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Project title: Self-sorting of Carbon Nanotubes for High Performance Large Area Transparent Electrodes for Solar Cells

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Abstract
Single-Walled Carbon Nanotubes (SWNTs) have superb electronic and mechanical properties; however, SWNTs come in different chiralities making them either metallic (MET) or semiconducting (SC). It is desirable to have only one type in electronic applications. We have recently developed a method to selectively separate the SC and MET SWNTs and form self sorted networks of each on different functionalized surfaces.

In order to deposit the SWNTs, they need to be purified and dispersed into solutions. Here, we systematically vary the dispersion conditions used to disperse SWNTs in solution and then use deposit films onto functionalized substrates resulting in sub-monolayer SWNT networks. We used field effect transistors (FETs) to evaluate the electronic properties of the networks. We show that changing the solution processing conditions changes the properties of SWNTs in solution, the length of SWNTs and the metallic and semiconducting fractions of SWNTs adsorbed on the surface. For optimal SWNTs transistor networks with high on/off ratio, and long unbundled SWNTs a short sonication time is required. However, comparable length and electronic performance can be obtained with increased yield with a slightly longer time. Longer sonication times reduce the length of the SWNTs and degrade the on/off ratio of self sorted SWNT networks by introducing defects, shortening the SWNTs and degrading the solvent.

The mechanism of pristine SWNT dispersion into organic solvents was explored. We have selected a protic amidines, a new class of SWNT solvent, and demonstrated these are effective to disperse SWNTs into solutions. We compared these results with commonly used amide solvents and demonstrate that electron charge transfer from the solvent to the SWNT effects the quality of the dispersion. We also compare the aprotic amidine solvent with an unsuccessful protic solvent and another amidine solvent with a planar chemical structure. These results show the chemical structure of the solvent molecule is critical to the quality of SWNT dispersion.

We also present further understanding of the mechanism of selective SWNT adsorption on a surface. The chirality, density, and alignment of the SWNTs were heavily influenced by adsorption onto amine functionalized surfaces that were exposed to varying pH solutions, as evidenced by atomic force microscopy (AFM) and Raman spectroscopy. This pH treatment altered the charge density on the surface, allowing for the examination of the contribution from electrostatic interaction to SWNT adsorption and SWNT characteristics. Secondary and tertiary amines with methyl substitutions were utilized to confirm that adsorption and chirality specific adsorption is largely due to the nitrogen lone pair, not the neighboring hydrogen atoms. Thus, the

nature of adsorption is predominantly electrostatic and not due to Van der Waals forces or localized polarization on the SWNTs.

The aminated silanes used in the previously mentioned studies can have difficult surface chemistry with and as an alternative, the nitrile group has been examined. These self-assembled monolayers (SAMs) sort and adsorb SWNTs just as efficiently as primary amines, but without the heightened sensitivity to water or contaminants. Preliminary analysis has shown that SWNTs adsorb more strongly to nitrile surfaces than amine surfaces due to higher density adsorption at constant volume deposition. Raman analysis suggested sorting has roughly the same efficiency on both surfaces. For roughly the same SWNTnt density and spin conditions, nitrile surfaces produced SWNTnts with higher mobilities, lower threshold voltages, higher operating currents, and similar on/off current ratios. This work can enhance our understanding of SWNT adsorption and open the door to scaling up for high-throughput and high-quality devices.

In addition to sorted SWNT networks, we studied composite CNT and conductive polymer poly(3,4-ethylenedioxythiophene) poly(styrenesolfonate) (PEDOT:PSS) transparent conducting electrodes. These materials were applied in separate steps creating a percolating CNT network surrounded by a think PEDOT:PSS film. This composite film had a higher conductivity then the sum of similar films simply adding the conductivities in parallel of the individual films, suggesting a synergistic interaction between the two materials. Sheet resistance below 100 ohm/sq at >80% transmittance has been achieved.

We have fabricated a transparent, stretchable and conductive skin using carbon nanotube electronics by spray deposition of CNTs onto a flexible elastomer. To render the CNT films stretchable, a one-time application of strain and subsequent release produces waves in the nanotubes aligned with the stretched axis, which accommodate strains while increasing the resistivity minimally. These skin-like devices could have applications in stretchable solar cells and other electronic devices.

