Materials and Methods

The SWNTs used in this work were grown by dual pulsed laser vaporization and purified by 2.6M HNO₃ reflux (45 hr) followed by cross-flow filtration (S1). The cross-flow filtration used 0.2 micron pore size, hollow fiber nitrocellulose membranes (Spectrum Laboratories) and a make-up solution of 1 wt.% Triton X-100 surfactant, pH 11 NaOH, deionized (18 M Ω) filtered (0.2 micron) water. Prior to film formation the nanotubes were further dispersed by ~15 min. of bath ultrasonication in 1 wt.% Triton X-100 solution to a concentration of ~2 x10⁻³ mg/ml.

For nanotube film formation we employ 0.2 micron mixed cellulose ester (MCE) filter membranes in a vacuum filtration apparatus (Millipore). Care is taken in pouring the nanotube solution into the filter funnel to avoid bubbles on the solution surface. Bursting surfactant bubbles disrupt the film when it is still wet and fragile. The solution is filtered down and the vacuum kept on until the film is mostly dried (~20 min). Water added before the film has "set" risks disruption of the film uniformity. Residual surfactant left in the "set" film is subsequently washed away with purified water. Near complete removal of the surfactant is indicated by the initially bubble laden permeate stream going water clear in the vacuum funnel.

Several methods have been developed for transfer of the nanotube film to substrates. In one technique the filtration membrane with the attached nanotube film is placed directly into an acetone bath, where the MCE membrane quickly dissolves. The nanotube film, left drifting in the bath is picked up on a wire mesh screen and transferred to a clean acetone bath, where it is left for 20-30 minutes to remove dissolved MCE diffused into the porous film in the first bath. The process is repeated through several

baths to ensure effectively complete removal of MCE. The final bath is typically a cleaner solvent than acetone (e.g. methanol), which may be selected for its compatibility with the particular substrate. The drifting film is picked up out of the final solvent on the substrate of interest and allowed to dry. The difficulty in precisely aligning a film picked up by this method has encouraged development of an alternative approach. In this case the nanotube film, with its still attached MCE membrane is placed, while wetted with water, into contact with the substrate of interest and aligned as desired. The membrane is covered with several layers of porous paper and a flat plate, which are compressively loaded to keep the film flat as it dries. Surface tension of the water as the assembly dries brings the nanotubes and substrate into intimate contact. Oven drying at 90°C for 45 min is adequate. This gives sufficient adhesion of the nanotube film to the substrate that they can now be transferred into fresh (sequential) solvent baths to remove the MCE membrane. More recently, to conserve solvent, we have incorporated a vapor bath, which heats the solvent in the bottom of a tall container, generating solvent vapor. The substrate/nanotube/membrane assembly rests on a water-cooled condenser near the top of the (loosely covered) container where effectively distilled, condensing solvent continually washes the nanotube film. Because the solvents are highly flammable, safety dictates that sources of spark and flame be kept away from the fume hood housing the vapor bath.

S1. A. G. Rinzler, et al., Appl. Phys. A 67, 29 (1998).

On line supporting text:

Regarding other methods of neat SWNT film production, the nanotubes are not soluble in any known, pure, evaporable solvent. Drop drying consequently suffers from inhomogeneities as the nanotubes flocculate in the solvent. Additional inhomogeneities appear as surface tension causes the last of the drying solvent to collect into discrete droplets. Airbrushing can be viewed as operating between two extremes in which the solids, entrained in the solvent, arrive at the surface either very wet, or very dry (the bulk of the solvent evaporating as the droplets progress from the nozzle to the surface). The first case (wet deposition) leads to the same problems encountered in drop drying. The second case (nearly dry deposition) deposits discrete clumps of balled up nanotubes, with minimum interpenetration of nanotubes between the optically dense clumps. Achieving the perfect, intermediate, in-flight drying consistency is elusive. Flocculation of the nanotubes in the solvent prior to exiting the nozzle remains a problem, as does material loss in the over spray at the edges of the work piece and in the aerosol generated. The Langmuir-Blodgett deposition method could perhaps yield films of comparable homogeneity but its reliance on layer-by-layer deposition would make it exceedingly slow in obtaining comparably thick films.