# Ultrasonic Spraying of Carbon Nanotubes using NMP

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## ABSTRACT

We have developed a method for spraying smooth thin films of carbon nanotubes without the aid of surfactants. The nanotubes are suspended in N-methyl Pyrollidone (NMP) and sprayed onto a heated substrate using an ultrasonic spray nozzle that is rastered over the spray area. The resulting nanotube films are washed in NMP or water to remove residual impurities.

The film thickness is controlled by the number of rasters, and is measured by atomic force microscopy (AFM). The films are then characterized by scanning electron microscopy (SEM), and their conductivity is measured.

***Keywords:*** nanotubes, spraying, thin films, NMP

## 1. INTRODUCTION

Thin films of carbon nanotubes (CNTs) have several potential applications, especially in the fields of organic electronics and photovoltaics. There are a several ways to create thin films of carbon nanotubes, including filtration, [1] nanotube ink printing, [2] spin casting, [3] and spraying. [4,5]

To spray nanotubes, the nanotubes must first be suspended in a solution. This is difficult because nanotubes have strong Van-der-Waals interactions with each other, and form rope-like bundles. [6] Nanotube suspension is frequently achieved by vigorously sonicating a solution containing bundled nanotubes combined with surfactants or long chain polymers like Sodium Dodecyl Benzene Sulfonate (SDBS), [4] or Sodium Carboxymethyl Cellulose (CMC). [5] The surfactants are thought to wrap around the nanotubes as they "unzip" from their bundles. [6] Nanotubes have also been suspended in organic solvents such as isopropyl alcohol, but when sprayed this results in films that are not uniform. [4]

Once the nanotubes are suspended, the solution is ultrasonically sprayed onto a heated substrate that evaporates the solvent (usually water) leaving a film of nanotubes and surfactant. Removing the surfactant can be challenging, since attempting to redissolve it in water or another solvent can create defects in the film, and extreme care is required to avoid delaminating the film from the substrate. Alternatively, an aggressive nitric acid has been used to remove the wrapping polymer, leaving a very smooth collapsed nanotube film. [5] Sometimes, though such a step may be undesirable, as it can modify the properties of the nanotubes (especially functionalized nanotubes) or damage the substrate material.

To avoid these challenges, we suspended nanotubes in N-methyl Pyrollidone (NMP), which has been shown to form relatively stable dispersions of individual carbon nanotubes. [7] Using an ultrasonic spray system we sprayed the nanotube suspension onto a heated substrate, quickly evaporating the NMP and leaving a film of randomly oriented nanotubes. Using this process we have achieved relatively smooth films with single walled, multi walled, and functionalized nanotubes. The roughness of these films is comparable with some of the previously published films sprayed from SDBS surfactant dispersions [4] but not as smooth as films sprayed from CMC dispersions followed by a nitric acid rinse. [5]

## 2. METHODS

The the nanotube suspension was prepared by adding a few milligrams of nanotube powder (SWeNT SG nanotubes from Southwest Nanotechnology) into a beaker containing 100–200 mL of NMP and then sonicate the mixture for about 20 minutes using a 350 W horn sonicator from Cole Parmer with a 0.5 in. tip. Longer sonication times will result in a higher concentration of nanotubes, but with shorter tube lengths. [4] NMP does not suspend nanotubes as well as other solvents, [8] but sonication results in a dark black mixture. After centrifugation at 12,000 RPM (~17,000 g) we carefully collect the supernatant by pipetting the top 75% of solution, being careful not disturb the pellet of still-bundled nanotubes.

Solution concentration can be measured, or at least estimated, optically. We used a spectrophotometer to perform absorption measurements of a small cuvette of the suspension at 763 nm with an assumed absorption coefficient of 0.043 L/(mg*cm). [6] Typical concentrations range from 5-50 mg/L.

The solution is then loaded into a syringe pump connected to a Sono-Tek 250 kHz ultrasonic spray nozzle. The nozzle atomizes the liquid and a pressurized airflow directs the droplets down onto a heated substrate. We generally adjust the hotplate temperature to be around 180 °C. (NMP boils around 202 °C.)

We used an x-y stage to raster the nozzle over the substrate at a speed of 1 in/s, with a sweep separation of 0.25 in, and a working distance of 2–3 in. The nozzle power was 2.5 Watts with a flow rate of 0.25 mL/min. The flow rate, temperature, and speed were adjusted so that the NMP evaporates quickly and does not stay wet for the next pass. (Higher flow rates can be used with higher temperatures.)

