

# Self-Assembled Gold Nanowires from Nanoparticles: An Electronic Route Towards DNA Nanosensors

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## ABSTRACT

We present a new technique for fabricating gold nanowires using carbon nanotubes as the template. By applying an ac voltage to an electrically contacted single walled carbon nanotube, we generate highly non-uniform ac electric fields in the vicinity of the nanotubes. These ac electric fields serve to polarize 2 nm gold nanoparticles dispersed in solution. The induced dipole moment in the nanoparticles is attracted to the high-intensity field regions at the surface of the nanotube, thus causing a gold nanowire to grow on the surface of the nanotube. Interestingly, we find gold nanowires grow even on nanotubes that are not electrically contacted but in close proximity to the electrodes. Future applications of this work may include DNA sensors based on functionalized Au nanoparticles.

**Keywords:** Dielectrophoresis, nanowires, nanoparticle, nanotubes

## 1. INTRODUCTION

Nanowires and nanotubes represent fundamental building blocks in nanotechnology. A key challenge in the application of these devices in massively parallel integrated circuits lies in their manufacturability. In particular, at the moment it is difficult to control the spatial location of nanowires on a chip with nanometer resolution. Most research level manufacturing techniques consist of one of two approaches. In the first approach<sup>1</sup>, catalyst sites are lithographically patterned, and nanotubes grow from these sites. While a significant first step, this method does not achieve resolution on the placement of nanotubes beyond the limits of lithography. Additionally, the direction the nanotubes grow in is difficult to control. A second method consists of growing nanowires in bulk<sup>2</sup>, dispersing them in solution, and allowing the solution to evaporate on a solid surface. The nanowires are later contacted by lithography. While appropriate for research applications, this technique results in nanowires at random locations on a chip.

Some new techniques have been proposed and demonstrated to overcome some of these limitations. One technique uses dc and ac electric fields to align the nanowires during or after growth<sup>3 4 5</sup>. This controls their orientation and, to a lesser extent, their spatial position. A second, more promising technique is to chemically functionalize the ends of the nanowires so they bind to metal electrodes already in place<sup>6</sup>. This controls their orientation, and position, although where the nanowires bind are limited by the spatial limit of how well the chemical groups can be attached to the electrodes. Additionally, there may be significant boundary resistance if the functional groups (e.g. COOH, NH<sub>2</sub> moieties) are not conducting.

We present here a new technique of fabricating gold nanowires from the bottom up using pre-existing carbon nanotubes as the templates and engineering ac electric fields at the nanometer scale to assist a self-assembly<sup>7 8</sup> process. This technique, based on dielectrophoresis<sup>9</sup>, controls with nanometer resolution where the nanowires are fabricated, and they are in electrical contact with external electrodes immediately following fabrication. When combined with nanotubes that are located specifically on a chip using chemically functionalized end groups, this technique could be useful for massively parallel fabrication of low-resistance Au nanowires. We recently showed that nanoelectrodes could be used to generate the ac electric fields<sup>10</sup>, allowing us to manipulate 2 nm Au nano-particles with nanometer resolution using dielectrophoresis. Previous researchers have used lithographically fabricated electrodes. In this work, we, we take a step further and manufacture Au nanowires using this effect, using the carbon nanotube as the template, and demonstrate electric contact to these nanowires with no post-growth processing needed. Our method is robust, reproducible, and extremely simple. As such, it should find broad applicability.

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## 2. DIELECTROPHORESIS

Dielectrophoresis (hereafter DEP) is an electronic analog of optical tweezers<sup>11</sup> using audio frequency, RF, and microwave electric fields generated from microfabricated electrodes on a chip. The detailed theory of the effect of dielectrophoresis is presented in reference<sup>9</sup>, and an extensive literature review was recently written by one of us<sup>12</sup>. The physical principles of dielectrophoresis are well-established. In figure 1, the principle is illustrated schematically. If a polarizable object is placed in an electric field, there will be an induced positive charge on one side of the object and an induced negative charge (of the same magnitude as the induced positive charge) on the other side of the object. The positive charge will experience a pulling force; the negative charge will experience a pushing force. In a uniform field, as depicted in figure 1 A, the pulling force will cancel the pushing force, and the net force will be zero. However, in a non-uniform field, as depicted in figure 1B, the electric field will be stronger on one side of the object and weaker on the other side of the object. Hence, the pulling and pushing forces will not cancel, and there will be a net force on the object. This is the dielectrophoresis (DEP) force.