Finally, we present work on graphene transparent conducting electrodes from solution based process. This method is inexpensive and compatible with flexible substrates. We bath sonicated graphite flakes in an organic solvent and optimized the conditions to obtain large and thin flakes with reasonable concentrations. These were used to create transparent conducting films, which, after annealing, had comparable conductivities to highest reported literature values.

Introduction

The application of carbon nanotubes (CNT) to the fabrication of transparent conductive electrodes (TCE) for photovoltaic applications has been investigated in the recent years for their potential to address some of the shortcomings of current Indium-Tin-Oxide (ITO) technologies, namely the high material and fabrication costs and the brittleness of the deposited layers. Their excellent charge-transport properties are particularly suitable for applications relating to display drivers, photovoltaics, and circuits. CNTs have the prospect to meet low fabrication cost targets for the low cost of earth-abundant carbon and for their potential to be dispersed into solution for large area coating. Additionally, they have excellent thermal, mechanical, and electrical

properties that make them an ideal candidate for TCEs: they are stable at the high temperatures required to process inorganic devices; they have excellent strength and flexibility; and they have an electrical conductivity three orders of magnitude greater than metals like copper.

Despite their potential, state-of-the-art CNT-based TCEs have still poor performance with a sheet resistance more than ten times higher than ITO electrodes at comparable light transmittance (~80%). The key problem in reducing the sheet resistance of CNT-based layers is that as-synthesized CNTs usually contain a mixture of approximately 67% semiconducting CNTs (sc-CNT) and only 33% metallic CNTs (met-CNT), where the difference in electronic properties depends on the chirality of the nanotubes. Moreover, the ability to tune the alignment and absorption onto surfaces will lead to optimized optoelectronic properties. And finally, a big driver for alternatives to ITO is a dramatic reduction in cost. To facilitate cost-efficient electronics, large area devices will require cheaper materials such as polymers, along with faster, cheaper solution processing rather than high temperature sputtering.

However, accurate (directed) assembly and orientation in a reproducible fashion of SWNTs over large areas remains an unsolved issue. We have spent considerable effort mitigating this problem by fabricating CNT films with tunable and reproducible chirality, alignment, and density through a spin-assembly method from solution on various substrates. This more elegant approach beyond "random CNT networks" leads to better conductivity with higher transparency since with an optimized CNT network, a thinner film is required.