## 3. CHARACTERIZATION

The resulting nanotube films were optically transparent or completely black, depending on the sprayed thickness. Characterization of the films was performed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM images showed that the nanotubes were randomly oriented, forming a uniform carpet (Figures 1, 4). AFM allowed us to characterize the film's roughness and thickness, which we measured by gently scratching a film and then measuring the edge. Film thickness ranged from about 200 nm to over a micron.

One challenge with making films with such dilute concentrations is that in the spraying process, the NMP solvent evaporates, leaving impurities native to the NMP or introduced in the processing deposited directly on the nanotubes. These impurities showed up under SEM as dark splotches (generally forming circular rings patterns, presumably at droplet edges as shown in Figure 2). These splotches went largely unnoticed when we were spraying concentrated solutions of SWeNT SMW100 multiwall nanotubes, but became clearly evident with the less-concentrated solutions of single wall nanotubes. We confirmed by AFM that these "coffee stains" were actually raised rings of material, as shown in Figure 3.

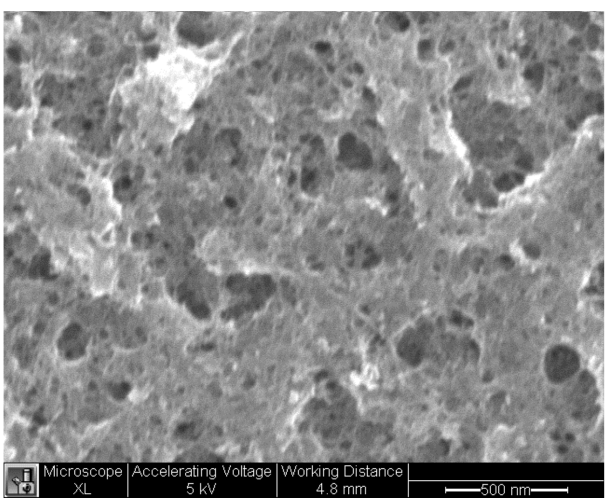


Figure 1: Sprayed film of SWNT's (SEM)

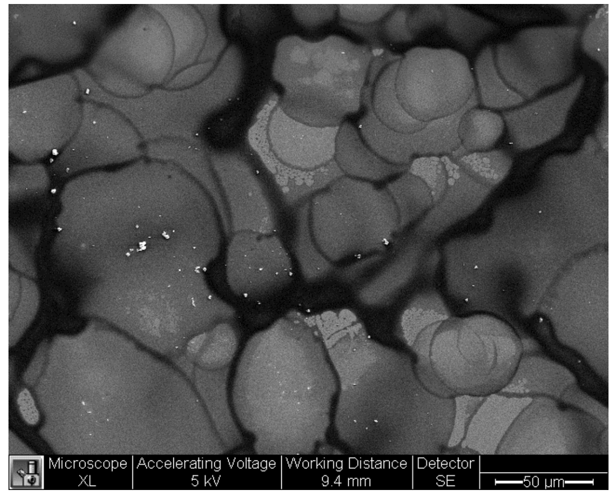


Figure 2: Droplet edges on sprayed film (SEM)

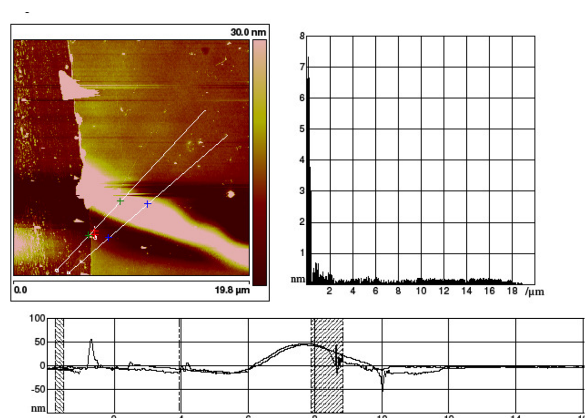


Figure 3: AFM showing height of a droplet edge

Because the impurities were presumably dissolved in NMP previously, we tried dipping the wafers in a hot NMP bath to re-dissolve them. Subsequent AFM and SEM images showed that the nanotubes had been cleaned up significantly (Figures 4, 5). The rings were gone, and the nanotube films looked much cleaner. We have also achieved similar results by soaking the film in hot water for 30 min.

