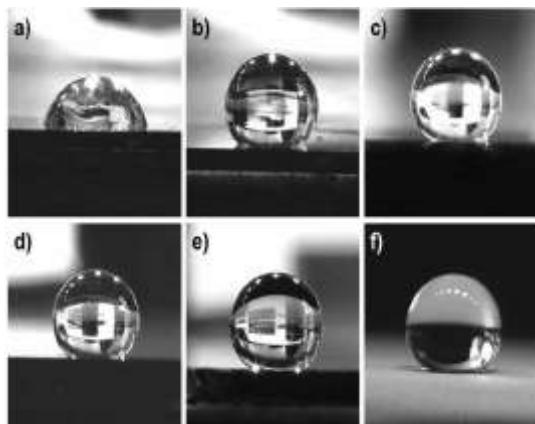
prepare emulsions by supported SWNT shows great advantage in achieving high emulsion volume compared with using only SWNT, and might open new opportunities for utilizing these materials as supports for heterogeneous catalysis to be used in biphasic systems. These catalyst/emulsifiers would be easily removed from the reaction system, breaking the emulsion, and obtaining the two liquid phases containing products. Also, the solid-stabilized emulsions of the o/w type can be used to conduct *in situ* polymerization with nanotubes kept in a highly dispersed state at the oil/water interface.



### **Single-Walled Carbon Nanotube Pillars: A Superhydrophobic Surface**

Published in: *Langmuir* 2009, 25, 4792-4798 (Liang Zhang and Daniel E. Resasco)

A series of SWNT arrays have been constructed by disproportionation of carbon monoxide on Co-Mo catalyst films deposited on flat Si wafer substrates. The arrays include a two-dimensional SWNT thin film prepared by spraying aSWNT suspension, as well as random SWNT networks, and vertically aligned SWNT. In addition, a novel SWNT array has been developed and termed SWNT “pillars”. These pillars are prepared by controlled synthesis of SWNT over a templated substrate. When water droplets are deposited on these surfaces, it is observed that the static contact angle changes dramatically with the type of SWNT array. The higher is the degree of surface roughness (at the nano and microscales) of these structures, the higher is the contact angle. The novel SWNT pillars exhibit superhydrophobicity (i.e., contact angle  $\sim 160^\circ$ ). To quantify the effect of surface roughness, two simple models have been employed. The



Wenzel model can be used to quantify the behavior of the SWNT thin films while the Cassie-Baxter model is used for the SWNT arrays with three-dimensional structure (grass, forest, and pillars).

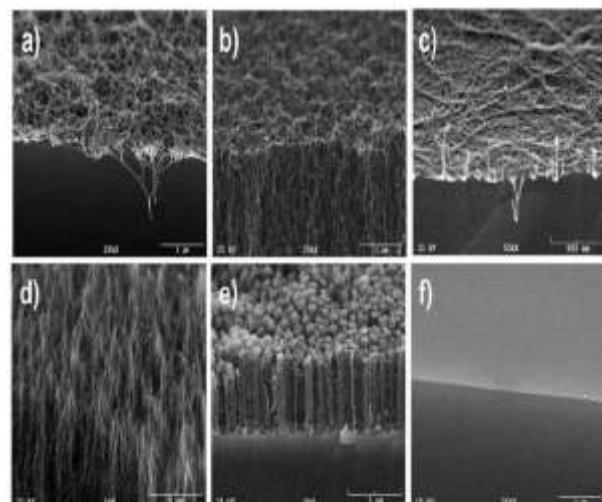
Extensive efforts have been dedicated to develop synthesis methods for growing SWNT directly on substrates with specific arrangements, for example, vertically oriented forests. This is particularly challenging for SWNT compared to MWNT, since the former are much more sensitive to catalyst structure and carbon feedstock than the latter. In this contribution, we show an example of dramatic changes in physical properties observed when the microarrangement of nanotubes is varied, while using the same nanomaterial, which in this case is SWNT prepared by CO disproportionation on Co-Mo catalysts supported on silica.

A previous study indicates that MWNT display an interesting range of hydrophobicity when varying parameters like ionic strength, nature of the electrolyte, or pH of the water droplet. Moreover, it was found that the droplet behavior can be switched from superhydrophobic to hydrophilic by application of an electric field. In this contribution we demonstrate dramatic changes in hydrophobicity of SWNT microstructures of varying arrangement. These microstructures include 2-dimensional SWNT films, random networks of SWNT (grass), vertically aligned SWNT (forest), and a novel array of bundled SWNT (pillars).

Essentially total water repellency has been observed on the surface of SWNT pillars grown from morphology-controlled catalyst surfaces synthesized by the nanosphere templating method. In concurrence with previous studies on superhydrophobic systems, in which a combination of microscale roughness and nanoscale roughness appears to be essential, we propose here that the highest hydrophobicity achieved with the SWNT pillar structure can be ascribed to a double structural roughness of the surface. The first level of roughness is at the nanoscale and is a consequence of the presence of entangled SWNT on the top of each pillar. The second level of roughness is at the microscale and is associated with the orderly spaced pillars.

We have developed a series of SWNT microstructures, including 2-dimensional SWNT film, random SWNT network (grass), vertically aligned SWNT (forest), and SWNT pillars, by controlled synthesis of SWNT directly on flat substrates and/or treatment after synthesis. Our study has demonstrated that the static contact angle on these surfaces

changes dramatically with surface roughness of SWNT structures and depends on whether this roughness is in the nano- or microscale. The contact angle of a drop sitting on the flat SWNT thin films is described by the Wenzel model.



By contrast, the behavior of the different three-dimensional arrays can be described in terms of the Cassie-Baxter model. Therefore, the hydrophobicity of SWNT grass, forest, and pillars is greatly enhanced by both a primary roughness at the nanoscale and a secondary roughness at the microscale, which is particularly effective in the case of the SWNT pillars.

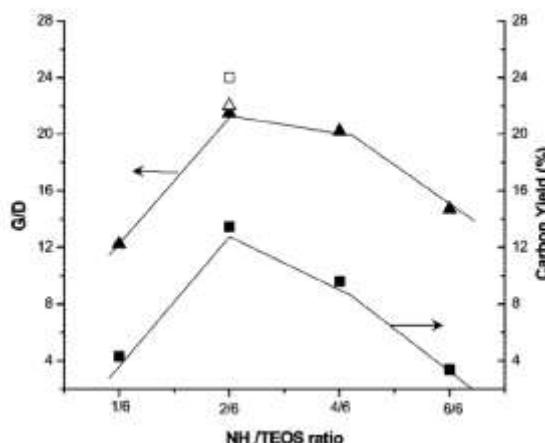
### **Sol-Gel Synthesis and Characterization of Co-Mo/Silica Catalysts for Single-Walled Carbon Nanotube Production**

Published in: *Chem. Mater.*, **2009**, 21, 2238-2246 (Veronica M. Irurzun, Yongqiang Tan, and Daniel E. Resasco)

A series of silica-supported Co-Mo samples prepared by the sol-gel method has been compared as catalysts for the synthesis of single-walled carbon nanotubes (SWNT). The concentration ratio of ammonium hydroxide to the silica precursor tetraethoxysilane (TEOS) has an important effect on the resulting morphology of the silica support and, consequently, on the nature of the Co-Mo catalytic species. In turn, these morphology changes have significant effects on carbon yield, quality, and type of the single-walled carbon nanotubes obtained by the disproportionation of CO at 750 °C. In addition, a catalyst with an open microscale structure has been prepared by using carbon fibers as burnable sacrificial templates. This open structure results in several-fold enhanced carbon yield, while keeping the same nanotube quality as those obtained on conventional powder catalysts.

In this contribution, a series of silica-supported Co-Mo catalysts prepared by the sol-gel method has been compared. The sol-gel method has been extensively used in the preparation of supported metal catalysts because it typically results in highly homogeneous materials with high degree of metal dispersion. For example, Pd/SiO<sub>2</sub> catalysts prepared by the sol-gel method have not only exhibited higher surface area, narrower pore size distribution, and higher support thermal stability than impregnated catalysts but also higher resistance to metal particle sintering and lower deactivation during methane combustion.<sup>15</sup> Particularly relevant to the current work, this method has been also used to obtain active phases of Ni-Mo and Co-Mo<sup>16</sup> bimetallic catalysts supported on silica for the oxidative dehydrogenation of alkanes. It has been observed that catalysts prepared by the sol-gel method can stabilize the bimetallic active phases much more efficiently than those prepared by other methods. Therefore, sol-gel appears as a suitable method to produce Co-Mo/SiO<sub>2</sub> catalysts for the synthesis of SWNT, which requires stabilization of small clusters.

To obtain metal catalysts supported on high-surface area silica by the sol-gel method the

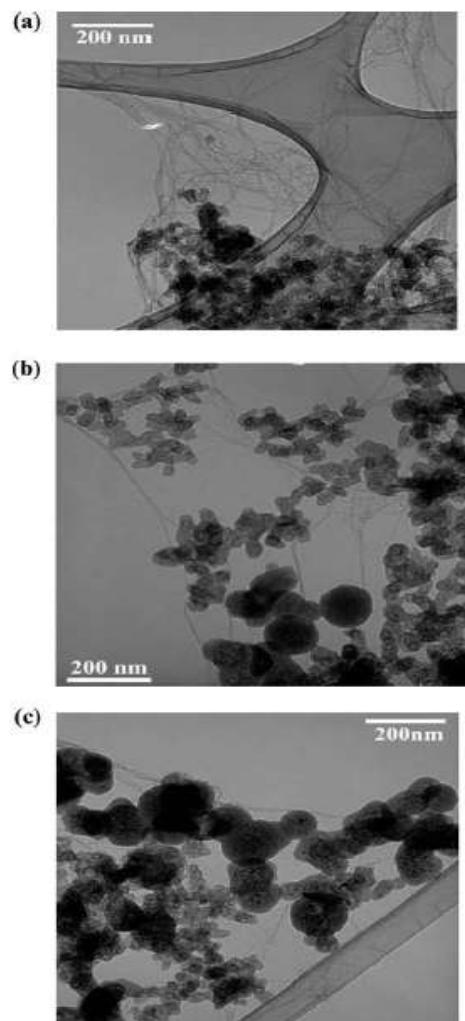


polymerization of an alkoxy silane such as tetraethoxysilane (TEOS), also known as tetraethyl orthosilicate, is carried out in the presence of the appropriate metal precursors. When exposed to water, the alkoxy-silane hydrolyzes and, at different pH values, forms different monomeric species. These species range from  $[\text{Si}(\text{OH})_3(\text{OH}_2)]^+$  at pH 0 to  $[\text{SiO}_2(\text{OH})_2]^{2-}$  at pH 14. Depending on the conditions, these species can condense and form oligomers at a different rate and with different configurations. To accelerate the polymerization, an increase in pH can be brought about by addition of a base, which causes a rapid hydrolysis followed by polymerization.

Simultaneously with this polymerization process, the metal ions (e.g., Co and Mo) precipitate, thus forming a homogeneous and well dispersed mixture

In this study, the effect of varying the ratio of the added ammonium hydroxide concentration has been studied, while keeping the other parameters constant. The concentration of ammonium hydroxide has an important effect on the rate of polymerization, and consequently, we expect that it will affect significantly the resulting morphology. In addition, a catalyst with an open microscale structure was

prepared by the sol-gel method, using a burnable sacrificial template which, after calcination, renders an open structure. This approach, known as sol-gel nanocoating, has been extensively employed by previous workers to prepare structured materials. It gives us the opportunity to investigate the influence of the microstructure, while keeping the composition unchanged. The five catalysts prepared with varying structure were used to catalyze the growth of singlewalled carbon nanotubes (SWNT) and to compare the resulting SWNT quality and yield. We have shown that the sol-gel preparation method has versatility to widely vary the morphology of Co-Mo catalysts used in the synthesis of SWNT. In turn, these changes in morphology result in reproducible changes in nanotube quality and yield. By increasing the ammonia concentration in the sol-gel step, the silica particle size increases as the rates of hydrolysis and polymerization of TEOS are accelerated. Therefore, when the  $\text{NH}_4\text{OH}/\text{TEOS}$  ratio is high a large fraction of Co-Mo species remains encapsulated under the silica. By contrast, at low  $\text{NH}_4\text{OH}/\text{TEOS}$  ratios, the rate of silica polymerization is low, which results in an enhanced agglomeration of Co and Mo species. Both extremes are detrimental for SWNT production. An optimum preparation is found at intermediate  $\text{NH}_4\text{OH}/\text{TEOS}$  ratios.



## ***Silica Supported Single-Walled Carbon Nanotubes as a Modifier in Polyethylene Composites***

Published in: *Journal of applied polymer Science*, **2009**, 11, 589-601 (Neal D. McDaniel, Max P. McDaniel, Leandro Balzano, Daniel E. Resasco)

Composites have been made from singlewall carbon nanotubes in a polyethylene (PE) matrix, in which different methods of preparation were used to disperse the nanotubes. The study includes using either the refined pure nanotubes (P-NT) as the source, or the original silica supported nanotubes (SS-NT). SS-NT contained nanotubes still incorporated in and around the silica as originally grown. Composites were then made by (1) coprecipitation from a suspension of P-NT or SS-NT in a PE solution, or (2) by forming a polymerization catalyst from the SS-NT, and using it to polymerize ethylene, which ruptures and expands the silica as polymer builds up in the pores. Extrusion was also studied as a method of additional dispersion. Nanotubes were found to have a powerful effect on the melt rheology, increasing the low shear viscosity dramatically. Increasing the nanotube concentration also increased the flexural and tensile moduli, decreased the elongation, and increased the electrical conductivity. Consistent trends were observed from all of these diverse properties: SS-NT had a stronger effect than P-NT, and within the SS-NT group the choice of silica type also had a major effect. Polymerization was generally preferred as the method of dispersing the nanotubes. The conductivity, which in some cases was quite high, was found to be pressure sensitive. Conductive NT/PE composites could be molded into films or extruded into other shapes, or comolded with other PE

Polyethylene (PE) is the most widely used plastic because it is least costly, easily molded by many different processes, and exhibits a wide variety of useful properties such as high chemical, electrical, and impact resistance.

The properties of PE are sometimes further modified by adding inorganic reinforcing agents, such as calcium carbonate, clay, talc, mica, powdered metals, and carbon black. Such fillers usually increase stiffness and diffusional barrier performance, block light transmission, and the latter two are sometimes added to generate electrical conductivity. A major problem associated with blending fillers into molten PE is the difficulty of dispersing the individual particles into the polymer matrix. Indeed, the quality of dispersion turns out to be the critical variable when designing such composites. High shear extrusion mixing is usually employed for this purpose. The carbon NT are especially problematic in this respect because they are only a few angstroms in diameter, as opposed to microns for other materials. To take full advantage of their high aspect ratio, they must be dispersed at the nanometer level. However, they have a much stronger Van der Waals affinity for each other than they have for the PE matrix. This makes it especially hard to break up clusters of NT, effectively disperse them, and keep them dispersed in the polymer

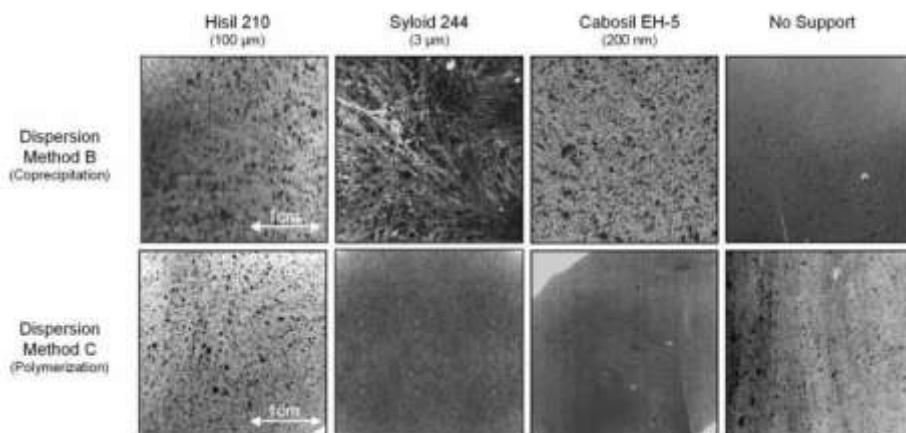
To accomplish such dispersal, several experimental methods have been tested in this study using single- walled Nanotubes: extrusion mixing PE and NT, Coprecipitating PE and NT. Dispersing NT via polymerization, and Immobilizing P-NT in an oxide gel.