Results

I. Solution Processing of Single Walled Nanotubes

In order to facilitate the integration of single walled carbon nanotubes (SWNTs) into transparent conductors and electronic devices they need to be purified and dispersed into solutions. Understanding the effect solution processing steps can have important implications in the design of SWNT films for these electronic applications. We systematically vary the sonication time used to disperse SWNTs in solution and then use deposit films onto functionalized substrates resulting in sub-monolayer SWNT network field effect transistors (FETs) with a range of device properties. Changing the solution processing conditions changes the properties of SWNTs in solution, the length of SWNTs and the metallic and semiconducting fractions of SWNTs adsorbed on the surface. For optimal SWNTs transistor networks with high on/off ratio, and long unbundled SWNTs a short sonication time is required. However, comparable length and electronic performance can be obtained with increased yield with a slightly longer time. Longer sonication times reduce the length of the SWNTs and degrade the on/off ratio of self sorted SWNT networks by introducing defects, shortening the SWNTs and degrading the solvent. This study shows that careful consideration is required for the scalable processing of SWNT electronic devices.
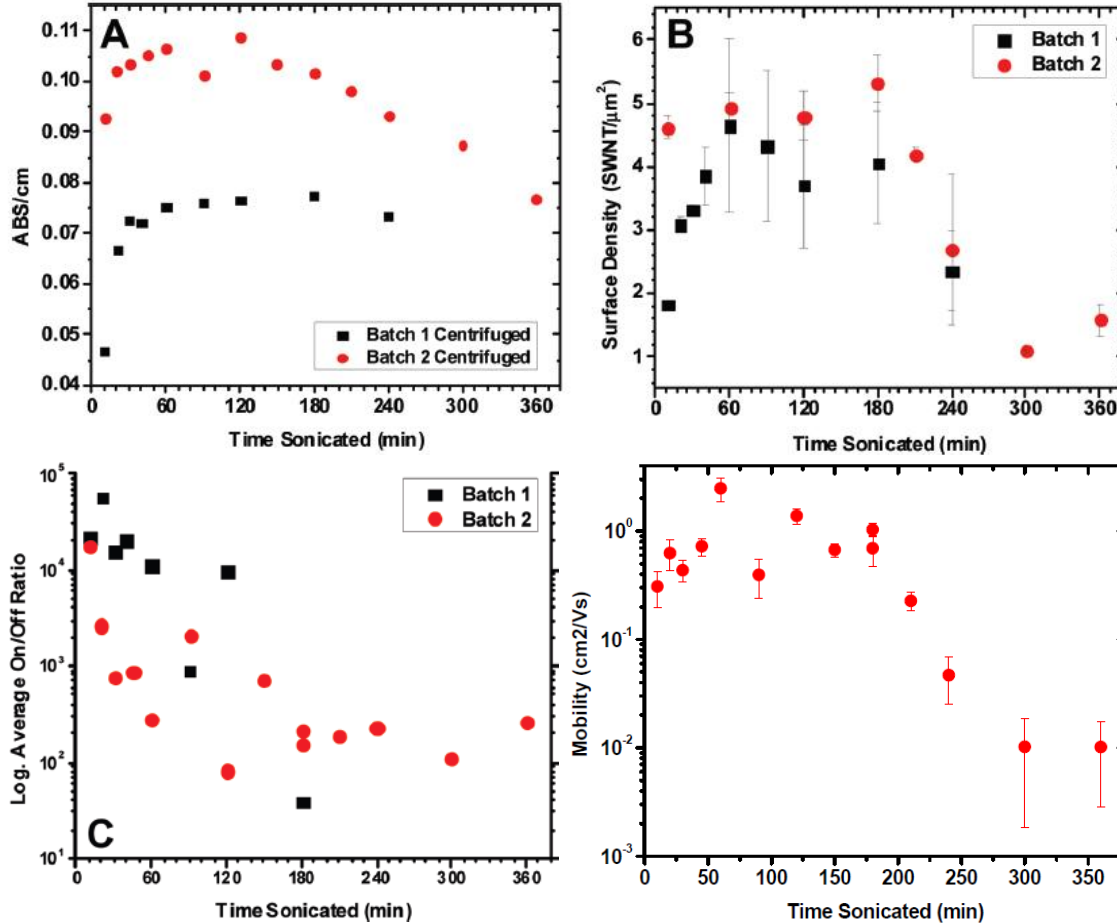
Figure 1: A. The optical UV-Vis NIR absorption of solutions of SWNTs in organic solvent.
The absorbtion increases sharply and then decreases as the solution become more bundled. B.
The surface density of SWNTs as a function of time sonicated. C. The On/Off ratio of
transistors fabricated from solutions sonicated for various times. The decrease indicated
diminished sorting of the semiconducting SWNTs. D. The mobility of the devices made from
different sonication times.

II. New Solvents for the dispersion of SWNTs

The dispersion of SWNTs into solution is necessary for the economic processing of nanotubes
electronic and structural applications. This can be performed using functionalization of the
SWNT walls and end caps or with a third phase dispersant such as a surfactant or a polymer.
Unfortunately, functionalization and dispersants alter the exceptional electronic and structural
properties of the SWNT. Disperse the SWNTs directly into solvents would be best. However,
SWNTs are insoluble in most common organic solvents due to their large molecular weight and
strong van der Walls forces between SWNTs resulting in the aggregation into large bundles.
Select solvents have been identified which have been shown to disperse SWNTs via match with
physical properties. The best of these solvents are aprotic and contain the amide (NC=O)

