Nanopipettes for Metal Transport

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Here we demonstrate, for the first time experimentally, a nanopipette action for metals using multiwalled carbon nanotubes. The process relies on electromigration forces, created at high electron current densities, enabling the transport of material inside the hollow core of carbon nanotubes. In this way nanoparticles of iron were transported to and from electrically conducting substrates.

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The ability to manipulate materials on the nanometer scale is very important for the fabrication of future nanoscale devices. On the atomic scale the scanning tunneling microscope (STM) has evolved into a powerful tool for manipulations of single atoms and molecules [1–3]. Although such manipulations may seem to be the ultimate goal, it is less useful for the manipulation and fabrication of nanometer scale features containing thousands of atoms. On this scale carbon nanotubes have been proposed to function as "fountain pens" or atomic pumps [4] for atoms, providing a continuous source of material. In their model, hot electrons created by a laser would drive material contained inside a carbon nanotube. The possibility of an electromigration process was discarded due to the need for, supposedly, too high electrical fields.

Here we demonstrate experimentally how carbon nanotubes can be used as "nanopipettes" in order to deposit and retrieve solid material on a nanometer scale. The process relies on electromigration forces [5] forcing material to move inside the hollow core of a multiwalled carbon nanotube (MWNT).

Our setup is based on a recently developed instrument [6] providing a movable STM probe inside a transmission electron microscope (TEM) with a regular side-entry stage, here a CM200 field emission gun supertwin TEM with a Compustage. The STM is controlled by commercial software and electronics from Nanofactory Instruments AB [7]. A sharp gold tip is attached to the movable end of a piezoelectric tube (see Fig. 1), facing the sample and oriented perpendicular to the electron beam of the TEM. The sample consists of MWNTs filled with iron [8] that are attached to a metal wire by using electrically conducting glue. The movable tip is used to approach individual MWNTs and to make an electrical contact. By driving a high current through the nanotube the entrapped iron will start to migrate in a direction opposing the electric field, i.e., in the direction of the electron flow. Figure 2 shows a gold tip in contact with iron filled carbon nanotube inside the TEM. As a current is passed through the nanotube, the iron core first breaks up into smaller particles [Figs. 2(a) and 2(b)] and these then begin to move in the direction of the electron flow [Fig. 2(c)]. A movie of this process is available in the EPAPS [9]. It was also observed that the moving iron particles could change the microstructure of the nanotubes.

We have measured the threshold currents for iron diffusion in various sized nanotubes [Fig. 3(a)]. By studying the current, instead of the voltage, we can avoid the limitations of two-point measurements. The values follow a parabolic behavior, indicating that there is a threshold in the current density [of about 7×10^6 A/cm^2, Fig. 3(b)] rather than in the current. At these high current densities electromigration processes become important [10]. The electrical resistance of the nanotubes in this study ranged from about 4–40 kΩ (two-point measurement at the electromigration threshold with biases of around 1 V). The resistance depends on the dimensions of the tube and is plotted as a function of the nanotube diameter in Fig. 3(c). The data reveal a resistance that is inversely

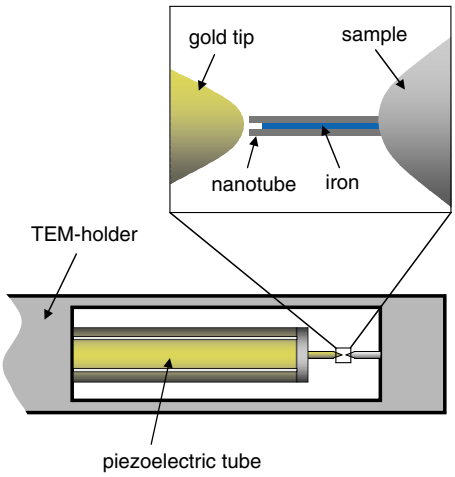

FIG. 1 (color). Schematic drawing of the setup used here. A sharp metal tip is attached to a piezoelectric actuator and is used to make electrical contacts to individual, iron filled, carbon nanotubes protruding from the sample.

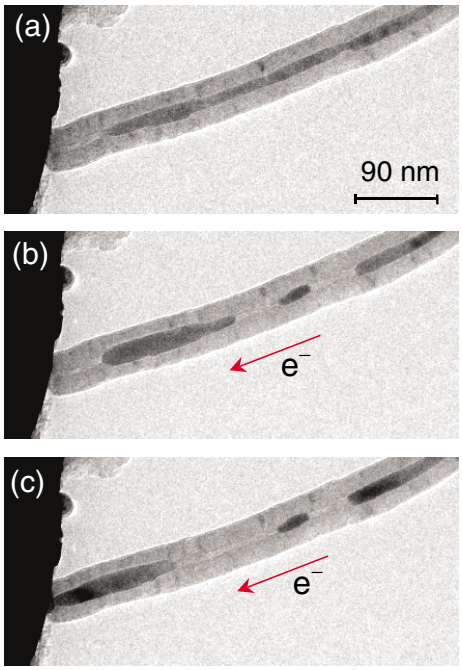

FIG. 2 (color). Sequential TEM images showing the induced movement of iron. A gold tip (on the left, positively biased) is in electrical contact with an iron filled carbon nanotube (on the right): (a) a current of electrons flows from the right to the left (at time $t = 0$); (b) the iron core breaks up (at $t = 2$ min); (c) iron migrates in the same direction as the electron flow (at $t = 3$ min).