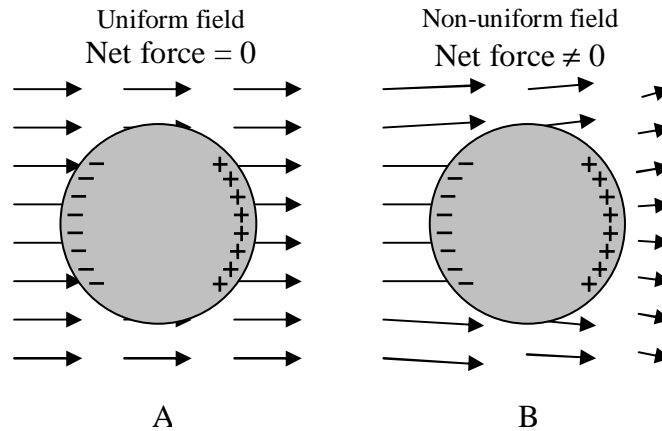


Fig. 1: Schematic description of dielectrophoresis.

More quantitatively, in the presence of an electric field gradient, there is a force on the dipole proportional to  $(\vec{p} \cdot \nabla) \vec{E}$ , where  $\vec{p}$  is the dipole moment, and  $\vec{E}$  the electric field. Since  $\vec{p} \propto \vec{E}$ , the force is proportional to  $(\vec{E} \cdot \nabla) \vec{E} \propto \nabla(\vec{E}^2)$ . There is thus a net DEP force in the direction of the higher intensity field. Since the direction of DEP force is not determined by the direction of the electrical field, an AC electric field is usually used to induce a dipole moment which experiences a force towards either the high-field intensity region (positive DEP) or the low-field intensity region (negative DEP). Generally, the DEP force is expressed as following:

$$\vec{F}_{DEP} = 2\pi v \epsilon_m K(\omega) \vec{\nabla}(\vec{E}_{RMS}^2) \quad (1)$$

where  $v$  is the volume of the particle,  $\vec{E}_{RMS}$  the RMS value of the electric field (assuming a sinusoidal time dependence), and  $K(\omega)$  the real part of what is called the Clausius-Mosotti factor, which is related to the particle dielectric constant  $\epsilon_p$  and medium dielectric constant  $\epsilon_m$  by

$$K(\omega) \equiv \text{Re} \left[ \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*} \right] \quad (2)$$

Here the star (\*) denotes that the dielectric constant is a complex quantity, and it can be related to the conductivity  $\sigma$  and the angular frequency  $\omega$  through the standard formula:

$$\epsilon^* \equiv \epsilon - i \frac{\sigma}{\omega} \quad (3)$$

From equation 2 the Clausius-Mosotti factor can vary between -0.5 and +1.0 for spherical particles. The particles move toward higher intensity field regions when the CM factor is positive and toward lower intensity field regions when it is negative.

### 3. NANO-MANIPULATION WITH CNTS

For the dielectrophoretic force to be of use it must dominate the Brownian motion, which can be treated as a random force whose maximum value is given roughly by<sup>9 13</sup>

$$F_{thermal} = k_B T / \sqrt[3]{v} \tag{4}$$

where  $k_B$  is the Boltzmann constant,  $T$  the temperature, and  $v$  the particle volume. The thermal Brownian motion becomes increasingly important compared to the DEP force as the particle size approaches the nanoscale. This sets a rather strict requirement on the minimum particle size that can be manipulated, and very large electric field gradients are needed to manipulate nano-sized particles. For electrodes made with traditional lithography, very high applied voltages are required to generate the large electrical field gradients needed in order for DEP to overcome the thermal motion of nanoparticles.