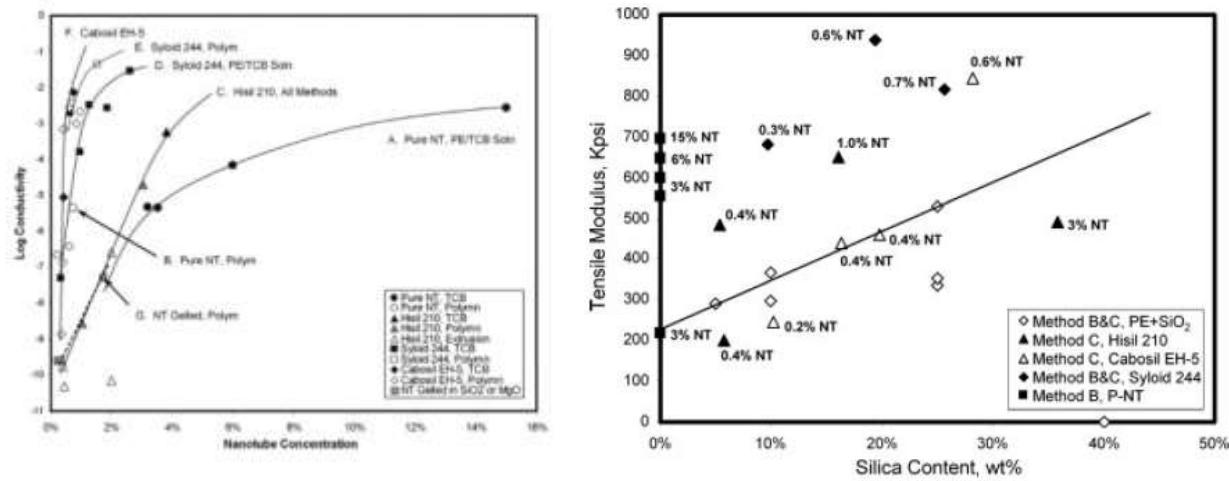
In addition to extrusion blending the NT into molten polymer, NT was also dispersed by sonication into solutions of PE, followed by “quenching,” i.e., fast coprecipitation in cold alcohol.

In another approach, the polymerization mechanism itself was tested as a means of dispersing the NT. NT was first made on Co/silica catalyst, which was then converted into a polymerization catalyst and allowed to polymerize ethylene. Again PE was generated at low yield and this material was then extrusion blended into PE. In situ polymerization yielded a source of NT that was found to be more compatible with PE. Improvements in physical properties of PE were reported. This report is another attempt to produce superior dispersion in PE by in situ polymerization. However, unlike previous reports that incorporated refined and isolated NT, which exists in agglomerated bundles, the present study instead used the original silica-supported NT in its nascent form. In situ PE was then generated, not as a compatibilizer for extrusion mixing with other PE, but to make the final NT/PE composite.

These nanotube-PE composites have been investigated by rheological, flexural, tensile, and electrical tests, each yielding similar conclusions. In PE, refined NT (P-NT) are much less effective as a filler than SS-NT. Furthermore, results among the SS-NT composites indicate that the choice of silica can also have a major influence on the final properties. The following order of effectiveness was consistently observed: Cabosil EH-5 > Syloid 244>> Hisil 210. Within a given family of composites using the same silica, results suggest that polymerization is the preferred method of dispersion.

All attempts to further homogenize the composite by intensive extrusion resulted in improved visual uniformity, but a loss of rheological and electrical properties. This again suggests that visual uniformity and “micro-dispersion” are not the same. SS-NT based composites yielded far better results than P-NT. This suggests that refining the NT allows their agglomeration, which is very difficult to reverse. Converting the original SS-NT catalyst into a polymerization catalyst provides an efficient and low-cost method of dispersing the NT. The measured conductivity was also found to be pressure sensitive, probably from microscopic surface roughness, despite the glossy macroscopic appearance. NT greatly increased the low-shear melt viscosity of PE. The effect of inert fillers like silica and carbon black on the melt rheology is well-known and is not comparable to that observed in this study from NT.





### Nanotubes: Giving catalysis the edge

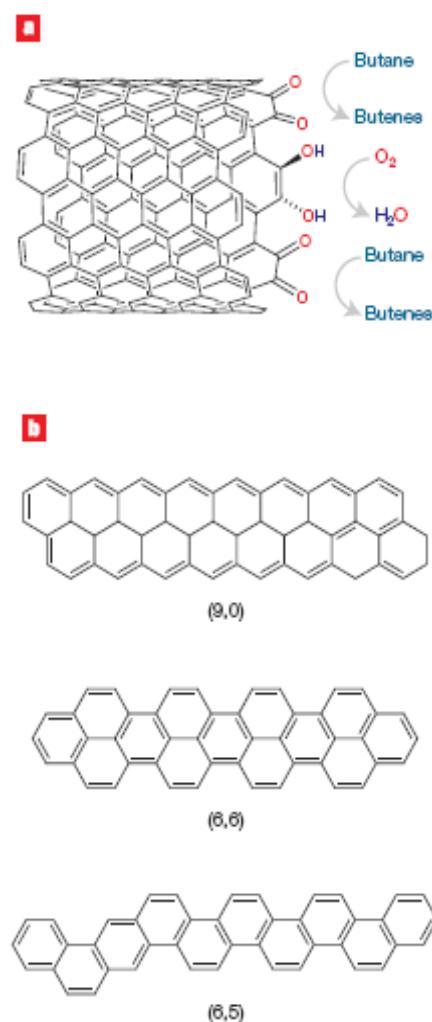
Published in: *Nature Nanotechnology* **2008**, 3, 708-709 (Daniel E. Resasco)

During catalysis, the distribution of products in a chemical reaction is determined by the catalyst's ability to modify the activation energy barriers of the possible reaction paths. However, the tendency of a catalyst to favour certain pathways while inhibiting others is more important than accelerating the overall rate. Needless to say, manipulating the activation energy of a specific reaction path is challenging and requires a detailed understanding of the very heart of the catalyst — its active site.

D. Su and colleagues report an elegant example of using the tools of nanotechnology to address this issue. By modifying the surface functionality of carbon nanotubes, they have created a highly selective oxidative dehydrogenation catalyst, clearly demonstrating that it is possible to selectively inhibit a particular reaction path by precise modification of the active site. Su and co-workers examine the oxidative dehydrogenation of an alkane, butane (C<sub>4</sub>H<sub>10</sub>), to produce the corresponding alkenes, butene and butadiene (C<sub>4</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>6</sub>), by creating one or two new carbon–carbon double bonds in the molecule. Unfortunately, alkenes are oxidized to produce carbon dioxide and water faster than the alkanes are dehydrogenated to produce the alkenes. Su and colleagues compare the catalytic activity and selectivity of multiwall carbon nanotubes in three different forms: pristine, oxidized and phosphorusmodified. Over pristine nanotubes, and in the presence of excess oxygen, butane is almost totally oxidized to CO<sub>2</sub> and water, and only a very small fraction is converted to alkenes. However, when the nanotubes contain oxygen functional groups, the selectivity towards alkenes significantly increases and becomes greater still when phosphorus is added. The authors find that phosphorus-modified nanotubes are much less active than oxidized nanotubes for the unwanted combustion step.

Other notable attributes of these nanotube catalysts include their remarkable stability under reaction conditions (no deactivation in 100 h) and their ability to withstand low O<sub>2</sub>/hydrocarbon ratios without deactivation.

The carbon atoms that constitute the walls of carbon nanotubes, either singlewall or multi-wall, are arranged in a honeycomb-like hexagonal lattice. This is a stable and chemically inert configuration, and as such the interaction with adsorbates is weak. By contrast, the edges of the nanotubes, as well as any defect in the walls (for example, a missing carbon atom), are chemically active. It is expected that electrophilic surface species such as superoxides (O<sub>2</sub><sup>–</sup>) and peroxides (O<sub>2</sub>2<sup>–</sup>) catalyse the unwanted combustion of the alkenes, and it has been shown that these electron-deficient species are produced by the interaction of oxygen with open defect carbon sites or edges. Therefore, it is understandable that pristine nanotubes show low selectivity. On the other hand, oxidized nanotubes have a higher concentration of C=O groups, which themselves are not electrophilic. However, the oxygen can desorb at high temperatures, leaving behind dangling carbon bonds that generate electrophilic (unselective) species, and thus partially limit their selectivity to alkenes. The role of phosphates is then to prevent the generation of electrophilic species on the surface, reducing the  $B \rightarrow C$  step rate constant (combustion) and thus improving alkene selectivity. This concept opens up a great opportunity for further fundamental research, particularly if single-wall carbon nanotubes of controlled chiralities are used, because their structure is much better defined than that of the multi-wall nanotubes used by Su and colleagues. The distance between contiguous C=O sites attached to the edge of a nanotube will vary in a consistent way, depending on whether the dangling carbon bond is on a zigzag edge or an armchair edge.



**Figure 1** The oxidative dehydrogenation of butane over oxidized carbon nanotubes. **a**, Two hydrogen atoms are removed from butane (C<sub>4</sub>H<sub>10</sub>) by a pair of C=O sites (top) at the edge of a nanotube to leave a pair of OH groups (middle). These hydrogen atoms then react with oxygen to form water, regenerating the pair of C=O sites so that they can remove hydrogen atoms from another butane molecule (bottom). **b**, Different single-wall carbon nanotubes have different edges: a (9,0) nanotube has zigzag sites along its edge, whereas a (6,6) nanotube has 'armchair' sites; a (6,5) nanotube has one zigzag site on the left, with the rest being armchair sites.

On an  $(n,n)$  nanotube, all the edge sites are armchair; on an  $(n,0)$  nanotube, in contrast, they are all zigzag; on  $(n,m)$  nanotubes, there is a combination of the two. Therefore, an opportunity exists to create nanotube-based catalysts of controlled density and distribution of C=O pairs. As a result, it may be possible to further refine the structure-reactivity relationships of nanotube catalysts through studies similar to those carried out using model single-crystal catalysts, but with the added advantage of working with a practical catalyst that could eventually be used industrially.

***Wide-range optical spectra of carbon nanotubes: a comparative study***

Published in: *Physica Status Solidi B: Basic Solid State Physics* **2008**, 245, 2229-2232  
(K. Kamara's, A. Pekker, M. Bruckner, F. Borondics, A. G. Rinzler, D. B. Tanner, M. E. Itkis, R. C. Haddon, Y. Tan, and D. E. Resasco)

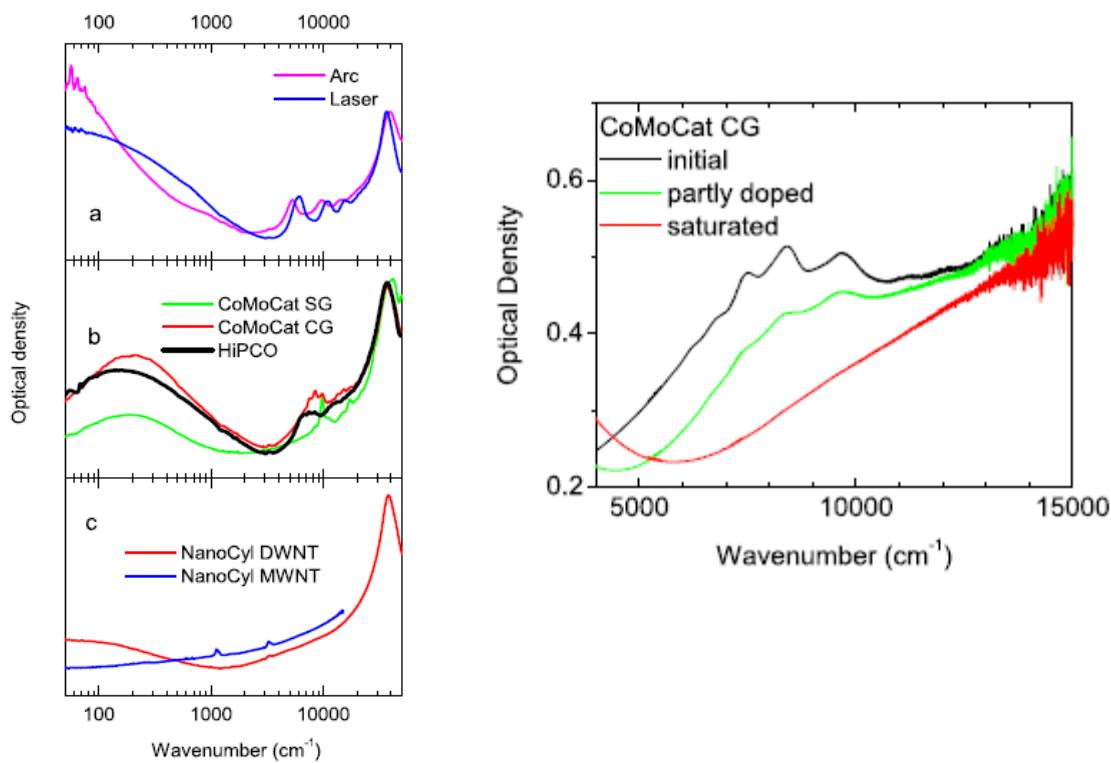
We present optical spectra from the far infrared through the ultraviolet spectral region of freestanding transparent carbon nanotube films: single-, double- and multiwalled, and containing varying amounts of tubes of different chirality. By comparing the spectral features in the far infrared and the near infrared/visible, we can estimate the metallic/semiconducting content. We show by spectroscopic methods that doping the tubes increases both the conductivity and the transparency for visible light. We also discuss the influence of sample preparation and subsequent treatment on application possibilities.

Optical spectroscopy is one of the most widely used methods in characterization of carbon nanotubes. Recently, it was demonstrated that absorption and especially fluorescence studies can detect individual nanotubes and identify them by chirality index]. Most studies concentrated on the NIR/VIS spectral range where transitions between Van Hove singularities occur: based on these observations, selectivity by semiconducting/metallic character was reported both for ionic doping and covalent functionalization. Relatively less attention was devoted to the low-frequency part of the spectrum. Here we want to emphasize the importance of far-infrared measurements as a sensitive indicator of intrinsic charge carriers in metallic tubes and extrinsic carriers in doped materials.

To study the effects of doping, we chose CoMoCat CG material because it contains few enough specimens to follow them individually, yet many enough to observe the effect of doping on several types of tubes. We followed the evolution of the spectra in the S11 region after exposing the film to nitric acid vapor. Nitric acid causes hole doping, similar to intercalated graphite]. The process arrived at saturation within five minutes. Changes consist of the disappearance of all interband transitions, and the appearance of a low-frequency absorption which we assign to free-carrier excitations connected with the emptying of the occupied states through hole doping by the acid. This treatment increases the dc conductivity and the free-carrier absorption, thereby distorting the apparent metal/semiconductor ratio; this is the reason why before

comparing spectroscopic features, all samples have to undergo thermal treatment in order to remove spurious dopants.

We have presented wide-range optical spectra of freestanding carbon nanotube films. From these data we can characterize various nanotube types by conductivity and transparency, the most important parameters of coating applications. We showed that laser or arc material is optimal when high conductivity is desired, HiPCO and CoMoCat show a wider transparency region, and double-wall tubes exhibit the least structure in transmission. The latter effect, loss of structure with increasing transparency, can also be achieved by doping. These possibilities (tunable conductivity and transparency window) make carbon nanotubes feasible alternatives to conducting transparent oxides.