functionality. We identify another new aprotic solvent containing the amidine (NC=N) moiety, 1,8-Diazabicycloundec-7-ene (DBU) , and show that this solvent effectively disperses arc discharge and HiPCO SWNTs. We compare the dispersion properties of DBU to a commonly used amide N-methyl-pyrrolidone (NMP) to demonstrate that electronic charge transfer of electrons is the mechanism for the dispersion of SWNTs in organic solvents via Raman spectroscopy. Also, we compare DBU with another similar aprotic amidine solvent, 1,5-Diazabicyclo(4.3.0)non-5-ene (DBN) which does not disperse SWNTs due to the chemical structure which does not allow SWNT access to the electron donating amidine moiety. Protic solvents such as 1,1,3,3-Tetramethylguanidine (TMG), which also contains an amidine moiety, do not disperse SWNTs. This study demonstrates chemical structure as well the physical properties of the solvent is necessary for the direct dispersion of SWNTs into solutions.
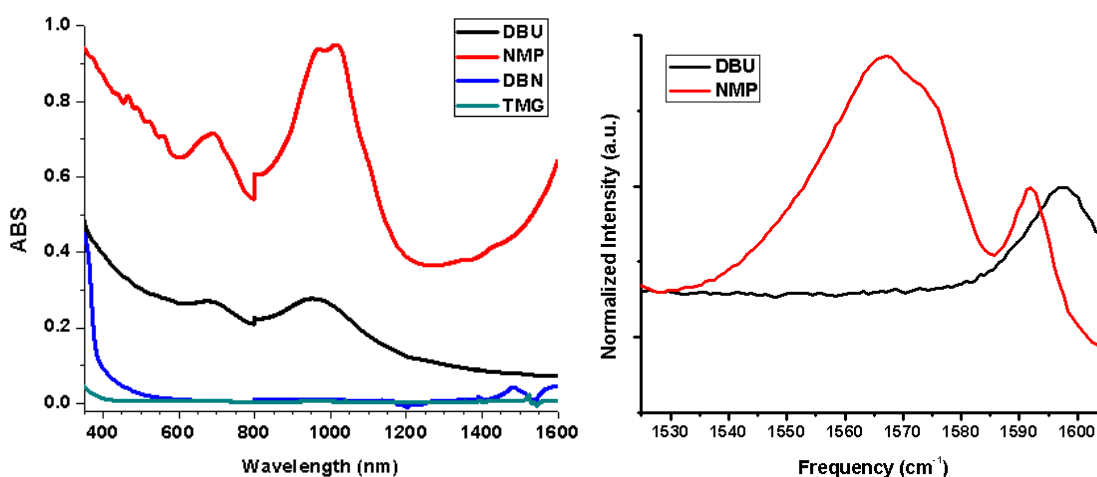

Figure 2: A. UV-vis NIR spectra of SWNTs dispersed into different solvents via sonication followed by centrifugation. DBU is an effective SWNT solvent, but not as effective as NMP. DBN and TMG do not solubilize SWNTs. B. Raman spectroscopy of the SWNT G-band from different dispersion taken in the solution phase. The downshifting of the G+ in the NMP spectra compared to DBU is indicative of increased electron donation.

III. Influence of Electrostatic Interactions on Spin Assembled Single-Walled Carbon Nanotube Networks (SWNTnts) on Amine Functionalized Surfaces

From our previous reports that amine-coated surfaces can selectively adsorb semiconducting nanotubes (SC-SWNTs)[1], it has been of interest to determine the origin of this preferential interaction. Other reports had suggested this origin to either be electron density donation from the amine lone pair, dispersive interactions with the hydrogen atoms, or purely electrostatic attraction. To examine this, we exposed these amine surfaces to various aqueous solutions of varying pH (ranging from 3 to 13) and subsequently deposited the SWNT solution.[2] To specifically examine whether the lone pair or the hydrogen atom was the dominant interacting species, we analyzed primary, secondary, and tertiary amines (the latter having no spare hydrogen atoms attached to the nitrogen).