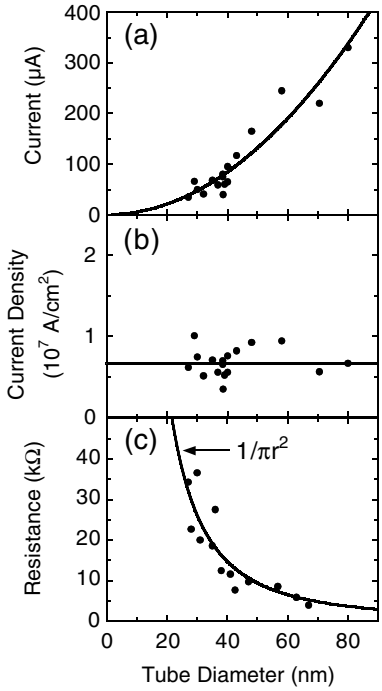

FIG. 3. Measured thresholds for iron migration: (a) current vs the nanotube outer diameter; and (b) current density (calculated using TEM images) vs the nanotube outer diameter. A threshold in the current density suggests a threshold in the electromigration force. The solid lines are a parabolic fit to the data in (a). (c) Measured resistance, at the electromigration threshold, vs the nanotube diameter. The solid line is a $1/\pi r^2$ fit, indicating a diffusive conduction mechanism.

proportional to the cross-sectional area. This is consistent with diffusive, multishell conduction in the tubes, i.e., all the walls are contributing to carrying the current (although only the outermost layers are in contact with the counter electrode). The variation of the resistance with the tube dimensions, including the length of the tubes, shows that these tubes are diffusive conductors with a resistivity of about $1 \times 10^{-5}\ \Omega\,\mathrm{m}$ [11]. This is a value comparable to that of natural graphite ($1.4 \times 10^{-5}\ \Omega\,\mathrm{m}$ [12]) and four point measurements of supported, unfilled, MWNTs ($0.9 \times 10^{-5}\ \Omega\,\mathrm{m}$ [13]). The diffusive conduction is likely caused by a high defect concentration, and the presence of iron, in our samples as opposed to arc-discharge grown ones [14].

By attaching a single MWNT to the movable probe [Fig. 4(a)] this can be used as a pipette to retrieve iron and to make iron deposits at selected sample positions. Figure 4 shows a series of TEM images were an iron nanoparticle is first retrieved, (b) and (c), and then deposited at a different location, (d) and (e), from where it can be retrieved again and deposited elsewhere, (f) and (g). This process can be repeated several times as long as the resistive heating is low enough in order to minimize thermal evaporation from the iron nanoparticle and thermal destruction of the nanotube. We have successfully made nanoparticle depositions onto gold and carbon substrates. The retrieval process is more delicate and requires low adhesion forces between the nanoparticle and the substrate. So far we have successfully performed repeated depositions and retrievals from carbon substrates while on gold substrates we have only been able to do deposits, due to the higher adhesion forces.

For electromigration phenomena [5], the force is often written as the sum of a direct electrostatic force, $\mathbf{F}_d$, and an electron mediated "wind force," $\mathbf{F}_w$:

$$\mathbf{F} = \mathbf{F}_d + \mathbf{F}_w = eZ_d\mathbf{E} + eZ_w\mathbf{E}, \tag{1}$$

where $\mathbf{E}$ is the electric field, and Z_d and Z_w are the effective valences for the direct and the wind force mediated processes, respectively. The direct force is present if there are charged particles (with an effective charge Z_d) or an accumulation of charge near the particle due to the scattering of current carriers. The scattering of current carriers against defects in the conductor will also create a wind force, due to momentum transfer, and this is included in the second term. Z_w, the "wind valence," then describes the force resulting from the momentum transfer caused by the scattering current carriers. The migration force can also be written as