### **Composites of Single-Walled Carbon Nanotubes and Polystyrene: Preparation and Electrical Conductivity**

Published in: *Chemistry of Materials* **2008**, 20, 3120-3126 (Maxim N. Tchoul, Warren T. Ford, Mai L. P. Ha, Israel Chavez-Sumarriva, Brian P. Grady, Giulio Lolli, Daniel E. Resasco, and Sivaram Arepalli)

Composites of single-walled carbon nanotubes (SWNT) and polystyrene have been prepared using three different types of SWNT: HiPco, CoMoCat, and pulsed laser vaporization (PLV). Nanotubes were incorporated into the polystyrene matrix by two methods: (1) evaporation of chloroform solutions of SWNT noncovalently functionalized

with poly[(*m*-phenylenevinylene)-co-(2,5-dioctoxy-*p*-phenylenevinylene)] (PmPV) and polystyrene; (2) coagulation in water of DMF solutions containing polystyrene and nitric acid oxidized SWNT. From measurements of the electrical conductivities of the composites over a range of concentration from 0.1 to 6 wt % SWNT, the percolation threshold of conductivity was 0.17–0.3% SWNT for the PmPV-coated materials and 0.4–0.5% for those made by coagulation. Of the three types of SWNT, composites made with HiPco tubes had the highest conductivity.

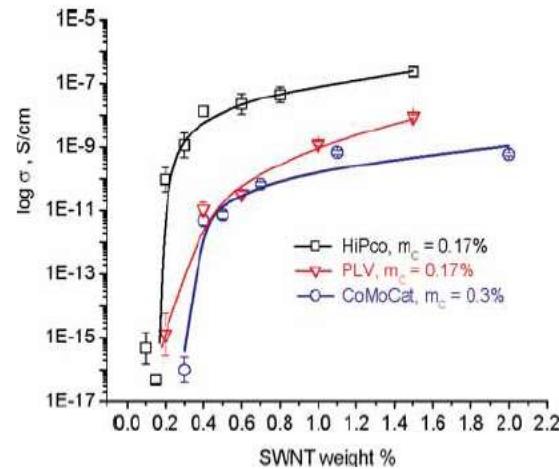
Carbon nanotubes possess high mechanical strength, high electrical and thermal conductivity, and unique optical and electronic properties. These

properties make carbon nanotubes valuable for a wide range of applications. Electrical conductivity of individual bundles of metallic carbon nanotubes reaches the value of  $104 \text{ S/cm}^2$  which is close to that of metals ( $59 \times 104 \text{ S/cm}$  for copper and  $9.9 \times 104 \text{ S/cm}$  for iron), even though the density of nanotubes is much lower. Thus carbon nanotubes are excellent candidates to blend with polymers to produce electrostatic dissipative materials and other useful components in electronics. However, the potentially superb properties of composites made with SWNT have not been achieved because of poor dispersion of the nanotubes. The experimental conductivities of CNT-polymer composites have percolation thresholds ranging from 0.0025% to several percent, depending on the

type of polymer and method of composite preparation. Values of 0.1–1% are most common. The conductivity of a composite  $\sigma$  vs volume fraction of nanotubes  $f$  follows the scaling law  $\sigma = C(f - f_c)^B$  where  $f_c$  is the volume fraction at the percolation threshold and  $B$  and  $C$  are constants. Because the percolation threshold is greatly dependent on the spatial distribution of nanotubes in the polymer matrix,<sup>14,15</sup> it is possible to use this parameter to assess the quality of nanotube dispersion in composites.

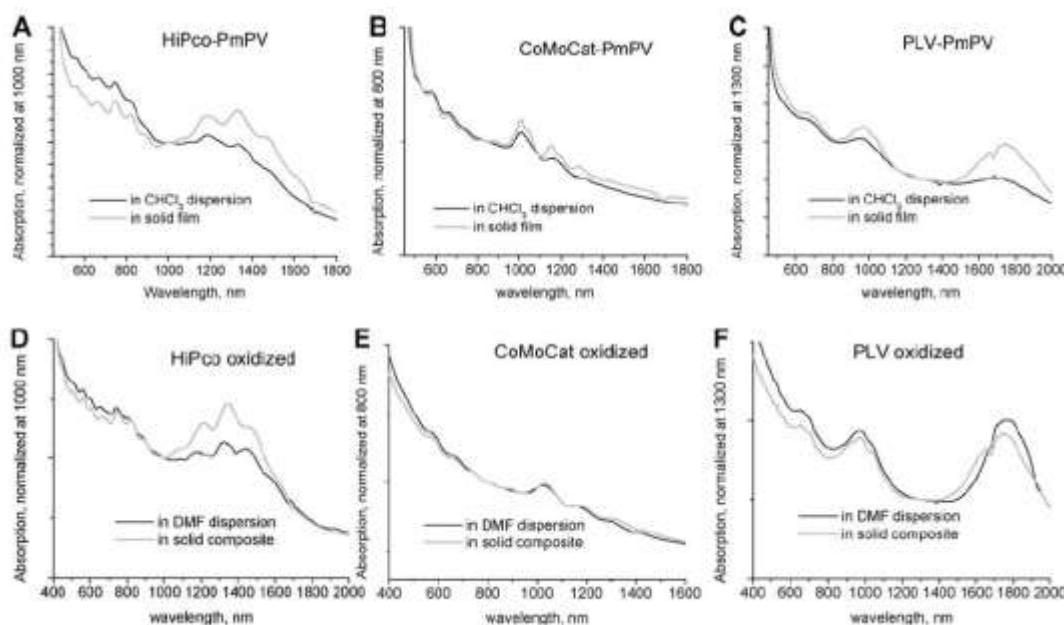
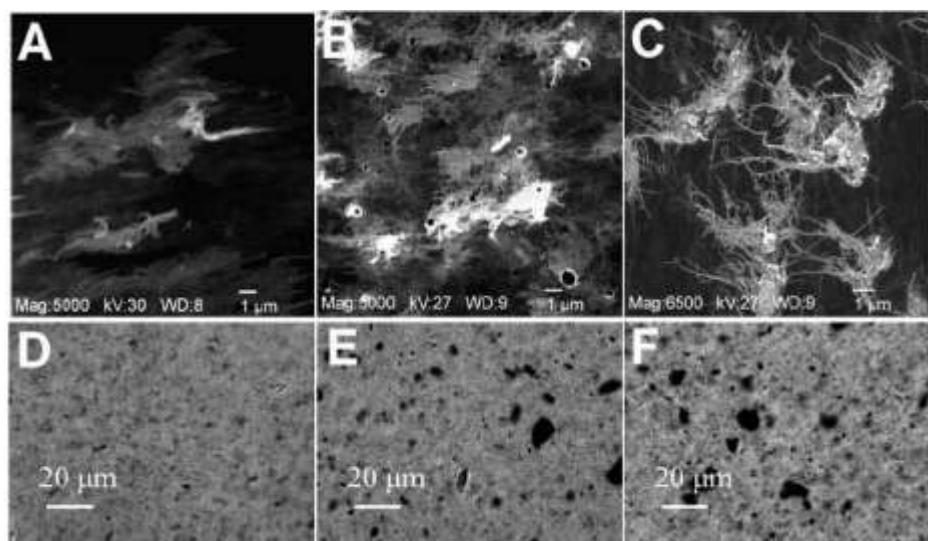
The basic approaches utilized for incorporation of nanotubes into the polymer matrix include melt mixing,<sup>9,10</sup> in situ polymerization,<sup>3,7</sup> and solution processing.<sup>6,8,12</sup> The latter two methods have given better results due to a more uniform distribution of nanotubes in a low-viscosity liquid phase that results in a more uniform mixing with polymer.

The objective of this research was to determine how SWNT of varied types can be dispersed into a typical amorphous polymer, polystyrene. We examined two methods of preparation of composites. First, we dispersed nanotubes in chloroform with the aid of poly[(*m*-phenylenevinylene)- co-(2,5-dioctoxy-*p*-phenylenevinylene)] (PmPV). Our second method of composite preparation is precipitation into water of a DMF solution of polystyrene and nanotubes that had been oxidized by nitric acid. We found previously<sup>18</sup>



that sonication of nanotubes in 8 M nitric acid for 60 min significantly increases their solubility in DMF while preserving the electronic structure of nanotubes.

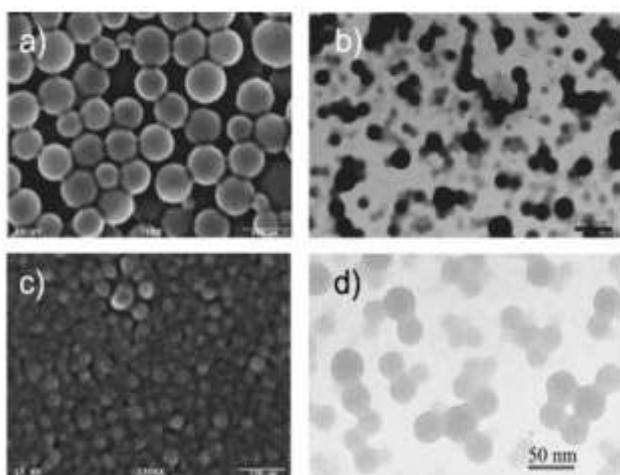
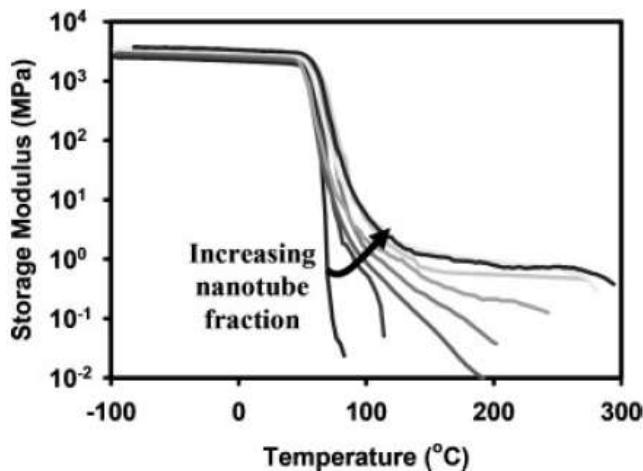
PmPV is a good stabilizing agent for dispersions of carbon nanotubes, enabling preparation of polystyrene composites via rapid evaporation of chloroform from dispersions of SWNT in polystyrene solution. However, the presence of PmPV may detract from the mechanical properties of the composite. The use of oxidized SWNT and no extra polymer or surfactant simplifies the composite content. The nitric acid treatment shortens the nanotubes, decreasing the aspect ratio compared with the PmPV dispersed nanotubes. The smaller aspect ratio nanotube bundles in polystyrene composites have a higher percolation threshold of electrical conductivity, which is consistent with percolation theory. The electrical conductivity in the plateau region above the percolation threshold depends on the type of SWNT material, which could be attributed to the differences in the fraction of metallic nanotubes.



## Composites of Single-Walled Carbon Nanotubes and Styrene-Isoprene Copolymer Lattices

Published in: *Macromolecular Chemistry and Physics* **2007**, 208, 446-456 (Mai L. P. Ha, Brian P. Grady, \* Giulio Lolli, Daniel E. Resasco, Warren T. Ford)

Composites of a styrene-isoprene copolymer and SWNTs were prepared by emulsion and miniemulsion polymerization in the presence of SWNTs, as well as by mixing dispersed SWNTs with a styrene-isoprene copolymer latex after polymerization. For the former, the surfactant was displaced from SWNTs to monomer droplets leading to SWNT aggregation. Mixing dispersed SWNTs with latex after reaction was able to preserve SWNT dispersion and gave a polymer composite with an electrical percolation threshold of 0.2%. Dynamic mechanical measurements of film samples in tension showed that the composites had a measurable modulus above  $T_g$ , indicating entanglement formation. The modulus above  $T_g$  was strongly temperature dependent, confirming shear measurements that have shown entanglements in SWNT/polymer composites involve both polymer and nanotubes.

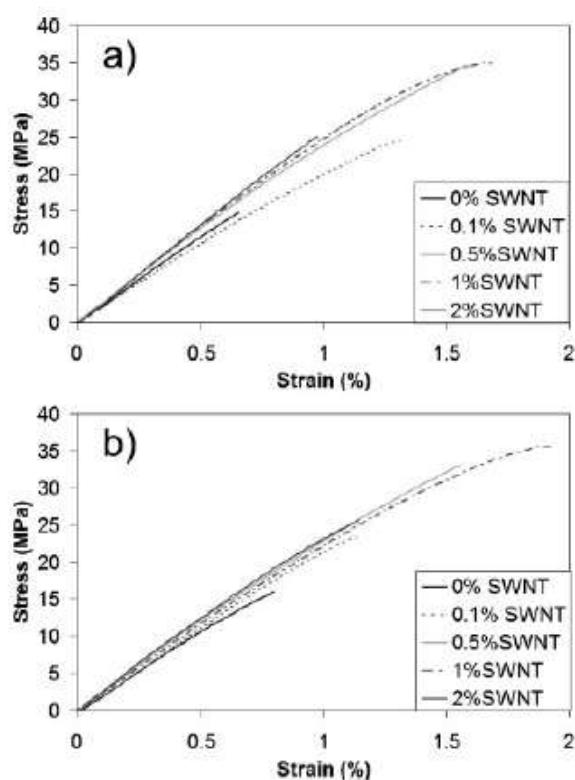


Diameter of CNTs varies over 1.4– 100 nm for MWNTs and 0.4–3 nm for SWNTs. Their aspect ratio can be 1 000 or more. Reported tensile strength and modulus range over 11–150 and 270–1 470 GPa, respectively. The fact that electrical properties of SWNTs are much better than MWNTs and the fact that inner tubes of MWNTs do not contribute significantly to some mechanical properties make SWNTs more attractive for certain applications. CNTs, besides their superb mechanical properties, also have excellent electrical properties: the

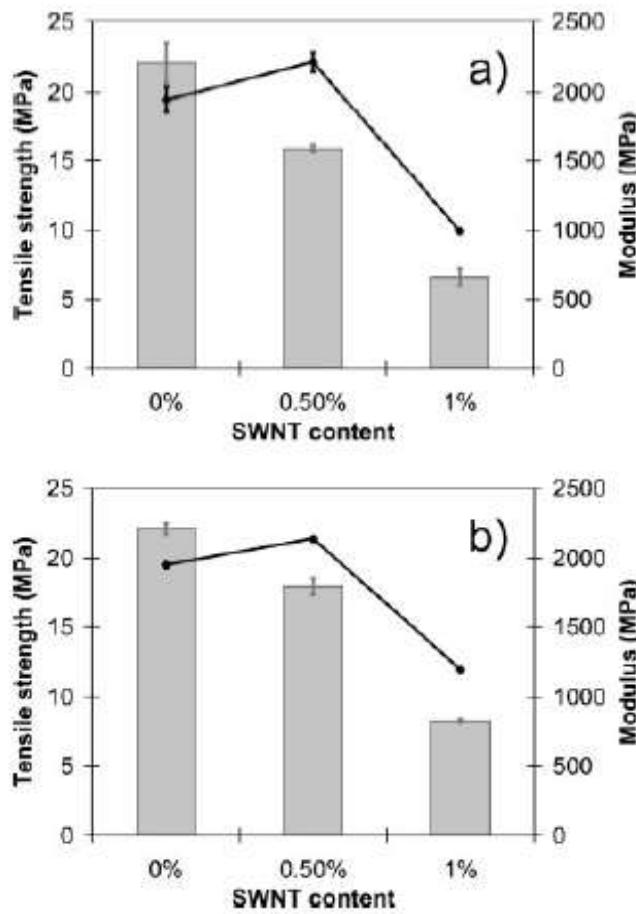
conductivity can be five times that of copper; and theoretically, metallic nanotubes can withstand a current 1 000 times higher than copper or silver. The thermal conductivity of SWNTs is also extremely high; higher than diamond or copper. Such properties suggest that nanotubes are an excellent material to incorporate with polymers.