In all cases, the SWNTnt density decreased with increasing pH until adsorption shutoff occurred. The adsorption trends are shown in Figure 3. This comes as a result of the charge on the surface and the charge of the SWNTs. The nanotubes became defective due to the dispersion process and contain many carboxylic acid defects and develop a net negative charge on their surface due to the Lewis basicity of the NMP solvent. At low pH, the amine surface became highly positively charged and attracted all defective SWNTs to the surface. This electrostatic interaction is very strong and all SWNTs adsorb quickly, with no opportunity to align or properly sort. As the pH increased, the interaction energy decreased, allowing less defective (less charged) SWNTs to wash away in the solution and not adsorb. Due to the diameter-range of the purchased arc discharged SWNTs, large diameters correspond to SC-SWNTs and these nanotubes should statistically contain more defects. Hence, as the pH was increased, more MET-SWNTs were washed away and the SWNTnts became predominantly filled with SC-SWNTs. This can be observed by Raman analysis, as shown in Figure 4.
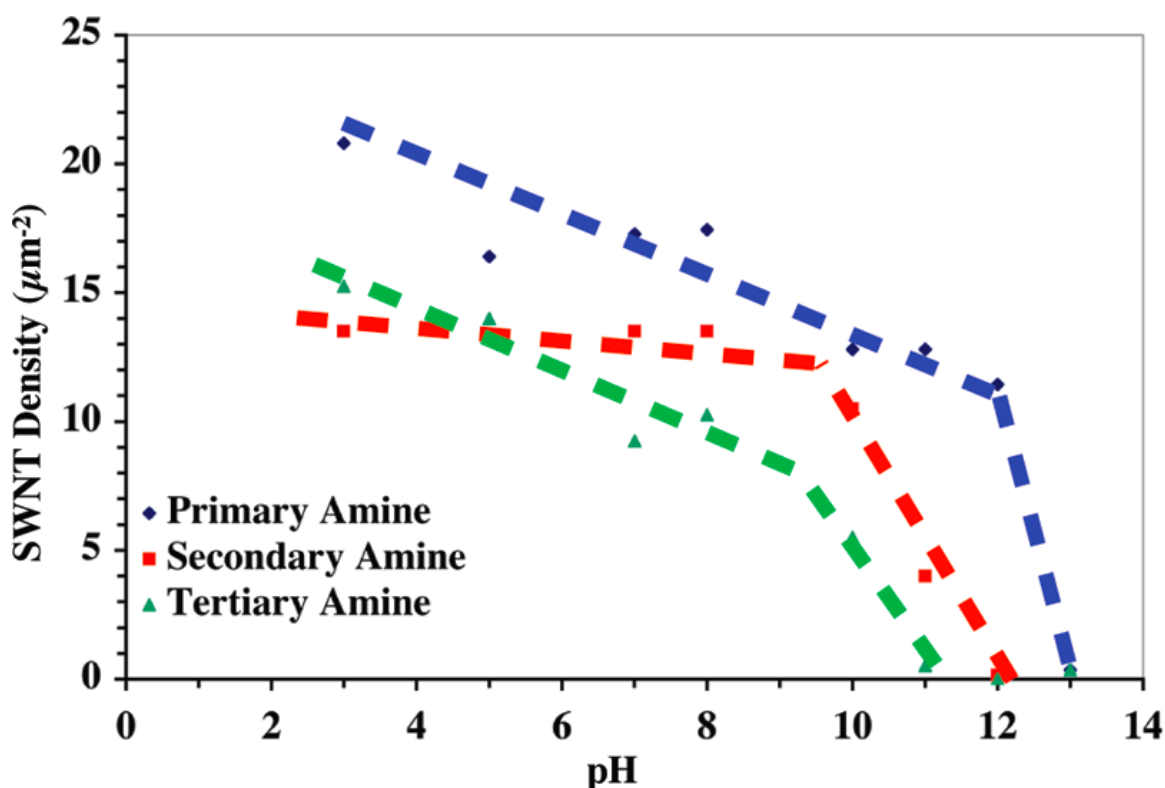