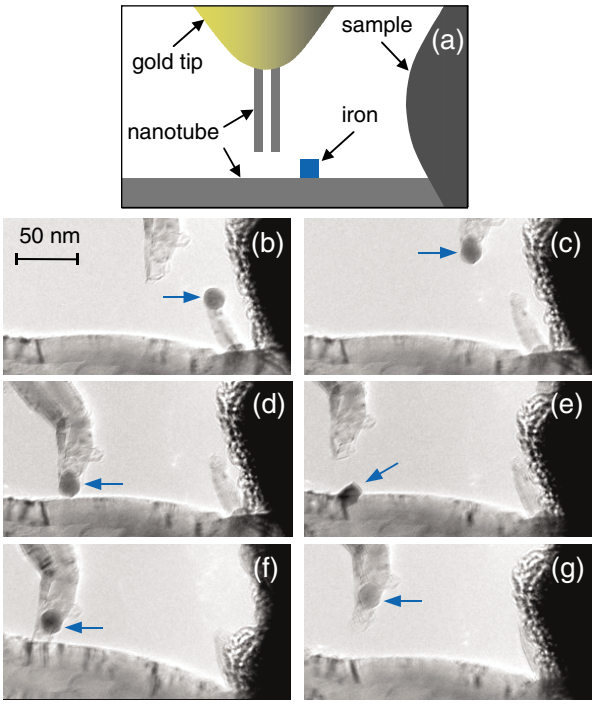

FIG. 4 (color). Sequential TEM images demonstrating the nanopipette action (the transferred iron is indicated by an arrow): (a) schematic drawing of the setup; (b) iron has been migrated to the end of a fixed nanotube; (c) iron is retrieved using a nanotube attached to the movable tip; (d) the nanotube is directed at the side of a large nanotube; (e) the iron is deposited. (f) The iron particle can be retrieved again and (g) it is ready to be deposited elsewhere.

$$\mathbf{F} = \mathbf{F}_d + \mathbf{F}_w = e\rho Z_d \mathbf{j} + e\rho Z_w \mathbf{j}, \qquad (2)$$

where ρ is the electrical resistivity and $\mathbf{j}$ the electron current density. Thereby the observed threshold in current density would indicate a threshold in the migration force that is independent on the particle size. This would appear in cases of self-diffusion driven by a dominating electromigration force (the influences of concentration and thermal gradients are negligible here since the direction can be controlled via the direction of the electron flow). Such a size dependence would also appear for the movement of solid particles since both the driving and frictional forces would be proportional to the area in contact with the nanotube. For self-diffusion in semiconductors [15], Z_d may dominate over Z_w, while, for metals, Z_d is low and the wind force is considered to be dominating [16]. In our case we would expect the iron to act as an electron donor (thus giving a $Z_d > 0$) and this would lead to a direct force on the iron particles that is oriented along the electric field direction. The observed migration is opposing the electric field and implies negatively charge particles or a dominating wind force from negatively charged current carriers (electrons), i.e., $Z_w < 0$. Theoretical work has shown that dopant atoms can indeed act as efficient scattering centers for electrons. They may even be the most important parameter determining the electrical conductance of carbon nanotubes [17]. In our case the diffusive conduction is in itself evidence of efficient electron scattering in the tubes [see Fig. 3(c)].

The high current densities employed here will lead to resistive heating. Temperatures of up to 2000 K have been measured in field emission experiments [18] at much lower currents, around 1 μA, than those used here. We have no way to measure the actual temperature of the nanotubes or the iron particles but the diffraction contrasts in the TEM images, during the migration, indicate that the iron particles remain crystalline during the migration (e.g., there is no change in contrast with and without applied current). Diffusion of atoms can quickly alter geometric shapes on the nanoscale, especially at elevated temperatures. We therefore believe that the iron moves in a combination of diffusion and movement of solid particles. The latter is further supported by the observation of structural changes in the nanotube structure in order to accommodate for the migrating iron particles.

Assuming an electromigration driven self-diffusion mechanism we can compare with values obtained for other systems. For metals [16] the wind valence, Z_w, is of the order of -10 to -20. If we in our case assume a value of -10 (per iron atom in contact with the inner carbon wall), we can get an estimate of the force $F_w \approx 1$ pN per atom, which corresponds to a shear stress of about 2×10^{-13} N/Å^2 $= 20$ MPa. This is about 1 order of magnitude lower than observed values for shear strengths on the nanometer scale for hard contacts [19], but comparable to values inferred from atomic-force measurements on graphite [20]. It should be noted that on this scale the friction force is proportional to the contact area, and a motion of solid iron particles is thus conceivable neglecting any additional forces due to the accommodation of the iron particles inside the tubes. The value is also nearly 3 orders of magnitude smaller than typical adhesion strengths between metals [21], which would explain why we have not been able to retrieve particles from metal substrates.

The process is likely to be a general effect such that other solids can be transferred to and from electrically conducting materials with sufficiently low adhesion forces. The transfer mechanism relies on thermally assisted electromigration, caused by high electron scattering at metal particles in the carbon nanotube structure. This process has previously been disregarded as a possible route to atom transfer (mainly due to an assumption that Z_d would dominate over Z_w) [4]. The electromigration can, however, be obtained irrespectively of a dominating Z_d or Z_w, as long as these do not cancel out. The method can be used to form 3-dimensional structures and provides a new route to the assembly of nanostructures and devices. Specifically, the iron nanoparticle deposition,

and repositioning, demonstrated here can serve as intentional seeds for in-place growth of carbon nanotubes in devices.

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