Encapsulation, i.e., polymerization in the presence of a solid filler, utilizing either miniemulsion or macroemulsion polymerization was not suitable for producing SWNT composites because of poor SWNT dispersion. Furthermore, TEM and SEM pictures indicate a significant reduction in latex particle size with the addition of nanotubes.

These observations indicate that the surfactant was transferred from nanotubes to latex during the reaction; the loss of stabilizing surfactant from nanotubes led to nanotube aggregation. This result should be regarded as specific to this surfactant/nanotube combination; sufficiently strong surfactant adsorption on the nanotube surface could prevent transfer of surfactant in this manner. However, this work shows that surfactant transfer must be prevented while performing encapsulating polymerizations with CNTs in order to obtain good properties. Mixing SWNTs dispersed in surfactant and polymer lattices is simple, and applicable for many polymers. The percolation threshold is similar to what others have found for well-dispersed systems (0.2 wt.% for electrical percolation, 0.033–0.14 wt.-% for rheological percolation). The mechanical properties improve with nanotube addition, particularly at low nanotube fractions. Above the  $T_g$  at high enough SWNT content, the composites have a measurable storage modulus in tension due to entanglements between nanotubes and polymer chains. Using DMA in tension to measure the mechanical properties of a nanotube composite film, it is possible to determine the rheological percolation threshold, its temperature dependence, and how these characteristics depend on orientation.



a) Microemulsion polymerization  
b) Macroemulsion polymerization



Mechanical properties of SWNT composite by a) Microemulsion polymerization  
b) Macroemulsion polymerization

## **Effect of Nanotube Functionalization on the Properties of Single-Walled Carbon Nanotube/Polyurethane Composites**

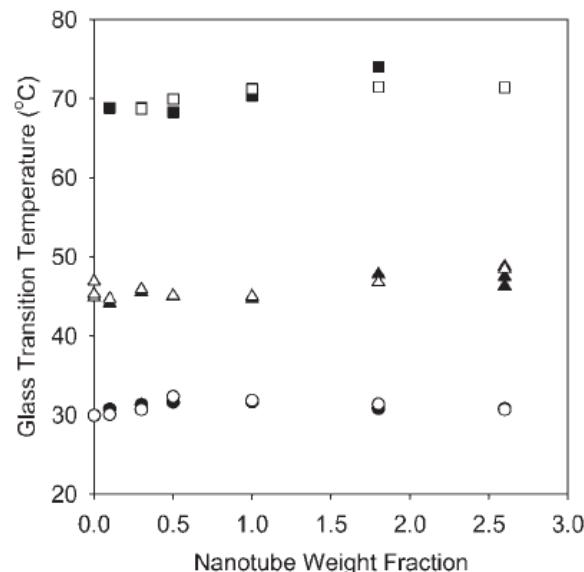
Published in: *Journal of Polymer Science* **2007**, 45, 490-501 (Fabian Buffa, Gustavo A. Abraham, Brian P. Grady, Daniel Resasco)

A commercially available aliphatic thermoplastic polyurethane formulated with a methylene bis(cyclohexyl) diisocyanate hard segment and a poly(tetramethylene oxide) soft segment and chain-extended with 1,4-butanediol was dissolved in dimethylformamide and mixed with dispersed single-walled carbon nanotubes. The properties of composites made with unfunctionalized nanotubes were compared with the properties of composites made with nanotubes functionalized to contain hydroxyl groups.

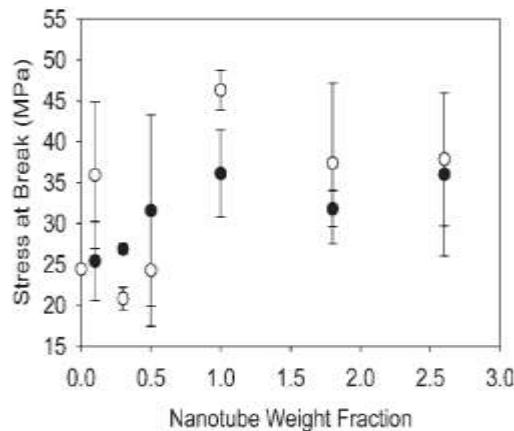
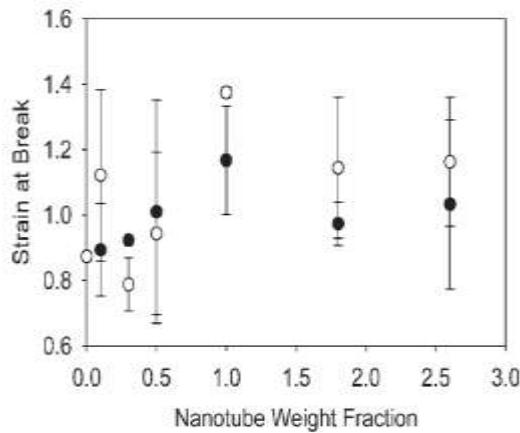
Functionalization almost eliminated the conductivity of the tubes according to the conductivity of the composites above the percolation threshold. In most cases, functionalized and unfunctionalized tubes yielded composites with statistically identical mechanical properties. However, composites made with functionalized tubes did have a slightly higher modulus in the rubbery plateau region at higher nanotube fractions. Small angle X-ray scattering patterns indicated that the dispersion reached a plateau in the unfunctionalized composites that was consistent with the plateau in the rubbery plateau region. The room-temperature modulus and tensile strength increase was proportionally higher than almost all increases seen previously in thermoplastic polyurethanes; however, the increase was still an order of magnitude below what has been reported for the best nanotube–polymer systems. Nanotube addition increased the hard-segment glass transition temperature slightly, whereas the soft-segment glass transition was so diffuse that no conclusions could be drawn. Unfunctionalized tubes suppressed the crystallization of the hard segment; whereas functionalized tubes had no effect.

Thermoplastic polyurethanes belong to a class of polymers termed thermoplastic elastomers. Thermoplastic elastomers have the ability to stretch and return to almost their original shape, though not nearly to the degree of crosslinked elastomers.

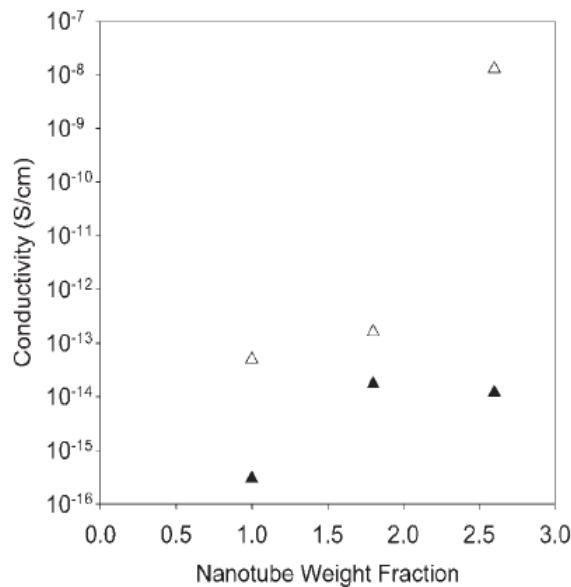
Thermoplastic polyurethanes are multiblock copolymers having the general repeat unit structure  $(AmBn)p$ . As with all multiblock thermoplastic elastomers, one of the block units is above its glass transition temperature ( $T_g$ ) at use temperature (the soft segment), and the other is below its  $T_g$  (the hard segment). Through changes in the individual block characteristics such as the molecular weight and chemical identity, polyurethanes can be made to be hard or soft. The purpose of this article is to measure the changes in the various mechanical, electrical, thermal, and morphological parameters with the addition



of single-walled carbon nanotubes to a particular polyurethane, and the complexity of polyurethane morphology and chemistry makes this a very difficult task. Single-walled carbon nanotubes, besides their superb mechanical properties, also have excellent electrical properties: the conductivity is 5 times that of copper. The thermal conductivity of SWNTs is also extremely high, higher than that of diamond or copper. Such properties suggest that nanotubes should be excellent materials for incorporation with polymers. The dispersion of the nanotubes in the polymer is a key issue. With polyurethanes, there are essentially three ways to disperse nanotubes in a polymer: (1) melt



Ultimate mechanical properties of polyurethane-nanotube composites made from functionalized (black) and unfunctionalized (white) nanotubes



Conductivity of composites from functionalized (black) and unfunctionalized (white) nanotubes

mixing; (2) the dispersion of the tubes in a solvent and dissolution of the polymer in the same solvent, followed by solvent evaporation; and (3) the reaction of the monomers or prepolymer (most thermoplastic polyurethanes are made by a two-step process) in the presence of dispersed nanotubes.

The purpose of this article is to investigate the effect of nanotubes on a particular polyurethane. This study differs substantially from previous studies, in that this polyurethane consists of a nonaromatic hard segment, and the hard-segment level is much higher than that explored previously. Nanotubes were also functionalized to contain hydroxy groups to presumably enhance the interaction with the urethane groups via hydrogen bonding and compared to the nonfunctionalized tubes.

The introduction of carbon nanotubes into a polyurethane with a high hard-segment content results in increases in the modulus, tensile strength, and strain at break.

The increases are proportionally the highest seen in any polyurethane to date.

Functionalization of the tubes leads to slightly better dispersion at high nanotube contents, although the manifestations of this improved dispersion are small. Functionalization also destroys the inherent electrical conductivity of the tubes as well. The glass transition of the hard segment increases slightly with nanotube addition, and the hard-segment crystallization rate decreases with unfunctionalized nanotube addition.

***Angle-resolved x-ray absorption near edge structure study of vertically aligned single-walled carbon nanotubes***

Published in: *Applied Physics letters* **2007**, 90, 103115 (Zhongrui Li, Liang Zhang, and Daniel E. Resasco)

Vertically aligned single-walled carbon nanotube (SWNT) forest was studied by using angular-dependent C K-edge x-ray absorption near edge structure (XANES) with linearly polarized x-ray beam. The XANES analysis found a crust of entangled nanotubes on top of the forest formed at the first stage of the forest growth, which shapes the morphology of the entire forest and constricts the nanotubes to grow to the same length. It indicates that this type of SWNT forest has a different growth mechanism from the multiwalled carbon nanotube forest.

Aligned carbon nanotubes have potential applications in field emission as well as in high-strength materials. Probing orientation of single-walled carbon nanotube (SWNT) systems is of paramount importance in these fields. By using linearly polarized x-ray beam, angular-dependent x-ray absorption near edge structure (XANES) spectroscopy provides such a capability to investigate the order of SWNTs. Since XANES detects transitions in carbon from the highly isotropic 1s core level, any polarization dependence will reflect the anisotropy of the final states. The dipole transition matrix elements thus have an angular dependence on the angle made by, for instance, the  $\pi^*$  orbital with respect to the electric field vector of the incident polarized x rays. Thus, changes in the intensity of the resonances upon rotating the sample in the plane of incidence of the beam provide evidence for bond orientation.

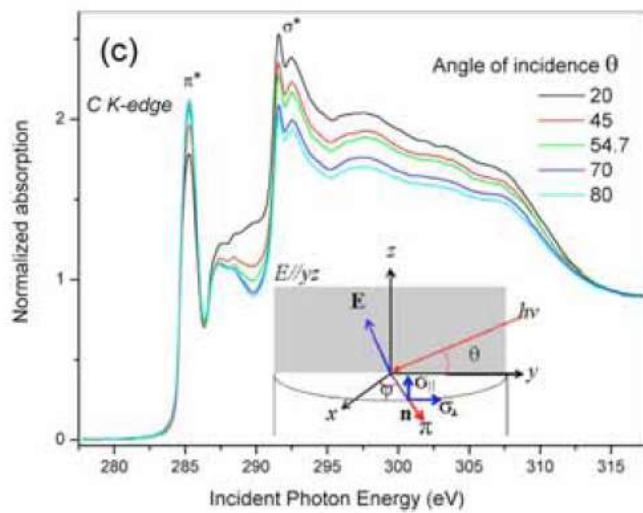
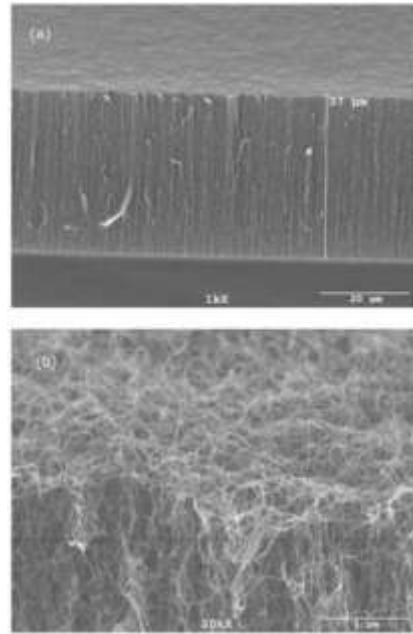
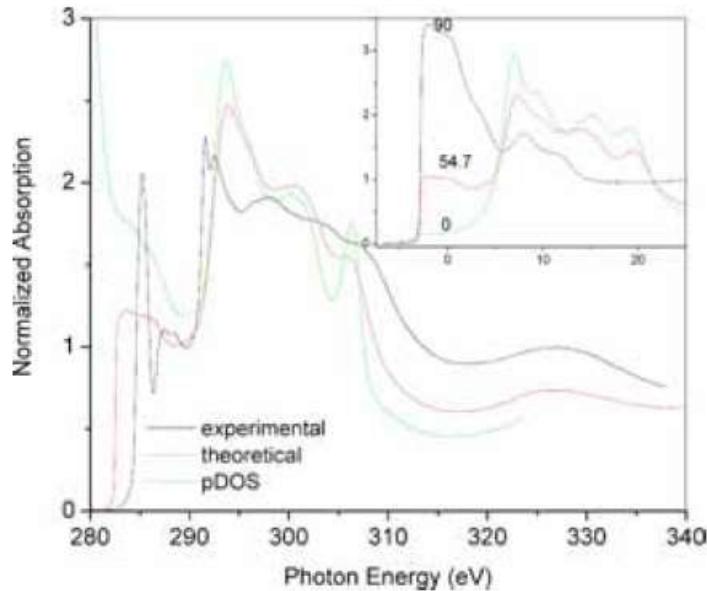
Angle-resolved XANES demonstrated very useful for the order measurement and the aligned growth mechanism study of carbon nanotubes. The angle-resolved C K-edge XANES spectra were taken in total electron yield (TEY) mode under UHV (low  $10^{-10}$  torr) at beamline 9.3.2 of Advanced Light Source in Lawrence Berkeley National Laboratory. The XANES data were collected at various angles ranging from  $\theta=10^\circ$  ("glancing") to  $\theta=80^\circ$  ("normal"), where  $\theta$  denotes the angle between the sample normal and the direction of the electric vector of the x-ray beam.

Using scanning electron microscope (SEM) and transmission electron microscope, the well vertically aligned SWNTs were observed to be about 37  $\mu\text{m}$  long and approximately 2 nm in diameter

Our observation for the vertically aligned SWNT forest is different from that of MWNT forest. For the case of the MWNT array, an increase of the x-ray absorption intensity with the increase of incidence angle was observed not only for the unoccupied  $\pi^*$

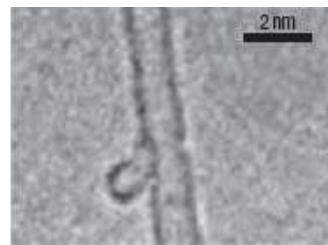
states but also for the  $\sigma^*$  state because of the enhanced DOSs of both unoccupied  $\sigma^*$  and  $\pi^*$  bands at the tip. However, our vertically aligned SWNT forest does not show enhanced density of states at tips by reason of the crust on the top of the SWNT forest. It also suggests that this type of SWNT structure has a different growth mechanism as compared with the MWNT array, which has no crust structure in its growth.