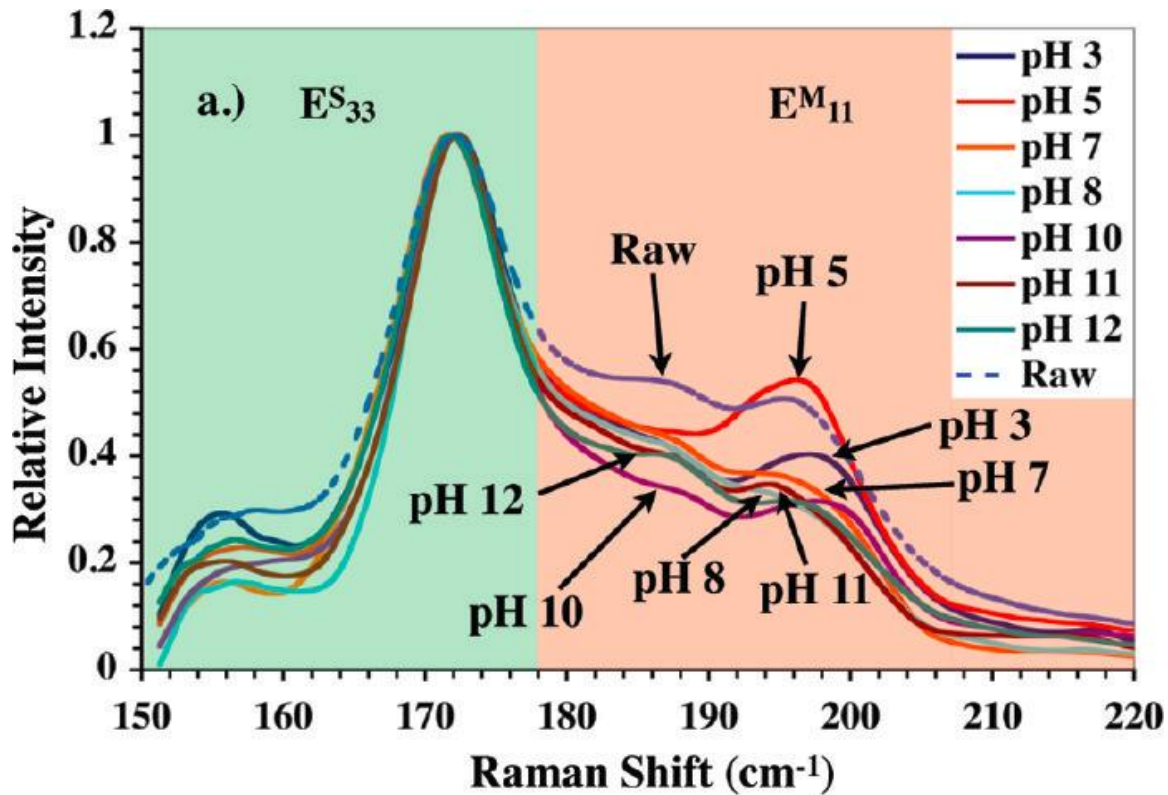Figure 3: SWNT adsorption as a function of bulk solution pH on all three amine surfaces.

Figure 4: Resonant Raman RBM analysis of SWNT networks on pH-treated primary amine surface at excitation energy of 1.96 eV.

This phenomena was observed on all three surfaces, but the secondary and tertiary amine surfaces had overall lower densities and shutoff occurred at lower pH than for the primary amine. The steric hindrance of the additional methyl groups on the secondary and tertiary amines blocked exposure between the amine lone pair and the SWNTs, yielding an overall lower interaction energy. This corresponded to lower SWNTnt densities. At pH 13, the primary amine was destroyed by the basic conditions and with no amines, no SWNTs could adsorb. Shutoff occurred at lower pH for the secondary and tertiary surfaces because the already reduced interaction energy was reduced too low at pH 12 and 11 (respectively) to attract any SWNTs and hence no network could form.