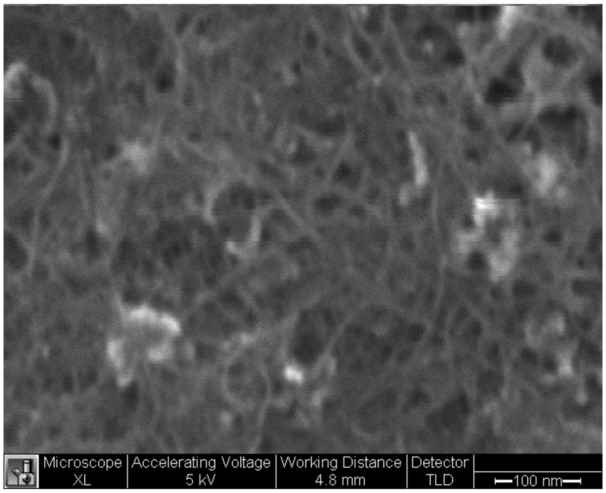


Figure 4: SWNT film after wash

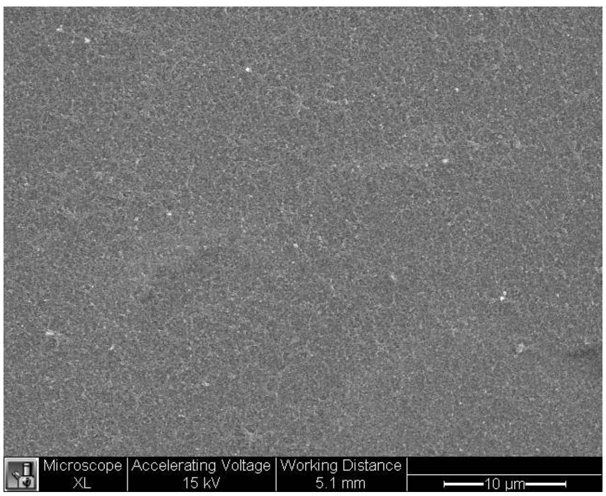


Figure 5: SWNT film after wash, showing absence of rings.

Energy-dispersive X-ray spectroscopy (EDX) analysis of the rings before the wash and the nanotube film after the wash showed that the rings were composed, at least in part, of a molybdenum containing compound (Figures 6, 7) that likely came from the nanotubes that were purchased from Southwest Nanotechnology. (The nanotubes were CoMoCAT tubes, grown from a molybdenum-stabilized cobalt catalyst.)

Film resistance measured by a 4-point probe, gave sheet resistances ranging from 2e3 to 6e3 Ω/□, and resistivities of around 0.1 Ω·cm.

AFM measurements (see Figure 8) of film thickness and roughness for several films is shown in Table 1. The roughness of these films ranged from 10–50 nm, which was comparable with some of the previously published films sprayed from SDBS surfactant dispersions [4] but not as smooth as films sprayed from CMC dispersions followed by a nitric acid rinse. [5]