In summary, the angle-resolved XANES of a SWNT forest in TEY shows that the C–C  $\pi^*$  resonance intensity decreases from normal to glancing incidence, while the C–C  $\sigma^*$  exhibits an opposite trend, which can be used to evaluate the order of SWNTs. A crust of entangled SWNT on top of the forest was found parallel to the surface as a result of different growth rates of individual tubes in the first step of the forest growth, which is responsible for the unique forestlike morphology exhibited by this type of SWNT structures. It is different from the growth of MWNT forest.



### ***Nano-buds, A novel hybrid carbon material***

Published in: *Nature Nanotechnology* 2007, 2, 156-161 (A. Nasibulin, P. Pikhitsa, H. Jiang, D. Brown, A. Krasheninnikov, P. Queipo, A. Moisala, D. Gonzalez, G. Lientschnig, A. Hassanien, S. Shandakov, G. Lolli, D. Resasco, M. Choi, D. Tománek, and E. Kauppinen)



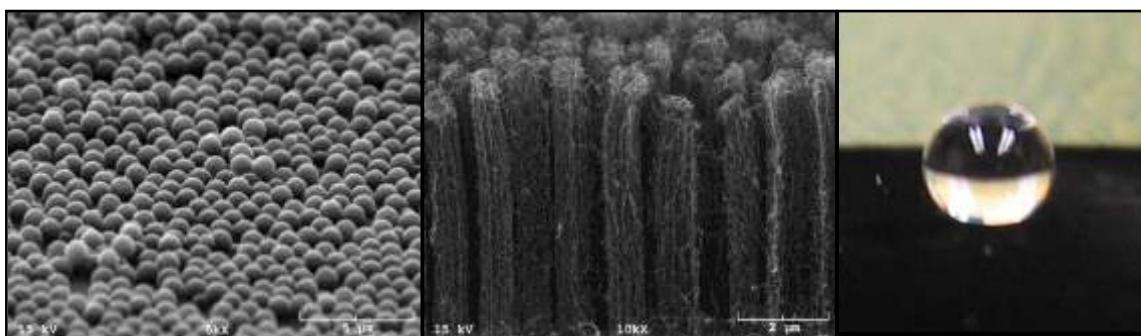
Both fullerenes and single-walled carbon nanotubes (SWNTs) exhibit many advantageous properties<sup>1</sup>. Despite the similarities between these two forms of carbon, there have been very few attempts to physically merge them. We have discovered a novel hybrid material that combines fullerenes and SWNTs into a single structure in which the fullerenes are covalently bonded to the outer surface of the SWNTs. These fullerene functionalized SWNTs, which we have termed NanoBuds, were selectively synthesized in two different one-step continuous methods, during which fullerenes were formed on iron-catalyst particles together with SWNTs during CO disproportionation. The field-emission characteristics of NanoBuds suggest that they may possess advantageous properties compared with single walled nanotubes or fullerenes alone, or in their nonbonded configurations.



The images show the TEM of the hybrid material and a possible bonding configuration.

### ***Nanostructured SWNT towers that exhibit superhydrophobic behavior.***

We have discovered that while the contact angle for water-graphite is about 86°, that for SWNT-water greatly depend on the mesostructure of the nanotube system. That is, the same type of SWNT have very different wetting behavior depending on the nanotube arrangement. For example, the contact angle for a 2D mat of SWNT is close to that of graphite (86°); it goes up drastically to 135° for the nanotube forest, and become superhydrophobic (~180°) for a new type of SWNT arrangement that we call SWNT “towers.”



To achieve this SWNT array we have prepared the Co-Mo catalyst on silicon wafer employing the *nanosphere lithography method* that results in tailored distribution of catalysts and produces the distribution of SWNT shown in the image. These micro-

towers of SWNT exhibit the “Lotus effect” that impart super-hydrophobicity to the surface.

## Kinetic modeling of the SWNT growth

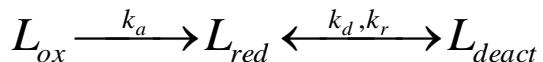
### Steps considered in the model:

Specifically, the different stages considered in this model are the following:

#### a) *Catalyst Activation:*

This step takes into consideration the in-situ creation of the active sites that take place in the CoMoCAT process by the transformation of the CoMoOx precursor into the active species (i.e. reduced Co clusters) and will be modelled in terms of the conversion of oxidized sites ( $L_{ox}$ ) into active (reduced) sites ( $L_{red}$ ). We define the new gas/solid interface as interface 1 (see schematic).

The balance of surface sites can be summarized as follows:



where  $L_{ox}$  is the molar concentration of surface sites (mol ox. sites/g. cat) present on the catalyst before the introduction of CO,  $L_{red}$  is the concentration of reduced active sites, and  $L_{deact}$  is the concentration of reduced but deactivated sites. It is assumed that the reduction step is irreversible, but the deactivation is reversible by the  $\text{CO}_2$  - C reaction. As mentioned above, only the reduced sites are active for the CO decomposition.

#### b) *Decomposition of CO over the surface of the reduced Co cluster (interface 1) generating surface carbon species:*

The surface fugacity of these carbon species is not simply in equilibrium with the gas phase CO, but rather is the result of the several phenomena that occur on the surface; they are i) the CO decomposition that generates surface C, ii) the C diffusion (both across the surface and into the metal particle), and iii) the reverse Boudouard reaction of C with gas phase  $\text{CO}_2$ . The first one causes an increase in the carbon surface fugacity, the last two act as releasing paths for carbon and help keeping a fraction of the the surface clean.

#### c) *Carbon diffusion, nucleation and growth of SWNT:*

After the surface fugacity has reached a certain threshold, nucleation of ordered forms of carbon occur (e.g. hexagons. The formation of these nuclei generates a new interface between the catalyst surface and the nanotube ( $L_{red}$ /SWNT, interface 2 in the schematic). The carbon flux is maintained because the nanotube structure provides a thermodynamic sink for the carbon and as a result the carbon fugacity at the interface is kept low

#### d) *Growth Termination:*

Based on the concept of two interfaces one can envision two forms of nanotube growth termination. The first type of termination would occur at interface 1 by deactivation of the catalyst active sites,  $L_{red}$ . The second type would occur at interface 2 when the carbon concentration,  $CF$ , raises and approaches  $CS$ , thus eliminating the driving force for diffusion. As discussed below, the raising in  $CF$  may be due to a mechanical interference of the nanotube growth with its environment, which would hinder the free path of C through the catalyst-nanotube interface 2.

The kinetic equation that describes the activation step can be expressed as:

$$-\frac{dL_{ox}}{dt} = \psi_a \cdot L_{ox}$$

with

$$\psi_a = \frac{k_a p_{CO}^{m_a}}{1 + K_a \cdot p_{CO_2}} \quad ; \quad k_a = k_{a_0} \exp(-E_a/RT)$$

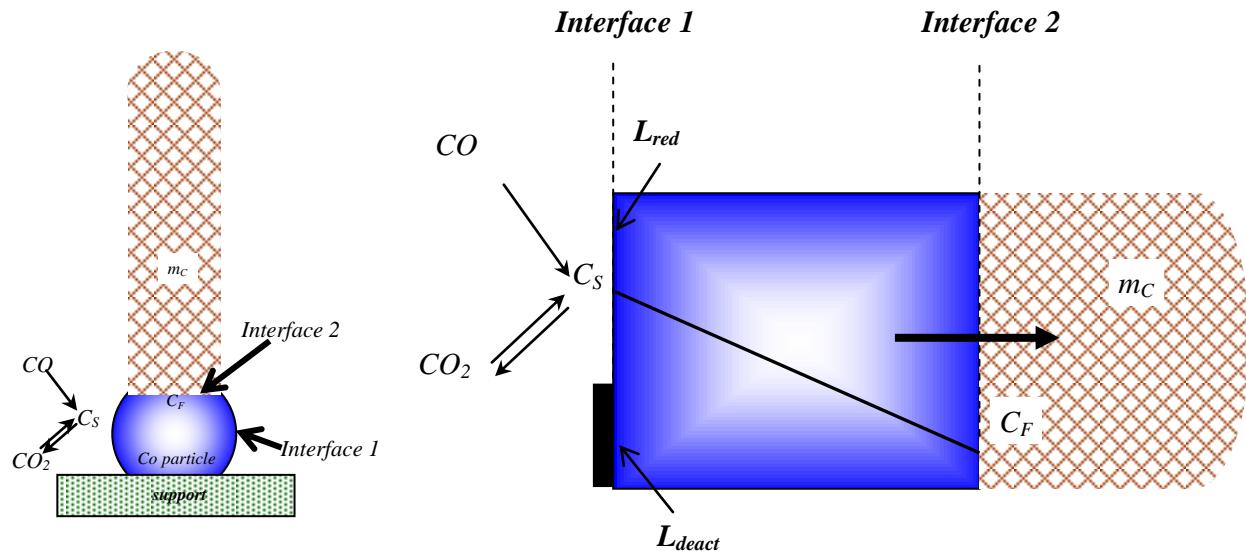
And the variation of active sites

$$\frac{dL_{red}}{dt} = \psi_a \cdot L_{ox} - \psi_d \cdot L_{red} + \psi_r \cdot L_{deact}$$

with

$$\psi_d = k_d p_{CO}^{m_d} \quad ; \quad k_d = k_{d_0} \exp(-E_d/RT)$$

$$\psi_r = k_r p_{CO_2}^{m_r} \quad ; \quad k_r = k_{r_0} \exp(-E_r/RT)$$



After having developed an expression for the catalyst activity for the specific case, we can calculate the net rate of CO disproportionation on the surface using a typical rate expression for the Boudouard reaction:

$$(-r_{CO})_t = (-r_{CO})^0 \cdot a = k_1 \cdot \left( p_{CO} - \frac{p_{CO_2}}{K_{eq} p_{CO}} \right) \cdot a$$

$$k_1 = k_{1_0} \cdot \exp(-E_1/RT) \quad ; \quad K_{eq} = \frac{k_1}{k_2} = \exp(-\Delta G/R)$$

The term  $(-r_{CO})^0$  represents the reaction rate of CO decomposition when the catalyst activity is 1, i.e. when is totally activated and before any deactivation process. Therefore,  $(-r_{CO})^0$  is a constant value for a given operating conditions. In the case that the catalyst initially will be totally activated ( $a_0=1$ ), this value is the initial reaction rate.

## Carbon diffusion and formation of SWNT at interface 2

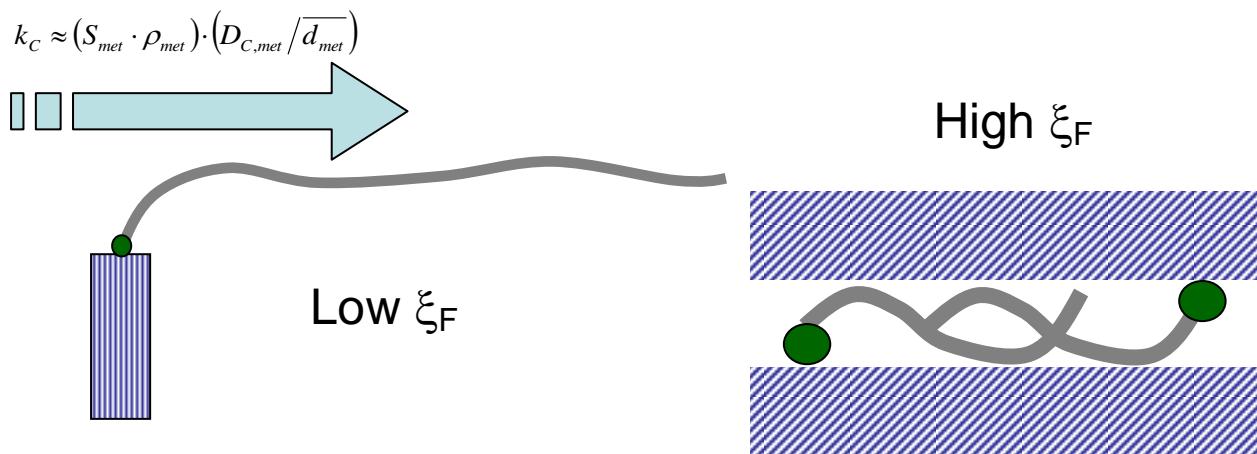
This stage represents the diffusion of carbon atoms through the metallic crystallites and in turn determines the rate of formation of SWNT. The rate for this step can be expressed as:

$$r_C = \frac{dm_C}{dt} = k_C (C_S - C_F)$$

where  $k_C$  is the effective transport coefficient of carbon on the Co particles and depends on the average size of the Co crystallites,  $d_{met}$ , the metallic exposed area,  $S_{met}$ , and of the carbon diffusivity of carbon on the metallic particle.  $D_{C,met}$ . In general,

When the SWNT growth is conducted on a high-surface-area porous catalyst, the growth process is eventually impeded by the lack of space for displacement inside the pores and tube-tube interactions. To take into account these effects, we assume that the value of  $C_F$  is proportional to the amount of carbon accumulated with a proportionality constant  $\xi_F$  that depends on the structure of the catalyst substrate and how the growing SWNT accommodate in such structure. Therefore,

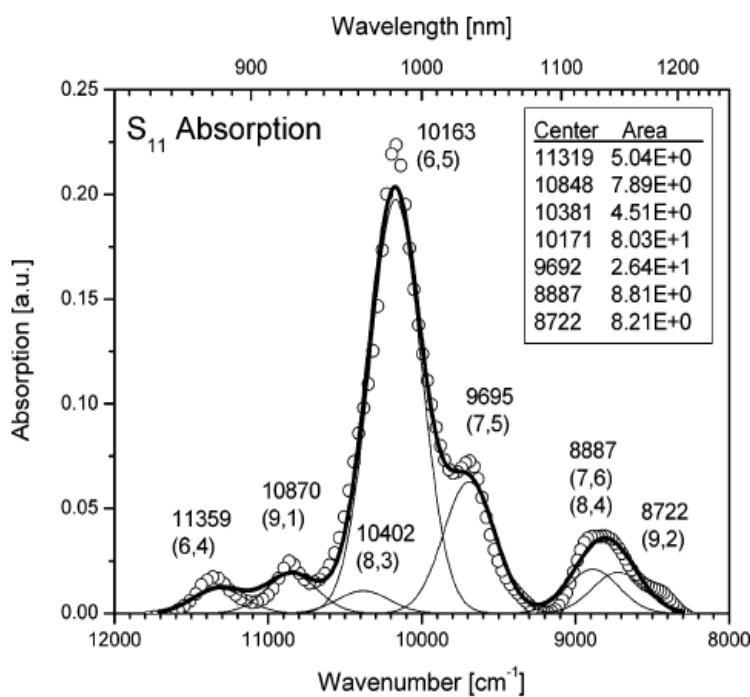
$$C_F = \xi_F \cdot m_C$$



## **Tailoring $(n,m)$ Structure of Single-Walled Carbon Nanotubes by Modifying Reaction Conditions and the Nature of the Support of CoMo Catalysts**

Published in: *Journal of Physical Chemistry B* **2006**, 110, 2108-2115 (Giulio Lolli, Liang Zhang, Leandro Balzano, Nataphan Sakulchaicharoen, Yongqiang Tan, and Daniel E. Resasco)

One of the most attractive features of single-walled carbon nanotubes (SWNT) is that their electronic properties strongly depend on their diameter and orientation of the carbon hexagons that form their walls. These characteristics are uniquely specified by the chiral vector identified with the integers  $(n,m)$ , but most synthesis methods result in a wide distribution of  $(n,m)$  species. In this project, the  $(n,m)$  population distribution of single-walled carbon nanotubes obtained on supported CoMo catalysts has been determined by photoluminescence and optical absorption.