When devices were made from these samples, it was found that the initial claims of increased sorting efficiency with increasing pH were confirmed.[3] At pH 3, the high metallic contribution yielded high off currents and low on/off current ratios (between 10-100). At higher pH, the off currents were reduced significantly, yielding significantly higher on/off ratios (above 10^4). These trends can be observed in Figure 3, which compares pH 3 to pH 10-12 for the primary amines at constant SWNTnt density.
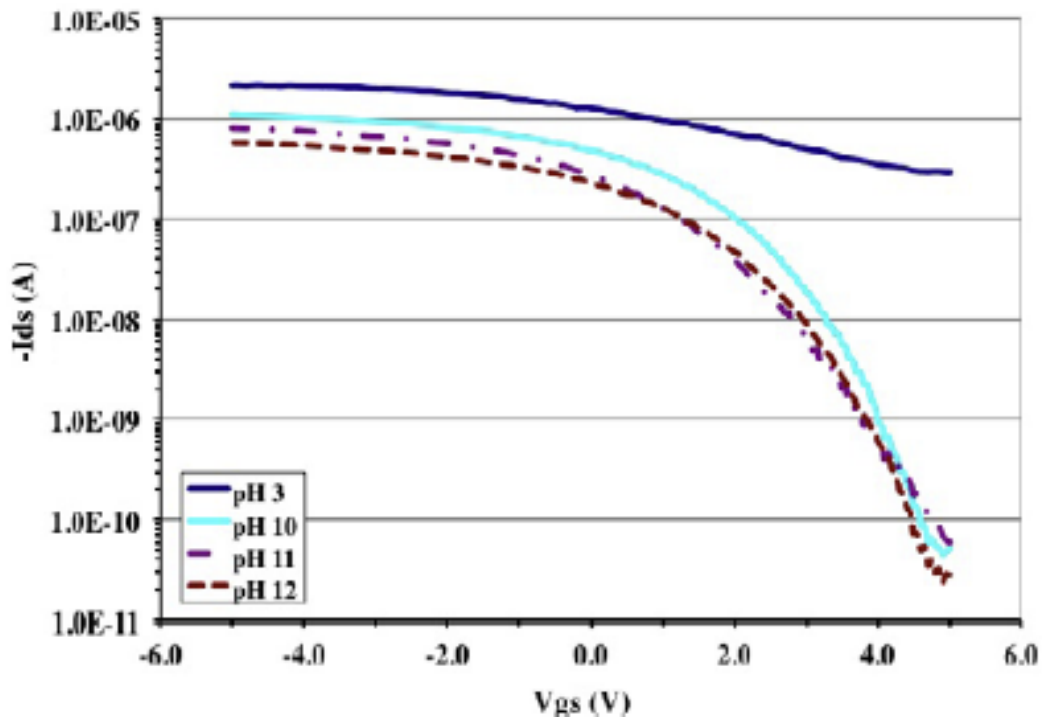
Figure 5: Average transfer curves for primary amine surfaces with constant SWNTnt density. Vds = -1V, W = 100 μm, L = 20 μm. Each curve is an average of 20 devices.

References:
1. LeMieux, M. C.; Roberts, M.; Barman, S.; Jin, Y. W.; Kim, J. M.; Bao, Z. Self-Sorted, Aligned Nanotube Networks for Thin-Film Transistors. Science 2008, 321, 101–104.
2. Opatkiewicz, J. P., LeMieux, M.C., Bao, Z. Influence of electrostatic interactions on spin-assembled single-walled carbon nanotube networks on amine-functionalized surfaces. ACS Nano, 2010, 4, 1167-1177.
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VI. Transparent Conducting Graphene Films Using Solution Processing

Recently, graphene has also attracted great attention as a transparent conducting material due to the same reasons as CNTs, as graphene is the 2D analog of the 1D CNT. Despite its relatively recent discovery in 2003, graphene has almost matched, if not reached, CNTs in performance as a transparent electrode. Remarkably, Bae et al. have shown a roll-to-roll production of 30 inch graphene films with a sheet resistance of 30 Ω/□ at 90% and have incorporated these films in touch screen panels.[1] This process, however, requires CVD growth of graphene on a copper foil, which must then be etched to transfer the graphene film to a flexible substrate. In contrast, solution based methods of producing graphene are low-cost and directly compatible with flexible substrates; however, their sheet resistance is larger by an order of magnitude or more compared to CVD grown films.

In this work, high concentration graphene solutions were prepared from bath-sonicated exfoliation of graphite flakes in N-Methylpyrrolidone (NMP). The effects of sonication time and centrifuge conditions were investigated to determine the optimum solution characteristics, such as concentration, flake size, and flake thickness. Then, using these solutions, we spray coated graphene thin films on glass and characterized their sheet resistance and optical transparency. Finally, annealing was used as a means to improve the sheet resistance of these films produced by solution methods.