One way to solve this problem is to use extremely thin and narrow electrodes that can generate very large electrical field gradient. In this paper we use one-dimensional single walled carbon nanotubes as electrodes. The basic principles of our fabrication process are shown in Figure 2. An ac voltage is applied to a single walled carbon nanotube (SWNT) immersed in a colloidal solution of Au nanoparticles. The ac voltage generates an ac electric field perpendicular to the walls of the carbon nanotube. This ac electric field induces an (ac) dipole moment in the Au nanoparticle. For the cylindrical geometry of a nanotube, this is towards the surface of the nanotube. Thus, upon the application of an ac voltage, nanoparticles are trapped electronically at the surface of the nanotube. In our experiments on Au nanoparticles, the Au nanowire so formed remains after drying and after the voltage is turned off.

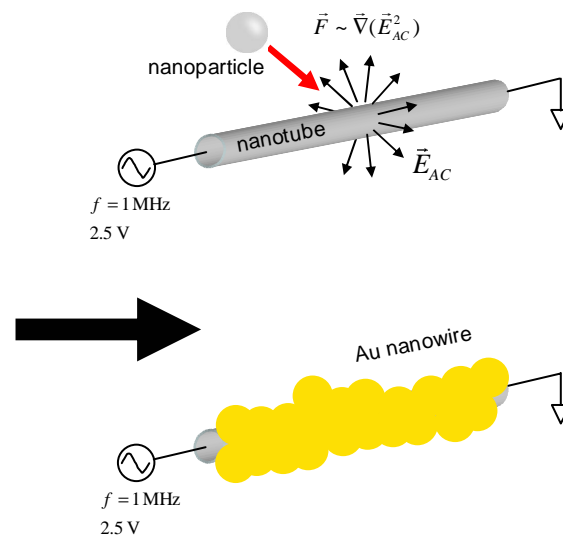


Fig. 2: Physical principle of the Au nanowire growth.

The radial electric field in the vicinity of the nanotube is given approximately by<sup>10</sup>

$$\vec{E}_{RMS} \sim \frac{V_{RMS}}{r} \hat{r} \quad (5)$$

where  $V_{RMS}$  is RMS value of the ac voltage applied to the nanotube,  $r$  is the radial distance away from the center of the nanotube, and  $\hat{r}$  is a unit vector pointing in the radial direction. From this, we can calculate the gradient of the electric field squared, finding:

$$\vec{\nabla}(E_{RMS}^2) \sim -\frac{V_{RMS}^2}{r^3} \hat{r} \quad (6)$$

Based on this simple calculation, for an applied voltage of 1 V, the DEP force at the surface of the nanotube experienced by a 1 nm dielectric particle can be estimated using equation 3 as the order of 100 pN, whereas the effective thermal Brownian motion random force for a 1 nm particle from equation 6 can be estimated as the order of 1 pN. This simple calculation, then, predicts that the DEP forces on even the smallest of nanoparticles should be large enough to overcome the thermal motion if nanotubes are used as the electrodes.

#### 4. EXPERIMENTAL METHODS

We now describe our technique in detail. Our nanotube growth procedure and recipes are described in detail in reference<sup>10,14</sup>. Briefly, our nanotubes are grown from lithographically patterned nanoparticle catalyst sites using chemical vapor deposition<sup>1</sup> (CVD) on an oxidized Si wafer. The grown carbon nanotubes were characterized by a scanning electron microscope (SEM) (Hitachi S-4700) using beam energies of 1 keV. Typical nanotube lengths were between 1 and 50 microns in length. AFM images of growth results show that the diameter of as grown nanotubes is less than 1.5 nm, indicating that the nanotubes grown from the nanoparticle catalysts are single walled nanotubes (SWNTs). After the location of the nanotubes with respect to the catalyst pads was determined under SEM, optical lithography was used to electrically contact the nanotubes using thermal or electron-beam evaporation of 10 nm Ti/100 nm Au and liftoff. The catalyst pads were used as optical alignment marks. The electrode geometry included a 5-10 micron gap between two Au electrodes. Each Au/Ti electrode was electrically contacted with a 25 micron gold wire using bond pads  $\sim 1 \text{ mm}^2$  located approximately 1 cm away from the gap. In some cases, more than one nanotube was contacted on both ends. In other cases, a nanotube would be contacted by one electrode but not the other. Additionally, there were cases where nanotubes were near the electrodes, but not contacted at all.