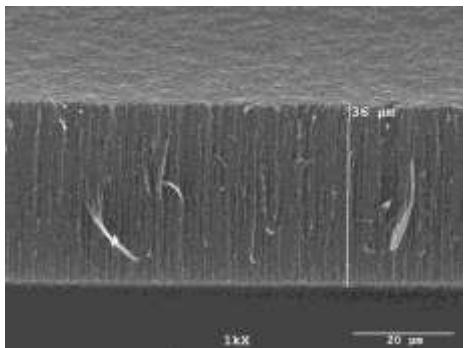


It has been found that the  $(n,m)$  distribution can be controlled by varying the gaseous feed composition, the reaction temperature, and the type of catalyst support used. When using CO as a feed over CoMo/SiO<sub>2</sub> catalysts, increasing the synthesis temperature results in an increase in nanotube diameter, without a change in the chiral angle. The nanotube distribution shifts from a dominant (6,5) at the low-temperature end (700-750 °C, see spectrum above) to (7,6) and to (8,7) at 850°C. Interestingly, the nanotube diameter increases with temperature, but the chiral angle stays close to the armchair line. We have previously explained the increase in diameter with temperature in terms of a faster rate of metal agglomeration at higher temperatures that cause a shift to larger diameter caps during the nucleation that precedes the nanotube growth. By contrast, by changing the support from SiO<sub>2</sub> to MgO, nanotubes with similar diameter but different chiral angles are obtained. Finally, keeping the same reaction conditions but varying the composition of the gaseous feed results in different  $(n,m)$  distribution. The clearly different distributions obtained when varying catalysts support and/or reaction conditions demonstrate that the  $(n,m)$  distribution is a result of differences in the growth kinetics, which in turn depends on the nanotube cap-metal cluster interaction.

## Vertically oriented forests of SWNT.

Published in *Chemistry of Materials* **2006**, 18, 5624-5629 (Influence of a Top Crust of Entangled Nanotubes on the Structure of Vertically Aligned Forests of Single-Walled Carbon Nanotubes

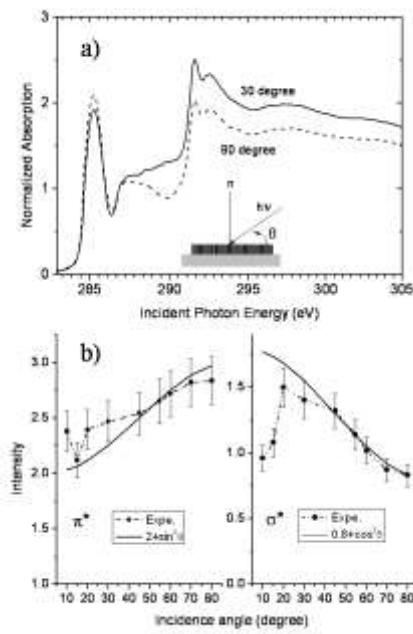
Liang Zhang, Zhongrui Li, Yongqiang Tan, Giulio Lolli, Nataphan Sakulchaicharoen, Felix G. Requejo, B. Simon Mun, and Daniel E. Resasco



CO disproportionation on Co-Mo bimetallic catalysts has been used in the synthesis of vertically oriented forests of SWNT (see SEM image of forest). This is the first time that these forests are obtained by a CVD method at atmospheric pressure. Resonant Raman and transmission electron microscope (TEM) were employed to characterize the as-produced SWNT, which display a high purity and very low concentration of other carbon forms. Combination of AFM and SEM gives evidence for the crucial role of the surface distribution of the bimetallic (Co/Mo)

catalyst particles on the substrate during the growth of SWNT.

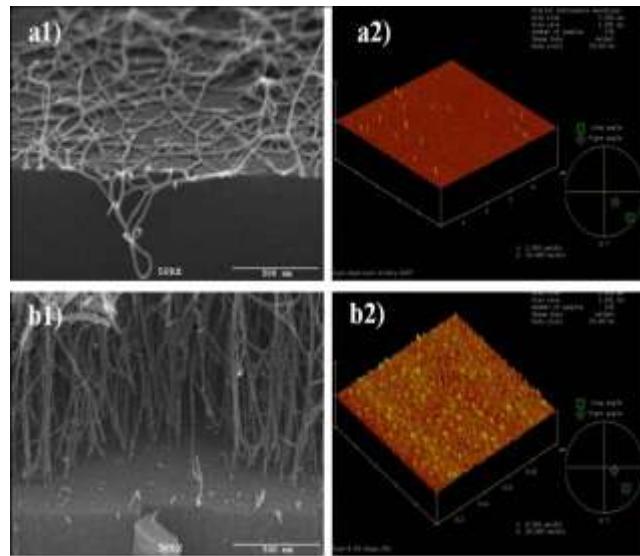
A detailed analysis of the structure of SWNT forests as a function of growth time reveals that a two-step process is responsible for the formation of a SWNT forest. The first step is the weaving of a crust of entangled SWNT which grow with different rates and with random orientation over the surface. The second step is a concerted growth of vertically aligned SWNT constrained by the uniform top crust. Several techniques were employed to examine the growth process and the results are all consistent with this mechanism. The angle-resolved x-ray absorption near edge structure results (see Figure below) show that a fraction of the tubes on top of the forest are parallel to the surface, rather than perpendicular as the majority of the tubes in the forest. Direct SEM observations agree with this morphology. Several examples are presented to demonstrate that the crust influences the morphology of the resulting forest. Catalysts which are non-uniformly distributed on the substrate produce curved crusts instead of the consistent forest with a flat top obtained when the catalyst layer is uniform.



**Controlling the growth of vertically oriented single-walled carbon nanotubes by varying the density of CoMo catalyst particles**

Published in *Chemical Physics Letters* **2006**, 422, 198–203 (Liang Zhang, Yongqiang Tan, Daniel E. Resasco)

A simple method to grow vertically aligned arrays of various forms of single-walled carbon nanotubes (V-SWNT) is reported. CO disproportionation on Co-Mo bimetallic catalysts has been used in the synthesis. Resonant Raman and transmission electron microscope (TEM) were employed to characterize the as-produced SWNTs, which display a high purity and very low concentration of other carbon forms. Combination of AFM and SEM gives evidence for the crucial role of the surface distribution of the bimetallic (Co/Mo) catalyst particles on the substrate during the growth of SWNT (see AFM and SEM images).



**D) Combining experimental and theoretical simulations to understand the Growth of Single-Wall Carbon Nanotubes**

Published in *Journal of Nanoscience and Nanotechnology*, **2006** 6, pp. 1247-1258(12); Authors: Balbuena, Perla B.; Zhao, Jin; Huang, Shiping; Wang, Yixuan; Sakulchaicharoen, Nataphan; Resasco, Daniel E.

Classical molecular dynamics simulations were carried out to analyze the physical state of the catalyst, and the growth of single-wall carbon nanotubes under typical temperature and pressure conditions of their experimental synthesis, emphasizing the role of the catalyst/substrate interactions. It was found that a strong cluster/substrate interaction increases the cluster melting point, modifying the initial stages of carbon dissolution and precipitation on the cluster surface. Experiments performed on model Co–Mo catalysts clearly illustrated the existence of an initial period where the catalyst is formed and no nanotube growth is observed. To quantify the nature of the Co–Mo<sub>2</sub>C interaction, quantum density functional theory was applied to characterize structural and energetic features of small Co clusters deposited on a (001) Mo<sub>2</sub>C surface, revealing a strong attachment of Co-clusters to the Mo<sub>2</sub>C surface, which may increase the melting point of the cluster and prevent cluster sintering.

**DOE Interest.** SWNT exhibit exceptional chemical and physical properties. Tight control of their structural properties by tailored catalytic surfaces is opening a vast number of opportunities for research and it is also generating technological applications in diverse fields such as nanoelectronics, nanosensors, field emission, fuel cell electrodes, tailored catalyst supports, smart surfaces, etc.

**Future Plans** We plan to continue improving our ability to control of producing nanotubes with specific structure by manipulating catalyst composition and structure. Our next focus will be on utilizing nanoparticles catalysts of controlled size and composition.

### Publications:

- “Solid Nanoparticles that Catalyze Biofuel Upgrade Reactions at the Water/Oil Interface,” Steven Crossley, Jimmy Faria, Min Shen, Daniel E. Resasco, *Science*, 327, 68, **2010**.
- “Quantifying the Semiconducting Fraction in Single-Walled Carbon Nanotube Samples through Comparative Atomic Force and Photoluminescence Microscopies,” Naumov, Anton V., Kuznetsov, Oleg A., Harutyunyan, Avetik R., Green, Alexander A., Hersam, Mark C., Resasco, Daniel E., Nikolaev, Pavel N., Weisman, R. Bruce, *Nano Letters*, 9, 3203-3208, **2009**
- “Adsorption of Glucose Oxidase onto Single-Walled Carbon Nanotubes and Its Application in Layer-By-Layer Biosensors” Tsai, Ta-Wei, Heckert, Gustavo, Neves, Luis F., Tan, Yongqiang, Kao, Der-You, Harrison, Roger, Resasco, Daniel E., Schmidtke, David W., *Analytical Chemistry*, 81, 7917-7925, **2009**
- “Cancer photothermal therapy in the near-infrared region by using single-walled carbon nanotubes.” Zhou, Feifan ; Xing, Da ; Ou, Zhongmin ; Wu, Baoyan ; Resasco, Daniel E ; Chen, Wei R; *Journal of Biomedical Optics* **2009**, 14, 021009/1-021009/7. ISSN:1083-3668.154.
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- “Single-Walled Carbon Nanotube Pillars: A Superhydrophobic Surface” Liang Zhang and Daniel E. Resasco, *Langmuir* **2009**, 25 (8), pp 4792–4798
- “Sol–gel synthesis and characterization of Co-Mo/silica catalysts for single-walled carbon nanotube production” V. M. Irurzun, Y. Tan, and D. E. Resasco, *Chem. Mater.* **2009**, 21 (11), pp 2238–2246
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B.; Itkis, M. E.; Haddon, R. C.; Tan, Y.; Resasco, D. E.. *Physica Status Solidi B: Basic Solid State Physics* **2008**, 245, 2229-2232

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- “Composites of single-walled carbon nanotubes and styrene-isoprene copolymer lattices” Ha MLP, Grady BP, Lolli G, Resasco DE, Ford WT , Macromolecular Chemistry And Physics 208, 446-456 **2007**
- “Effect of Nanotube Functionalization on the Properties of Single-Walled Nanotube/Polyurethane Composites Fabian Buffa, Gustavo A. Abraham, Brian P. Grady, Daniel Resasco, *J. Polymer Sci., B* 45 (4): 490-501 FEB 15 **2007**
- “Angle-resolved X-ray absorption near edge structure study of vertically aligned single-walled carbon nanotubes” Li ZR, Zhang L, Resasco DE , Mun BS , Requejo FG *Applied Physics Letters* 90 (10): Art. No. 103115 MAR 5 **2007**
- “A Novel Hybrid Carbon Material” Albert G. Nasibulin, Peter V. Pikhitsa, Hua Jiang, David P. Brown, Arkady V. Krasheninnikov, Anton S. Anisimov, Paula Queipo, Anna Moisala, David Gonzalez, Gunther Lientschnig, Abdou Hassanien, Sergey D. Shandakov, Giulio Lolli, Daniel E. Resasco, Mansoo Choi, David Tománek, and Esko I. Kauppinen, *Nature Nanotechnology* 2(3), 156-161 **2007**
- “Influence of a Top Crust of Entangled Nanotubes on the Structure of Vertically Aligned Forests of Single-Walled Carbon Nanotubes” L. Zhang, Z. Li, Y. Tan, G. Lolli, N. Sakulchaicharoen, F. G. Requejo, B. Simon Mun, and Daniel E. Resasco, *Chemistry of Materials* 18 (23): 5624-5629, **2006**
- “Exciton dynamics probed in carbon nanotube suspensions with narrow diameter distribution” Hertel, T., Zhu, Z., Crochet, J., McPheeters, C., Ulbricht, H., Resasco, D. *Physica Status Solidi (B) Basic Research* 243 (13), pp. 3186-3191, **2006**
- “Role of the catalyst in the growth of single single-wall carbon nanotubes,” Perla B. Balbuena, Jin Zhao, Shiping Huang, Yixuan Wang, Nataphan Sakulchaicharoen, and Daniel E. Resasco, *J. of Nanoscience and Nanotechnology*, 6, 1247-1258, **2006**.
- “Controlling the growth of vertically-oriented single-walled carbon nanotubes by varying the density of Co-Mo catalyst particles” Liang Zhang; Yongqiang Tan, Daniel E. Resasco, *Chemical Physics Letters* 422, 198-203, **2006**.
- “Tailoring (n,m) structure of single-walled carbon nanotubes by modifying reaction conditions and the nature of the support of CoMo catalysts.” Giulio Lolli, Liang Zhang, Leandro Balzano, Nataphan Sakulchaicharoen, Yongqiang Tan, and Daniel E. Resasco, *Journal of Physical Chemistry B*, **2006**; 110(5); 2108-2115.

**PERIOD 2002 - 2005**

**Controlling Structural Characteristics of Single-Walled Carbon Nanotubes  
(SWNT)  
by Tailoring Catalyst Composition and Synthesis Conditions**

(GRANT NUMBER DE-FG02-02ER15345)

PI: Daniel E. Resasco  
School of Chemical Engineering and Materials Science  
University of Oklahoma

**1. OVERALL RESEARCH GOAL:**

The main goal of this proposal is to advance the knowledge of the mechanism responsible for the formation of single-walled carbon nanotubes (SWNT) in order to get control over their structural parameters (diameter and chirality). Only through a detailed knowledge of the growth mechanism it will be possible to produce SWNT with tailored properties since they are directly related to the structural parameters.

**2. SPECIFIC OBJECTIVES FOR THE CURRENT FUNDING PERIOD**

- Investigate catalyst formulations, pre-treatment conditions, and reaction conditions conducive to produce single-walled nanotubes of specified diameter and chirality
- Determine the direct relationship between the Co-Mo interaction and the selectivity for nanotube production
- Evaluate the reproducibility of the nanotube structure that is obtained from batch to batch under the same synthesis conditions.
- Initiate an interaction with a theorist to simulate the controlled nanotube growth
- Develop novel methods for purifying and functionalizing nanotubes that may allow for a better characterization and application as catalyst supports.
- Test the nanotubes that we produce as catalyst supports for fuel cell applications
- Test their field emission properties (I-V curves)
- Extrapolation of the concepts learnt with SWNT to the production of other nanostructured materials, Si nanowires.

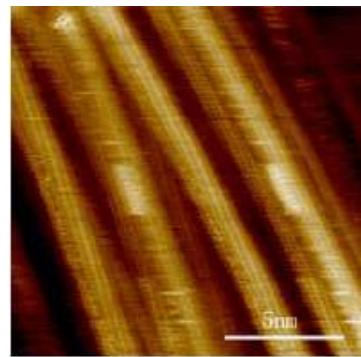
**3. SIGNIFICANT ACHIEVEMENTS AND RESULTS DURING THE CURRENT FUNDING PERIOD**

The production of single-walled carbon nanotubes (SWNT) with controlled diameter and chirality is a highly attractive target for scientists because the electronic properties of these unique materials are strongly related to their structure, which is typically described in terms of the chiral vector (n,m). In the last few years, we have

concentrated on the tailoring of specific catalysts and operating conditions to grow SWNT by the Boudouart disproportionation of CO (decomposition into C and CO<sub>2</sub>). Since the CO disproportionation is an exothermic reaction, at the high temperatures needed for the nanotube growth, the CO conversion can be limited by equilibrium. Therefore, since the reaction proceeds with a decrease in the number of moles, high CO pressures are required in order to counteract the effect of the temperature and drive the reaction in the forward direction. For example, at atmospheric pressure, the equilibrium conversion of a stream of pure CO is 83 % at 600°C, but only 15 % at 800°C and barely 1 % at 1000°C. For example, if the reaction is carried out isothermically starting with pure CO 700°C, the conversion of the CO at the equilibrium shifts from 48% to 75 % when the pressure is increased from 1 atm to 10 atm. However, at higher temperatures, the conversions are very low and the effect of pressure is less pronounced. Therefore, the pressure needed to keep a moderate equilibrium conversion at temperatures above 800°C is indeed high. For example, to reach 30 % CO conversion at 900°C, 20 atm are needed. Therefore, from a thermodynamic point of view, one would prefer to operate at low temperatures. However, it has been demonstrated that if the temperature is too low the selectivity towards SWNT drastically drops. Since the reaction is reversible, the buildup of CO<sub>2</sub> may adversely affect the SWNT production in a fixed bed reactor. We may expect a decrease in carbon deposition along the catalyst bed as the equilibrium condition is approached. Therefore, we have chosen to operate at low CO conversions, moderate pressures (1- 5 atm) and moderate temperatures (700-950°C).

