Nanowicks: Nanotubes as Tracks for Mass Transfer

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Abstract. We have used a manipulation stage to electrically contact individual nanotube bundles coated with metal nanoparticles for *in-situ* studies in a transmission electron microscope. When electrical current is passed through a bundle, unusual mass transport is observed along that bundle. Nanocrystals melt and disappear from a given section, with a correlated growth of similar nanoparticles further along the bundle. This unusual phenomenon, termed *nanowicking*, may provide a method for controlled nanoscale mass transport.

True nanoscale device fabrication presents a formidable challenge, and the tools presently available are quite primitive in comparison to the requirements of an economically useful technology [1]. Fundamental to any construction project is the ability to deliver appropriate quantities of required building material to the assembly site. In this work we describe the observation of directed movement of nanoscale quantities of metals along multiwall carbon nanotube templates or tracks, which we term *nanowicks*. Fully realized, this method of material transport may prove to be useful in many applications, including the formation 'by-design' of electrical and mechanical joints in complex nanostructures.

Our experiments are performed in a Philips CM200 transmission electron microscope (TEM) located at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory. The sample consists of a boule of multiwalled carbon nanotubes rigidly mounted with silver paint to the sample stage. The boule typically has 25 nm each of indium and tin evaporated onto it, and has been annealed overnight at 120 degrees Celsius. As a result of the annealing, the tubes are covered with nanocrystals of indium/tin alloy with a relatively low (bulk) melting point. From a practical standpoint, this alloy resembles (but is not derived from) commercially available lead-free solder. The sample stage includes a piezo-driven XYZ nanomanipulator. Mounted on the manipulator and opposing the sample is a conducting tip which can be driven to approach a nanotube of our choosing. After a successful approach, electrical contact is made between the tip and sample. Driving a current through the nanotube introduces Joule heating (presumably concentrated at the resistive tip/sample contact). One application is to use the local heating effect together with the locally available indium/tin to solder the nanotube to the tip, forming a

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reliable mechanical and electrical junction. As we demonstrate below, however, a much more interesting phenomenon is also observed.

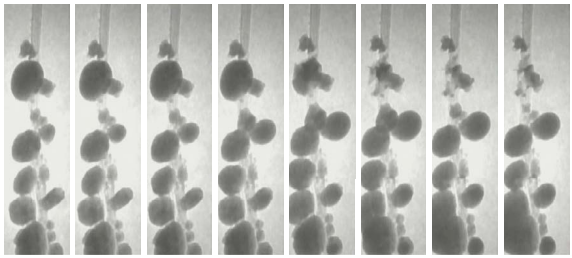

FIGURE 1. TEM image time series (time advances to the right). The field of view is approximately 360×1400 nm.

Figure 1 shows a time series of TEM video images taken from one of our experiments. A multiwalled carbon nanotube bundle has been approached from outside the field of view past the top edge of the images. The number of tubes in the bundle varies with position, but we estimate that there are about 6 tubes with characteristic diameters of 20 nm here. During this sequence, which spans about a minute, approximately 10 microamperes are passing through the nanotube bundle, and the total circuit resistance is ~ 30 kΩ. As time passes the mass on the bundle is observed to redistribute, as some globules shrink and others grow. Most striking is the near complete disappearance of a globule near the top of the images, and with corresponding enlargement of the globules directly beneath it. This behavior is repeated multiple times along the bundle. With a given power the metal will redistribute itself over a timescale of about a minute. After the movement has ceased, the applied voltage is increased and the transport is observed to continue from a new location further down the bundle. For this experiment the power dissipated varied from 5 to 200 μW.

We make four immediate observations from this experiment. First, mass always moves away from the tip-sample contact. Second, mass only appears where there is an obvious nucleation site, i.e. a preexisting crystallite. Third, although the TEM can not accurately measure mass or volume, it appears that mass is not lost. Using volume (derived from projected area, assuming spheres) and opacity as test metrics, we find that total nanoparticle mass is approximately conserved. At a minimum 80% of the mass that disappears from one site reappears elsewhere in our field of view. This observation implies directly that the mass is not moving around as vapor, nor even moving symmetrically up and down. Finally, the interesting movement is always localized in one place, not all along the bundle. Taking this transport process to be thermally activated, we conclude that there is a temperature gradient along the nanotube bundle. The most likely thermal source is localized heating at the contact point between the tip and tubes. Any Joule heating along the tube seems to be negligible in comparison.

