

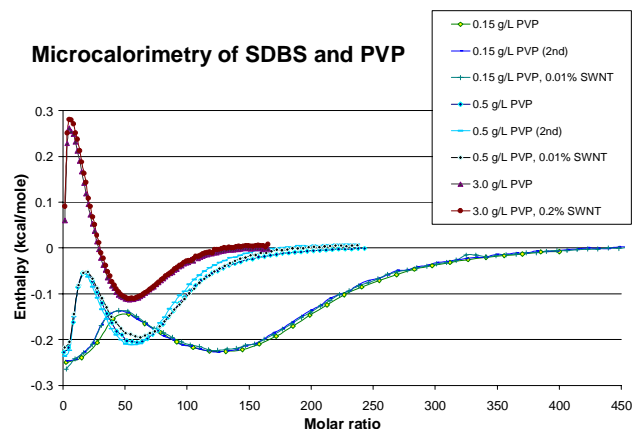
Large Area Aligned Arrays from Direct Deposition of Single Wall Carbon Nanotube Inks

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Supporting Information



Sodium dodecyl benzene sulfonate (SDBS), Polyvinylpyrrolidone (PVP, MW 10 kDa), and NaCl were obtained from Sigma Aldrich. Microcalorimetry experiments were performed using a MicorCal ITC-VP at the University of Albany Proteomics Facility in Rensselaer, NY. SDBS was added to de-ionized distilled water, and placed into the injection syringe of the microcalorimeter, and added to the sample cell containing PVP in de-ionized water. SWNT were added to the injection solution of water and SDBS for the relevant sample runs.

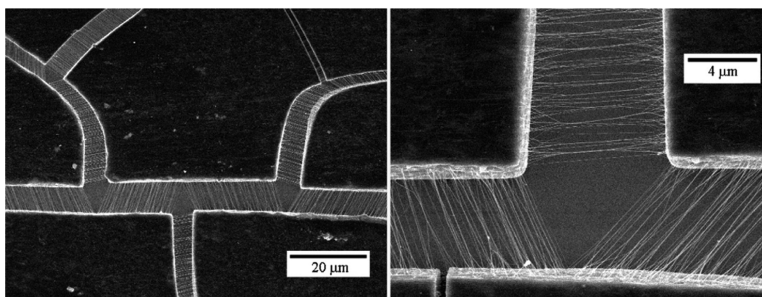
Communication

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In this work we disperse pristine single-wall carbon nanotubes (SWNTs) in water by noncovalent modification of the tube surfaces with polymer and surfactant, aided by brief low-power sonication. Some of the advantages of this method are that it avoids damaging the SWNTs substantially, maintains very long SWNTs (several micrometers), and yields high concentrations of SWNTs dispersed in water. These dispersions can be deposited in a variety of methods onto substrates such as silica, glass, and alumina. During thermal deposition, unique arrays of well-aligned SWNTs self-assemble across large fissures and once dry are observed by scanning electron microscopy (SEM).

SWNTs have unique electronic and mechanical properties which show promise in a wide variety of applications.^{1,2} One major hurdle in advancing toward such applications is the difficulty in suspending pristine carbon nanotubes in water and other polar solvents owing to the fact that pristine SWNTs are nonpolar. Various routes of chemical functionalization have allowed SWNTs to be suspended in polar solvents,³ but these covalent functionalization strategies cause defects in the nanotube sidewalls and shorten SWNTs via oxidative cutting. Extensive high-power sonication is another common method to aid in SWNT dispersion which creates defect sites and tube cutting.⁴

Water-based formulations of SWNTs and MWNTs, or inks, are essential to nanotube processing and fabrication of related devices when use of harsh organic solvents is not possible. Organic solvents cannot fully disperse nanotubes and have several drawbacks such as toxicity, flammability, and reactivity, which make water and to a lesser extent alcohols ideal solvents. Inkjet printing of carbon nanotube formulations can only be achieved with water or alcohols, since the polymer components of the printers are vulnerable to organic solvents. Recent work by Kordás et al.⁵ has shown water based printing of MWNTs, which relies on a covalent modification of the tube surfaces with oxidative acid treatment. Although these methods are common, they damage the nanotube lattice and reduce strength and conductivity, leaving reactive acid groups on the nanotube surface which can cause further deterioration and considerably shorten SWNT lengths. The water-based ink formulation presented here relies on no covalent modification of the nanotubes and is one of the first to be applied to depositing conductive carbon nanotube networks. The SWNTs dispersed are some of the longest ever suspended in solution^{6–9} which has several advantages for subsequent electronic devices. One of the most important advantages is that over a given distance there will be less tube–tube junctions, reducing the impedance of the deposited material. Increased length will also improve the mesoscale alignment of the SWNTs, making ordered arrays easier to produce.

There has been interest in aligned arrays of SWNTs in a polymer matrix since Ajayan et al. demonstrated controlled alignment

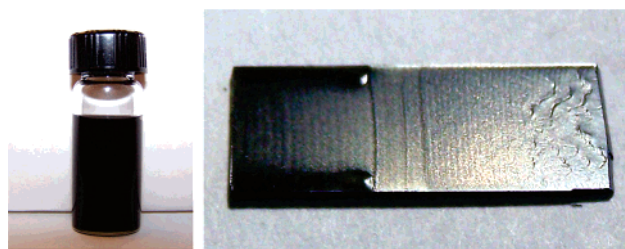


Figure 1. Vial of water-based ink after 1 month (left) and subsequent layer of ink deposited onto a silica substrate (right).

through stretching in 1994.^{10,11} Similar crack-alignment behavior has been shown in the fissures of dried aqueous suspensions of sodium dodecyl sulfonate (closely related to SDBS) with SWNTs,¹² although showing much less order and regularity than what is presented in this work.