Among a large number of catalysts investigated, we have found that bimetallic Co-Mo catalysts supported on silica exhibit the highest selectivity to SWNT. We have explained the excellent performance of the Co-Mo catalyst on the basis of the central role played by a surface cobalt molybdate. We have found that to be effective the catalyst requires both metals simultaneously present in a Co:Mo ratio significantly lower than unity to ensure that all the Co in the catalyst is forming a surface cobalt molybdate. This Co-Mo interaction inhibits the Co metal agglomeration that normally takes place at high temperatures. Cobalt agglomeration needs to be avoided to prevent the formation of less desirable carbon species such as graphitic nanofibers. The surface cobalt molybdate structure exhibits the right reducibility to resist decomposition unless it is in the presence of CO at high temperatures. These studies have been the basis for the development of a commercial process called CoMoCAT™ that can produce single-walled carbon nanotubes in large scale.

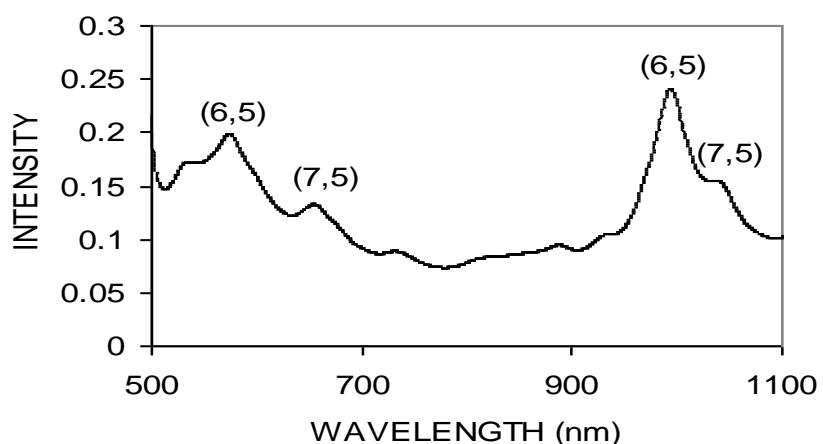
For many applications in nanoelectronics and nanosensors it is essential to have a nanotube material with specific electronic properties. The I-V characteristics of nanotubes are directly related to their diameter and chirality. Therefore, a process that allows controlling in a reproducible way the structure of nanotubes has a remarkable edge over non-selective processes. The nanotubes produced by the CoMoCAT™ process exhibit a uniquely narrow distribution of diameters, which can be controlled by adjusting the



STM Image of SWNT produced by SWeNT™'s low temperature method. Courtesy of Dr. Charles Lieber at Harvard University

process parameters. The narrowest distribution is obtained at the lowest synthesis temperature. This characteristic of the CoMoCAT™ product has been confirmed by photoluminescence analysis performed in collaboration with the group of Prof. Weisman at Rice University. Much effort was directed to improve the suspendability of these nanotubes, which due to their much thinner diameter and bundle size are very different from those prepared by other methods. We found that when dispersed in an appropriate solvent (i.e. Na-DDBS) only two types of nanotubes represent the majority of the semiconducting nanotubes present in the sample synthesized at 750°C. By contrast, a similar analysis of the competing HIPCO material displays a much broader distribution of both, diameter and chirality. The two types of nanotubes observed in CoMoCAT sample are the (6,5) and (7,5), whose diameters are 0.75 nm and 0.82 nm, respectively. This result is in perfect agreement with the 0.8 nm average diameter measured by Raman spectroscopy, TEM, and STM (see Figure of STM obtained at Harvard on our sample). Interestingly, the distribution of chiralities is also very narrow. Both, the (6,5) and (7,5) nanotubes have a chiral angle near 27 degrees. By contrast, the HIPCO material exhibits a much broader distribution of chiralities.

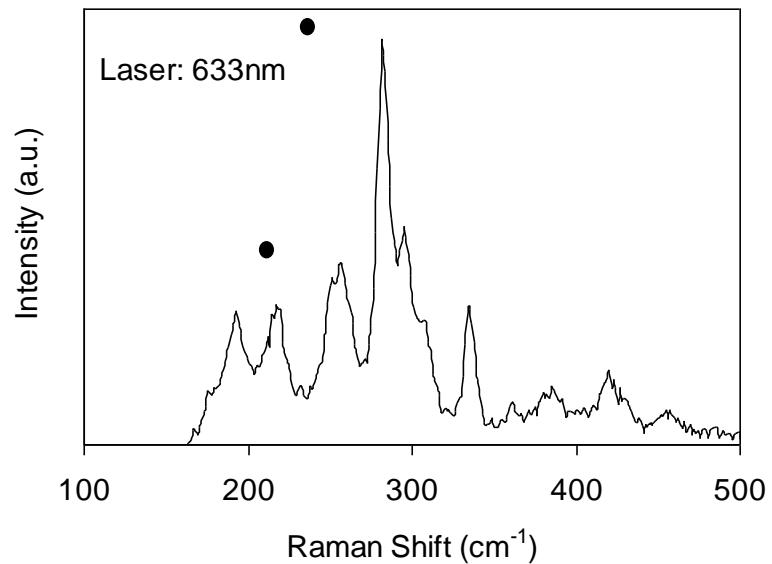
We have further characterized this material by optical absorption in aqueous suspension using a novel DNA-stabilization method. The single-stranded DNA-assisted dispersion results in isolated nanotubes in aqueous suspension, which allows for a good resolution in the optical absorption spectrum. As shown in Fig. 1, the spectrum in the 500-1100 nm range clearly exhibits the first and second van Hove optical transitions ( $S_{11}$  and  $S_{22}$ ) for the (6,5) and (7,5) nanotubes, the most abundant (n,m) semiconducting structures previously observed by us on this material by spectrofluorimetry and reported last year to DoE. It appears that in this particular sample the (6,5) is more abundant than the (7,5). Although the band at around 650 nm can contain contributions of both (7,6) and (7,5) nanotubes, which have  $S_{22}$  transitions at 647 and 644 nm, respectively, the band at 1025 nm is most certainly due to (7,5).



**FIGURE 1.** Absorption spectrum of the SWNT sample produced at 750°C suspended by sonicating in ssDNA aqueous solution obtained on the Bruker spectrophotometer purchased with DoE funds.

This in-house characterization has provided us with an excellent tool to quickly characterize the structure of the material that we produce. The IR-NIR-VIS spectrophotometer that we employ for this analysis was purchased with DoE funds directly related to this grant.

The Raman spectra of all the samples synthesized in the temperature range 700-900°C exhibit a low D band, indicative of good quality nanotubes, with strong bands in the breathing mode region. Figure 2 shows the portion of the spectrum below 500 nm, corresponding to the breathing mode region using a 633 nm excitation laser. The main band at 282 nm is consistent with the frequency expected for the (7,5) nanotube. We expect to be able to see a strong BM signal for this nanotube since the excitation wavelength (633 nm) is close to the resonance of the  $S_{11}$  band gap (644 nm). On the other hand, that for the other abundant nanotube in this sample (6,5) would be in resonance with a wavelength of 567 nm. The second intense band at 260 nm is most probably due to the (7,6) nanotube, for which the resonance occurs at a wavelength of 647 nm, very close to that of the excitation laser.



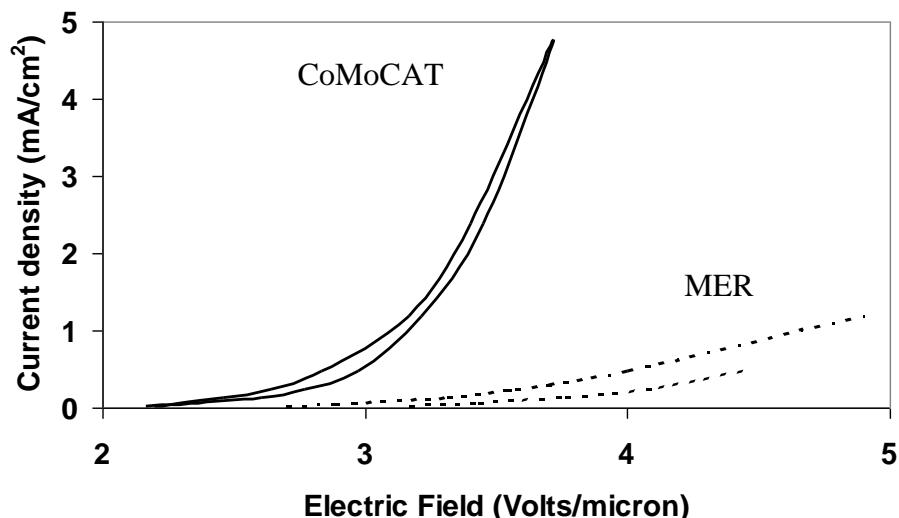
**FIGURE 2.** Raman spectrum of the SWNT sample produced at 750°C, purified in HF to remove the silica support. The two dots indicate the bands assigned to (7,5) and (7,6) nanotubes.

Due to the presence of the solid silica substrate that separates the growing nanotubes during the synthesis, the resulting bundles of SWNT are significantly thinner than what are typically obtained with methods in which the catalyst is in the vapor phase (i.e., arc discharge, laser ablation, HiPCO). While each of the bundles produced by any of the vapor phase methods contain 50 to 100 nanotubes, those

obtained in the CoMoCAT process only contain 10-20 nanotubes. A sample with thinner bundles has several important advantages over one with thicker bundles. For example, for applications in flat panel displays (field emission) thinner bundles result in much lower voltages requirements for a given operating emission current. Lower onset voltages in field emission have a great impact on the cost and viability of flat panel displays. Similarly, in the area of polymer composites, thinner bundles can produce conducting composites with lower nanotube loadings, increasing the transparency of the material and reducing the cost.

Figure 3 illustrates the field emission characteristics of a SWNT sample produced in the CoMoCAT process at 850°C, compared to a sample produced by a different synthesis method. The I-V characteristics were obtained in a vacuum chamber at about  $10^{-7}$  Torr on a 1 cm-diameter cylindrical electrode-counterelectrode system operating at a 0.25 mm spacing. A Keithley 237 source-measure unit was used for linearly ramping the voltage up to 1100 V and measuring the current with pA sensibility. In all cases, the samples obtained in the CoMoCAT process showed good stability, meaning little deterioration in the sample after reaching a current density of almost  $5 \text{ mA/cm}^2$ , as reflected by the low hysteresis of the I vs. V curve. By contrast, a sample prepared by arc discharge (MER sample) displayed a much lower current and lower stability under the same operating conditions.

Most interestingly, it has been found that the I-V characteristics can be systematically and reproducibly varied by varying the nanotube synthesis parameters.



**FIGURE 3.** Field emission at  $10^{-7}$  Torr. I-V characteristics of a SWNT sample (prepared at 850C by CoMoCAT) compared to a sample prepared by arc discharge (MER).

In summary, the CoMoCAT process exhibits the dual benefit of scalability and excellent control of nanotube structure. A very narrow distribution of nanotubes approaching monodispersity can be obtained.

### **Incorporation of SWNT in matrices and study of their properties:**

With these high-quality, well-characterized SWNT materials we have expanded our studies to explore the interactions of nanotubes of narrow-diameter-distribution with surfactants, polymers, DNA and other organic molecules. We have investigated the electrical, mechanical, and thermal properties, as well as their field emission characteristics to determine relationships between the diameter and chirality of the nanotubes and their physical properties. In addition, we are investigating the use of these tailored SWNT as unique catalyst supports with high thermal and electrical conductivities for applications as fuel-cell electrodes.

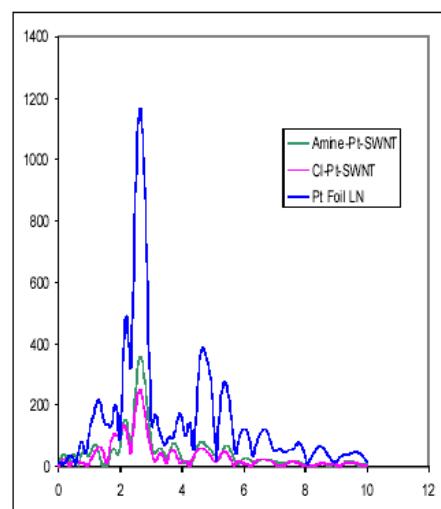
### **(n,m) speciation of SWNT:**

One of the most sought after capabilities that will open many opportunities for SWNT in nanoelectronics is to separate monodispersed samples of specific (n,m) characteristics. Only those SWNT for which n-m is a multiple of 3 are metallic and within the semiconducting, each (n,m) pair has a characteristic band gap and electronic response. To produce nanodevices it is important to be able to use specific (n,m) nanotubes. We have recently collaborated with researchers at Dupont who have been able to obtain from our SWNT monodispersed (6,5) nanotubes by selective interaction with DNA molecules of specific sequence (i.e. d(C,G)<sub>q</sub> with q=16-40).

### **Development of Fuel cell electrodes based on SWNT:**

We have shown that it is possible to obtain high platinum loadings with high dispersions supported on the single walled carbon nanotubes that we produce. To achieve these high Pt dispersions we developed a catalyst preparation method that involves the developing of electrical charge at the nanotube surface and subsequently employing the appropriate pH to effect either anion or cation adsorption of the Pt precursors.

In addition, we have built a fuel cell unit to evaluate the activity of the electrocatalysts. The adsorption method is based on the position of the point of zero charge (PZC) that can be varied depending on the purification



Comparison of the EXAFS results of Pt/SWNT (10wt.% Pt loading) and Pt foil.

method. The nanotubes are typically impregnated with a Pt precursor by ion exchange ( $H_2PtCl_6$  (chloroplatinic acid) and  $Pt(NH_3)_4(NO_3)_2$  (tetra-amonium platinic nitrate)). After the ion exchange process, the samples are typically freeze-dried first, and calcined in air. The Pt particles are finally reduced in  $H_2$  to obtain metallic Pt nanoparticles.

Depositions of as much as 30 wt.% Pt were achieved with very high dispersions. X-ray photoelectron spectroscopy analysis, which serves to quantify the surface concentration of Pt deposited on the SWNTs, indicates that the Pt content found on the SWNT surface is in good agreement with the total amount of Pt incorporated to the mixture, indicating a high metal exposure. Similarly, EXAFS data resulted in coordination numbers (N) for the Pt-Pt bond that are consistent with particles of about 1 nm in size.

By contrast, when the Pt is deposited by the conventional incipient wetness method on

Pt incorporation method / Support	Pt load (wt%)	R (Å)	$N_{Pt-Pt}$	$\sigma^2$ (Å <sup>2</sup> )
Ion exchange / SWNT-paste	10 (amine precursor)	2.77	5.85	0.0036
	30 (amine precursor)	2.79	7.78	0.0027
	10 (chloride precursor)	2.77	4.40	0.0039
Incipient wetness / Dry powder	10 (amine precursor)	2.80	8.01	0.0027

dried SWNTs, the NPt-Pt increases substantially. Thus, the impregnation of the Pt is more effective towards higher dispersions using our recently developed method. Likewise, TEM analysis of the SWNTs after the deposition of the Pt particles reveals the presence of particles as small as 1-2 nm are observed in those samples prepared by the adsorption method , while particles particles of the order of 5-10 nm are obtained by regular incipient wetness impregnation.