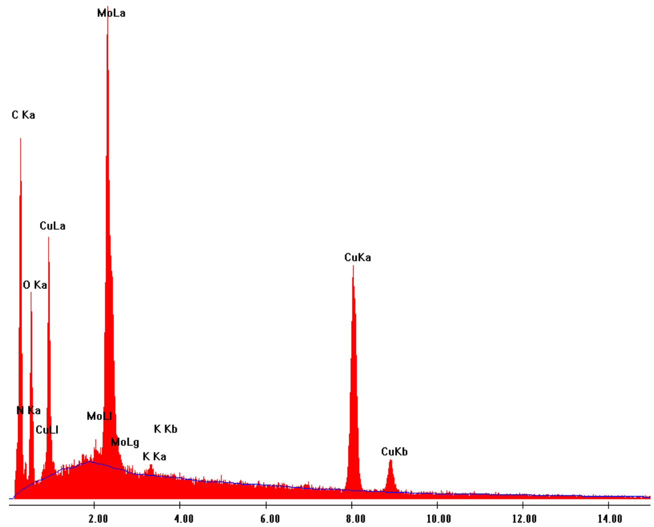


Figure 6: EDX of coffe ring showing Mo peak

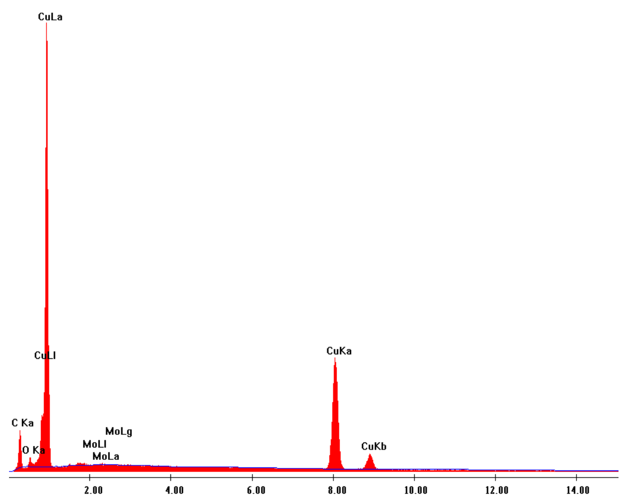


Figure 7: EDX of nanotube film after washing

| Film Thickness (nm) | RMS roughness (nm) |
|---|---|
| 220 | 42 |
| 300 | 17 |
| ~300 | 36 |
| 450 | 50 |
| 475 | 10 |
| 3000 | 43 |

Table 1: RMS roughness of nanotube films

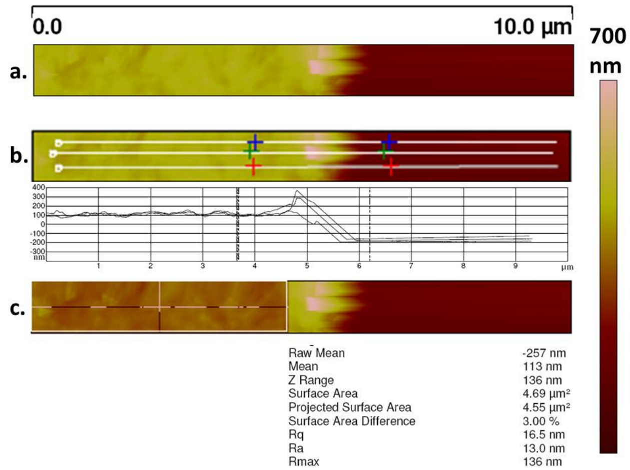


Figure 8: AFM measurements showing a) a scratched nanotube film; b) the thickness of the film; c) the roughness of the nanotube portion of the film.

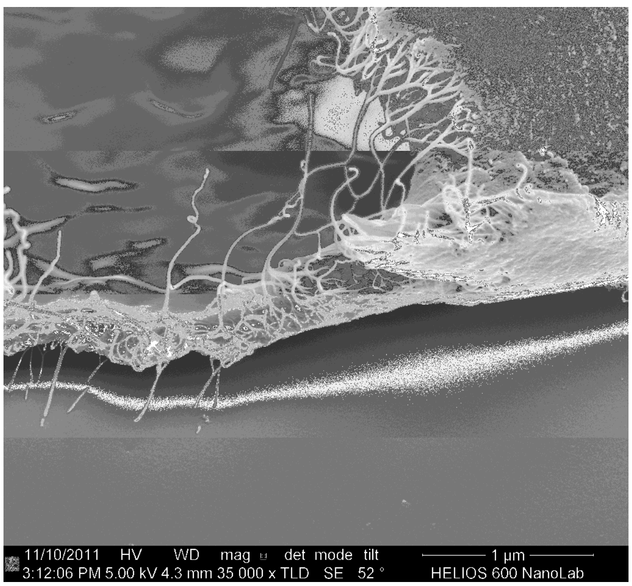


Figure 9: SEM image of a MWNT film that has been infiltrated with a polymer and then torn

## 4. CONCLUSION

Described is a method for ultrasonic spraying thin films of randomly oriented nanotubes without the aid of surfactants or wrapping polymers. Benefits of this method include not having to remove large amounts of surfactant from the sprayed nanotube film after deposition. Drawbacks include spraying at a high temperature of >180 °C, and long spray times because of low nanotube concentration. The technique works well with single wall nanotubes, multiwall nanotubes, and multiwall functionalized nanotubes.

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