We have determined that the optimal sonication time and centrifugation conditions were 120 min and 30 min at 5000 rpm, respectively. These conditions provide the best combination large and thin flakes with reasonable concentrations. Figures 8a and 8b show the effects of the centrifuge and sonication time on the solution concentration. The spray coating process was performed using a commercial air brush with the substrates heated at about 200 ºC. Good film uniformity was only obtained after determining optimum spray coating conditions. Figure 8c shows the film composition. As can be seen, the flake size was on the order of several hundred nanometers, and the thickness was estimated to range from 1-15 nm (one layer graphene to multilayer graphene) using atomic force microscopy (AFM). Due to the 2D nature of the flakes in the film, it is possible that excess NMP may become trapped between overlapping flakes, which can result in decreased film conductivity. As a result, we have annealed these films in air to remove any residual NMP. As shown in figure 8d, after determining the optimum annealing conditions, the sheet resistance of the films was reduced 30-50% after the annealing process. These best films had a sheet resistance of about 3,500 phm/sq at 60% transmittance (550nm), which is similar to the best solution processed graphene films.
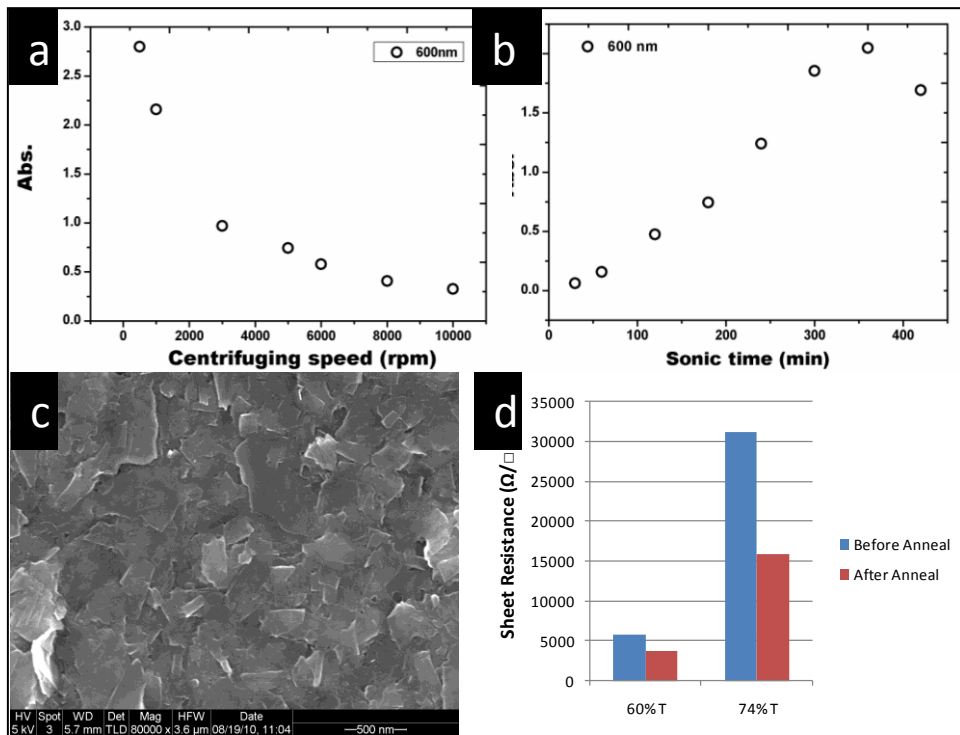

Figure 8: A. absorbance as a function of centrifuge speed. B. absorbance as a function of sonication time C. SEM image of typical graphene films D. sheet resistance for graphene films at two difference transparencies (550nm) before and after annealing.

References

1. Bae S. et al, *Nature Nanotech*, **2010**, *5*, pp 574–578.

Progress:

Our best results have achieved sheet resistance of below 100 ohm/sq at >80% transmittance. This performance brings us a step closer to replacing ITO as transparent electrodes.

Publications:

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2. Opatkiewicz, J. P., LeMieux, M.C., Bao, Z. Influence of electrostatic interactions on spin-assembled single-walled carbon nanotube networks on amine-functionalized surfaces. ACS Nano, 2010, 4, 1167-1177.
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