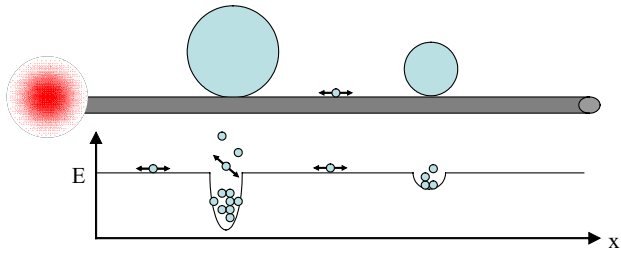

FIGURE 2. Toy model of the mass transport process.

The movement of molten metal globules immediately suggests the Young-Laplace equation as applied to two fluid spheres connected by a channel. The energy E associated with each sphere has a volume term and a surface term:

$$E \sim -aR^3 + bR^2 , \qquad (1)$$

where R is the radius of the sphere, and a and b are constants. This equation implies that such connected spheres, if similarly-sized, are not in mechanical equilibrium with respect to size changes. In order to minimize the total energy the smaller bubble will tend to shrink and the larger one will grow. Extending this argument gives the equation of Young and Laplace, which relates the pressure differential to surface tension and bubble radius: $\Delta P = 2\gamma/R$, where γ is the surface tension and R is the bubble radius. However, this mechanism does not agree even qualitatively with our observations. We see large globules shrink and small ones grow. In our experiments, the critical parameter appears to be position (i.e. local temperature), not globule radius.

The toy model shown in Fig. 2 thus presents itself. A nanotube bundle is locally heated on the left, with two representative liquid metal spheres distributed along its length. Each sphere, or nucleation site, represents a local minimum in the atomic potential. However, the minima are not always deep compared to kT. In the steady state, which obtains quickly, and without distributed heating, a linear temperature profile is expected. At some point along the bundle kT is comparable to the depth of the local minimum, and atoms are excited out of their bubble onto (or perhaps into the troughs between) the carbon nanotubes. There metal constituents randomly walk until they find the next spot where kT is small enough that they can condense.

Surprisingly, this primitive model can be used to extract an estimate for the thermal conductivity of our nanotube bundle. According to theoretical predictions, carbon nanotubes ought to be excellent thermal conductors, and much experimental work has been dedicated to confirming this technologically important property. While we do not know the details of the condensation potential, we can estimate that thermal energy differential $k\Delta T$ between a shrinking sphere and a growing one must be of the same order as the Young-Laplace energy $P\Delta V$ per atom. Furthermore, it follows from the heat equation that the temperature gradient $\Delta T/\Delta x$ is the heat flux Q divided by the thermal conductivity of the bundle κ. Thus, by combining our experimental

parameters (power dissipation ~ 30 μW, bubble separation Δx~ 100 nm, R ~ 100 nm, etc.) with the known characteristics of tin-indium alloy (density ρ ~ 7 g/cm^3, surface tension γ ~ 500 dyne/cm), we arrive at an estimate for κ. We find κ ~ 100 W/K m, which compares well with other values available in the literature on multiwalled carbon nanotube bundles [2-4]. Such a thermal conductivity implies a temperature differential of about 10 K between a site losing mass and one gaining mass, which is physically reasonable.

In conclusion, we report the discovery of nanowicks. Local temperature gradients, produced in our case by Joule heating, can be used to move or remove metal adsorbates on multiwalled carbon nanotube bundles. Possible applications of this process include the construction of electrical and mechanical joints in more sophisticated nanotube devices. Furthermore, we see that these bundles can support 'substantial' temperature gradients. By 'substantial' we mean that a temperature-driven transition between positive and negative mass divergence occurs over length scales of 100 nm or less. Finally, a toy model has been developed that provides an estimate of the bundle thermal conductivity in rough agreement with published values.

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