Polyvinylpyrrolidone (PVP) and sodium dodecyl benzene sulfonate (SDBS) work synergistically to suspend carbon nanotubes, though the actual mechanism of this synergy is not completely understood.¹³ Fleming et al. showed that sodium dodecyl sulfonate (SDS) forms ordered hemicylindrical aggregates while PVP forms strongly bound globular aggregates on a graphite surface.¹⁴ It is well established that PVP wraps around the micelle aggregates formed by SDS¹⁵ in water. There are a wide variety of polymers,^{16,17} peptides, and proteins¹⁸ that will wrap the nanotube surface. Additionally it has been demonstrated by O'Connell et al. that PVP will wrap SWNTs in an ordered manner when combined with SDS in water. Microcalorimetry of the SDBS and PVP interaction showed no change in the presence of SWNTs (see Supporting Information). Therefore it can be reasonably assumed that polymer wrapping of the SWNTs is occurring by displacing the SDBS micelles from the nanotube sidewalls. Further it can be inferred that the SDBS will stabilize the polymer-wrapped SWNTs in water.

The weight of the carbon nanotubes used was determined by a back-measurement technique to prevent loss of nanotubes in transfer. (It should be noted that the SWNTs were obtained from Thomas Swan & Co. which have iron catalyst content <2 %). The surfactant SDBS and water are added and sonicated in a low-power bath sonicator for 30 min. After the 30 min sonication the SWNTs are dispersed in the water by the surfactant, and the polymer PVP is added along with sodium chloride. After a recurring optimization process it was found that 15 mg of SWNTs was optimal for preparation of ~20 mL of nanotube ink, avoiding precipitation of SWNTs. The corresponding amounts of PVP and SDBS for 20 mL of deionized water are 150 mg and 75 mg, respectively, with 12 mg of NaCl. The appearance of the well dispersed ink is opaque black (Figure 1), which is a result of the ~0.1 wt % SWNTs in suspension.

The water-based suspensions of pristine nanotubes prepared in this manner are remarkably stable over periods of several months (Figure 1), after which only a few minutes in a bath sonicator are

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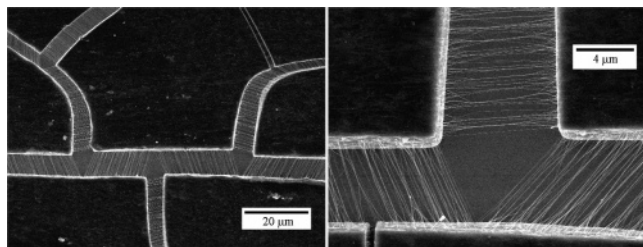


Figure 2. Two different views of the aligned SWNT arrays in the cracking of the dried ink material deposited onto silica substrate.

needed to redisperse any small amount of precipitate which has formed. These inks contain about 0.075% SWNTs by weight; the nanotubes are pristine and not significantly shortened by the brief low-power sonication. The ink dispersion is deposited onto a heavily doped silicon wafer capped with a silicon oxide surface in an oven at 80 °C for 48 h. After deposition the ink is then cured under a 60 °C lamp for several hours to remove any remaining moisture. Once the water has been evaporated during deposition, the resultant composite material is ~ 6% SWNT by weight.

Without the addition of the nanotubes, the dried composite material is not conductive. Therefore any conductance in the dried nanotube ink material can be attributed to the nanotube networks, since the catalyst content is less than 2% by weight of the dry nanotube material, the electronic contributions of iron should be negligible. Resistivity measurements for deposited ink material showed that for a layer thickness of 2 μm the resistivity (ρ) was equal to approximately 12 $\Omega\cdot\text{cm}$. With increasing thickness of the deposited ink layer, the resistivity drops to approximately 3 $\Omega\cdot\text{cm}$ for a 4–10 μm thickness. This suggests that the best results for this concentration of nanotubes is obtained from a deposition layer about 4 μm thick, which will give optimum conductivity using a minimum of SWNT material.

The deposited ink material exhibits significant cracking of the surface which can be seen throughout the sample. These cracks form during the curing process when the polymer–surfactant matrix contracts as it loses moisture. These fissures are one of the more interesting features of this ink, with bundles and even single nanotubes being suspended in ordered arrays across them as seen in Figure 2.

These ordered structures form throughout the dried composite material and occur in every dried sample prepared. Most of these fissures seen in this work are from one to several micrometers wide, which is a sufficient length to align the tubes perpendicular to the fissure axis. Occasionally fissures are found in excess of 30 μm wide with SWNT bundles aligned across them. The alignment of the SWNTs is due to the cracking mechanism. When a crack forms as two vertical planes in contact, SWNTs will contact these crack walls in the same location. As the crack widens, these points remain relatively stationary on the crack walls. The movement of these

walls is perpendicular to the vertical crack plane, pulling the SWNTs out of the composite matrix, stringing them across the crack. As a result of this movement, all of the SWNTs are normal to the vertical crack plane, and therefore all the SWNTs in a particular crack are parallel to one another.

Although the combination of PVP and SDBS is commonly used in the preparation of water-based ink formulations, this work is the first to use this formulation to create a SWNT conductive composite material. Additionally it is the first work to present controlled deposition of large arrays of well-ordered SWNTs from solution. This deposition process and the subsequent arrays are a major step toward creating functional SWNT devices from the solution phase.

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Supporting Information Available: Microcalorimetry data describing the SWNT-polymer–surfactant interaction mechanism. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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