## 4. PUBLICATIONS DURING THE REPORTING PERIOD

### 4.1. Refereed Articles in Periodical Journals:

- Qin, S; Qin, D.; Ford, W. T.; Resasco, D. E.; Herrera, J. E. "Functionalization of Single-Walled Carbon Nanotubes with Polystyrene via Grafting to and Grafting from Methods." *Macromolecules* (2004), 37(3), 752-757.
- "Polymer Brushes on Single-Walled Carbon Nanotubes by Atom Transfer Radical Polymerization of n-Butyl Methacrylate" Shuhui Qin, Dongqi Qin, Warren T. Ford, Daniel E. Resasco, and Jose E. Herrera, *Journal of the American Chemical Society* (2004), 126(1), 170-176.
- "Loss of single-walled carbon nanotubes selectivity by disruption of the Co-Mo interaction in the catalyst", J. E. Herrera and D. E. Resasco, *Journal of Catalysis* 221, (2004) 354-364
- Dispersion of Single-Walled Carbon Nanotubes in Aqueous Solutions of the Anionic Surfactant NaDDBS' Olga Matarredona, Heather Rhoads, Zhongrui Li, Jeffrey H. Harwell, Leandro Balzano, and Daniel E. Resasco *Journal of Physical Chemistry B* (2003), 107(48), 13357-13367.

- “Narrow (n,m)-Distribution of Single-Walled Carbon Nanotubes Grown using a Solid Supported Catalyst”, Sergei M. Bachilo, Leandro Balzano, Jose E. Herrera, Francisco Pompeo, Daniel E. Resasco, and R. Bruce Weisman, *Journal American Chem. Soc.* (2003), 125, 11186
- “Structural Characterization of Single-Walled Carbon Nanotubes” Daniel E. Resasco and Jose E. Herrera. *Encyclopedia of Nanoscience and Nanotechnology*, (2003) American Scientific Publishers (H. S. Nalwa Ed.), Vol. 10, pp 1-23.
- “Temperature dependence of the quality of silicon nanowires produced over a titania-supported gold catalyst” Nataphan Sakulchaicharoen and Daniel E. Resasco *Chemical Physics Letters* 377 (2003) 377-383
- “Role of the catalyst in the growth of single single-wall carbon nanotubes,” Perla B. Balbuena, Jin Zhao, Shiping Huang, Yixuan Wang, Nataphan Sakulchaicharoen, and Daniel E. Resasco, *J. of Nanoscience and Nanotechnology*, 6, 1247-1258, 2006.
- “Controlling the growth of vertically-oriented single-walled carbon nanotubes by varying the density of Co-Mo catalyst particles” Liang Zhang; Yongqiang Tan, Daniel E. Resasco, *Chemical Physics Letters* 422, 198-203, 2006.
- “Tailoring (n,m) structure of single-walled carbon nanotubes by modifying reaction conditions and the nature of the support of CoMo catalysts.” Giulio Lolli, Liang Zhang, Leandro Balzano, Nataphan Sakulchaicharoen, Yongqiang Tan, and Daniel E. Resasco, *Journal of Physical Chemistry B*, 2006; 110(5); 2108-2115.
- “Side-Wall Functionalization of Single-Walled Carbon Nanotubes with 4-Hydroxymethylaniline Followed by Polymerization of  $\epsilon$ -Caprolactone.” Buffa, Fabian; Hu, Hui; Resasco, Daniel E.. *Macromolecules* 2005, 38(20), 8258-8263.
- “Quantifying carbon-nanotube species with resonance Raman scattering” A. Jorio, A. P. Santos, H. B. Ribeiro, C. Fantini, M. Souza, J. P. M. Vieira, C. A. Furtado, J. Jiang, R. Saito, L. Balzano, D. E. Resasco, and M. A. Pimenta, *Physical Review B* 72, 72, 075207 2005
- “Dispersion of Single-Walled Carbon Nanotubes of Narrow Diameter Distribution.” Yongqiang Tan and Daniel E. Resasco *Journal of Physical Chemistry B* 2005, 109, 14454-14460
- “Single-Walled Carbon Nanotubes of Controlled Diameter and Bundle Size and Their Field Emission Properties.” Liang Zhang, Leandro Balzano, and Daniel E. Resasco, *Journal of Physical Chemistry B* 2005, 109, 14375-14381
- “Raman Spectroscopy of Individual Single-Walled Carbon Nanotubes from Various Sources” . Hennrich, Frank; Krupke, Ralph; Lebedkin, Sergei; Arnold, Katharina; Fischer, Regina; Resasco, Daniel E.; Kappes, Manfred M. *Journal of Physical Chemistry B* 2005, 109(21), 10567-10573

## **B) Patents Issued:**

- “Metallic catalytic particle for producing single-walled carbon nanotubes” United States Patent 6,962,892. November 8, 2005. Resasco; Daniel E.; Kitiyanan; Boonyarach; Harwell; Jeffrey H.
- “Method and apparatus for producing carbon nanotubes” United States Patent 6,955,800. October 18, 2005; Resasco; Daniel E. ; Kitiyanan; Boonyarach; Balzano; Leandro

#### 4.3. Presentations to Scientific Meetings:

- "Comparison of SWNT prepared by Catalytic Decomposition of Methane and Disproportionation of CO over Different Catalysts. Paper 4f - Chemical Engineering Issues in Carbon Nanotubes II. AIChE 2002 Annual Meeting, November 3 – 8, Indianapolis, Indiana. Supapak Xuto, Teerakun Boonphyoong, J. E Herrera, Sumaeth Chavadej, Boonyarach Kitayanan, Daniel E Resasco
- "Comparison between the activities of silica-supported CoMo and CoW catalyst for carbon nanotube production by CO disproportionation" 18th North American Catalysis Society Meeting, Cancun, June 1-6, 2003 E. J. Herrera, L. Balzano, and D. E. Resasco
- "Carbon Nanotube - Surfactant Interactions," AIChE 2003 National Meeting, San Francisco, November 11-16, Daniel E. Resasco, Olga Matarredona (speaker), Leandro Balzano, Francisco Pompeo
- "Modification of the Extent of Co-Mo Interaction and its Effect on SWNT Growth Selectivity," AIChE 2003 National Meeting, San Francisco, November 11-16, Daniel E. Resasco (speaker), Leandro Balzano, Jose E. Herrera
- "Comparison of Different Metallic Catalysts for Single-walled Carbon Nanotubes Production," AIChE 2003 National Meeting, San Francisco, November 11-16, Pisan Chungchamroenkit, Teerakun Boonphyoong, Jose E. Herrera, Boonyarach Kitayanan, Sumaeth Chavadej, Daniel E. Resasco
- "Influence of Catalyst Support and Reaction Conditions in the Synthesis of Silicon Nanowires by Decomposition of Silane On Gold," AIChE 2003 National Meeting, San Francisco, November 11-16, Nataphan Sakulchaicharoen, Siriporn Jongpatiwut, Jose E. Herrera, Daniel E. Resasco

#### 4.4. Invited Lectures:

- "Selective Production of Single-Walled Carbon Nanotubes by CO Disproportionation on Co-Mo Catalysts", University of Notre Dame, September 2003
- "Diseño de materiales catalíticos para la producción selectiva de nanotubos de carbono de pared única (SWNT)", 18 Congress on Catalysis Argentina-Brazil, Plenary Lecture, Villa Giardino, Cordoba, Argentina, October 2003
- "Large-scale production of Single-walled nanotubes and applications in fuel cells", Engelhard Corp., New Jersey, Nov. 2003
- "Co-Mo-Catalyzed Production of Carbon Nanotubes", Invited Lecture The SWRM Symposium on Catalysis for the 21st Century, Oklahoma City, October 2003

#### 4.5. Other non-reviewed documents:

web page [www.ou.edu/engineering/nanotube](http://www.ou.edu/engineering/nanotube)

#### 4.6. Media appearances:

- Feature article (front page) in Tulsa World about our large-scale production of single-walled carbon nanotubes.

### **5. Other Synergistic Activities**

#### 5.1. Awards:

- *Yale Award for Advancement of Basic and Applied Science*  
Yale Science and Engineering Association, Yale University  
April 2004

5.2. Technology Transfer: SouthWest NanoTechnologies, Inc. (SWeNT™) is a development-stage specialty chemical manufacturer formed to mass-produce Single Wall Carbon Nanotubes for high-volume specialty applications. The production process was designed by the research group of D. Resasco at the University of Oklahoma and co-developed with ConocoPhillips, SWeNT's™ strategic partner. The Company executed an exclusive worldwide license for the production process technology from the U. of Oklahoma and ConocoPhillips, including 2 U.S. patents and several pending and provisional applications. International counterparts exist in all major markets, including NAFTA, EU, Japan, China, Mexico, and Brazil; as well as 2 U.S. trademarks.



SWeNT™ will raise \$6-8 million to support 2.5-3 years of operations, and seeks advanced materials and/or chemical industry investors. Current support is from NASA, OCAST an Oklahoma state technology agency, ConocoPhillips (owns ~21%), the U. of Oklahoma (owns ~47%), and several individuals (collectively own ~32%).

### **6. Objectives for the next funding period**

- During the past year, we have developed handling protocols that have allowed us to determine more readily and effectively the distribution of SWNT present in any sample. This protocol included the development of covalent and non-covalent methods of functionalization that greatly enhance the dispersibility of the nanotubes. Without these handling methods in place the detailed (n,m) characterization was extremely tedious and had to be done in collaboration with other groups. With this capability in-house, we can now explore slightly different catalyst compositions and reaction conditions (CO/He/H<sub>2</sub> concentration,

temperature, pressure) to determine whether it is possible to obtain a variety of (n,m) nanotube structures while keeping narrow distributions.

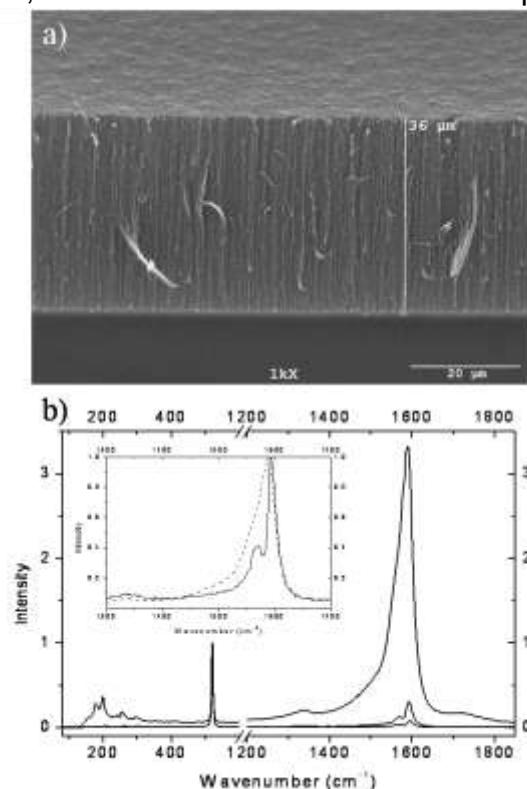
- At the same time, we plan to evaluate the properties of these nanotubes for the applications that we have developed in-house (fuel cell electrodes, field emission, electrical conductivity)
- We will continue collaborating with Prof. Perla Balbuena (Texas A&M) in a combined theoretical-experimental program to simulate the controlled nanotube growth and find relationships between the cluster structure and the nanotube chirality.

The main goal of this proposal is to advance the knowledge of the mechanism responsible for the formation of single-walled carbon nanotubes (SWNT) in order to get control over their structural parameters (diameter, chirality, and lenght). Only through a detailed knowledge of the growth mechanism it will be possible to produce SWNT with tailored properties since they are directly related to the structural parameters.

### Controlling the Length of Vertically Aligned Forests of Single-Walled Carbon Nanotubes

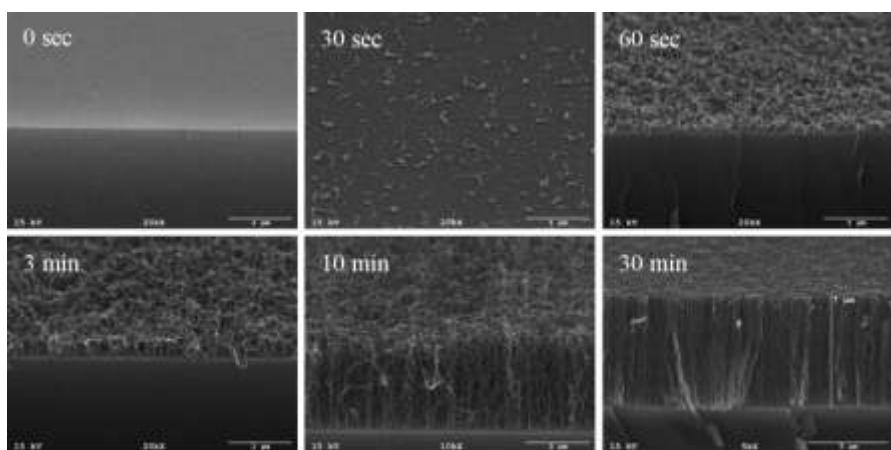
Despite large uncertainties in the measurements and differences in the synthesis methods employed, it is well recognized that, in an unrestricted state, the growth rate of single-walled carbon nanotubes is at least higher than several microns-per-second.<sup>i-iv</sup> By contrast, when the growth occurs via catalytic decomposition of carbon-containing molecules on high surface-area catalysts, such as CoMo/SiO<sub>2</sub>, the growth takes place in a scale of hours. As previously proposed,<sup>v</sup> while the amount of carbon deposits slowly increases with time, this does not necessarily mean that the growth of a given nanotube is so slow. It is plausible that the slow rate observed for overall rate of carbon deposition is in fact a slow rate of nucleation followed by a fast nanotube growth rate. Accordingly, new nucleation sites will appear on a high-surface area material and each site will give rise to a nanotube that grows relatively fast. Of course, the nanotubes that grow later will do it constricted by the presence of those that grew earlier.

As a result, control of nanotube length during growth appeared as an almost impossible task for a long time. However, recent studies of SWNT growth on flat



substrates have shown that, in fact, length of SWNT can be controlled.<sup>vi-xii,xiii</sup> In our previous contribution,<sup>xiv</sup> we indicated that the density and distribution of the catalyst moieties on the flat surface is crucial to determine whether the nanotubes grow in vertically oriented fashion (“forest” or V-SWNT) or a random network parallel to the surface (“grass”).

We found that different forms of SWNT arrays can be reproducibly obtained on flat silicon substrates when the Co-Mo catalyst particles have the appropriate distribution, which can be readily controlled by simply varying the concentration of catalyst solution.<sup>14</sup> The difference between this type of flat catalyst and the high surface-area catalyst, is that on a flat surface the nanotube growth is, in principle, less constricted by the catalyst structure due to the absence of porosity.



SEM Images of V-SWNT obtained for a series of reaction time period. The scale bars in those images are 1  $\mu$ m for 0, 30, 60 seconds and 3 minutes, 2  $\mu$ m for 10 minutes and 5  $\mu$ m for 30 minutes.

However, the growth of a nanotube is still constricted by the presence of the other nanotubes, which, as we show in this contribution, make them grow vertically oriented (V-SWNT). A question that remains unanswered is why all the SWNT that forms the “forest” appear to have the same length and what is most puzzling is the smoothness of the top of the forest clearly observed in the SEM images.<sup>vii,14</sup>

A detailed analysis of the structure of SWNT forests as a function of growth time reveals that a two-step process is responsible for the formation of a SWNT forest. The first step is the weaving of a crust of entangled SWNT which grow at different rates and with random orientation over the surface. The second step is a concerted growth of vertically aligned SWNT constrained by the uniform top crust. Several techniques were employed to examine the growth process and the results are all consistent with this mechanism. The XANES results show that a fraction of the tubes on top of the forest are parallel to the surface, rather than perpendicular as the majority of the tubes in the forest. Direct SEM observations agree with this morphology. Several examples are presented to demonstrate that the crust influences the morphology of the resulting forest. Catalysts which are non-uniformly distributed on the substrate produce curved crusts instead of the consistent forest with a flat top obtained when the catalyst layer is uniform.

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