Two types of nanoparticles suspensions were used in this work: Au nanoparticles of diameters 2 and 10 nm. Suspensions of commercially available<sup>15</sup> colloidal Au ( $d=2 \text{ nm}$  or  $10 \text{ nm}$ ) were diluted  $10^9$  times with D.I. water ( $18 \text{ M}\Omega\text{-cm}$ ) to a density of approximately  $10^5$  particles/mL. No electrolyte was used in either suspension.

An aliquot of suspension ( $6 \mu\text{L}$ ) is dropped onto the chip containing the electrically contacted single walled carbon nanotubes. A sinusoidal ac voltage of 2.5 volts at 1 MHz for is applied to the electrodes which are already in electrical contact with the nanotubes, and the solution is allowed to dry while the ac voltage is left on. This typically takes about 5 minutes. The samples are then imaged in an SEM.

#### 5. RESULTS AND DISCUSSION

In Figures 3, 4, 5 and 6 we show typical SEM images of the Au nanowire grown after the solution dries. Note that the Au nanowire grows on nanotubes that are not contacted electrically on both ends. The nanoparticles clearly attach to the nanotubes, forming an electrical contact from one electrode to the next. In a control experiment, an aliquot of nanoparticle solution was allowed to dry on a chip where no ac voltage was applied. In that experiment, we found no evidence that nanoparticles bind to the nanotube. Thus, the Au nanowire formation is clearly controlled by the application of an ac voltage.

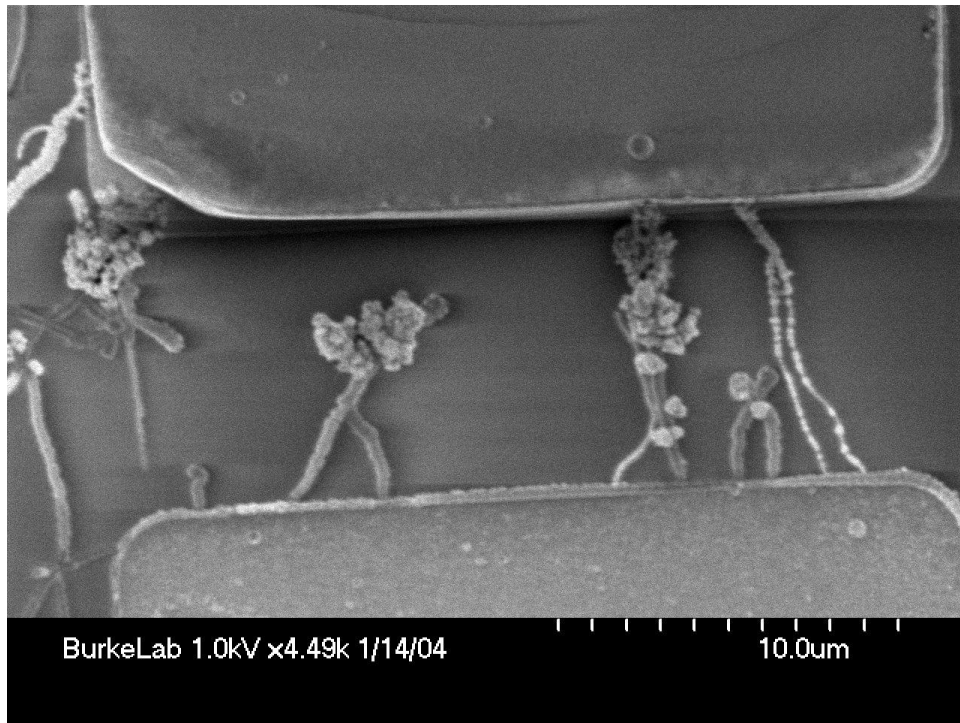


Fig. 3: SEM images of a SWNT after the Au nanowire growth, connected electrically with thin-film metal (Au) electrodes.

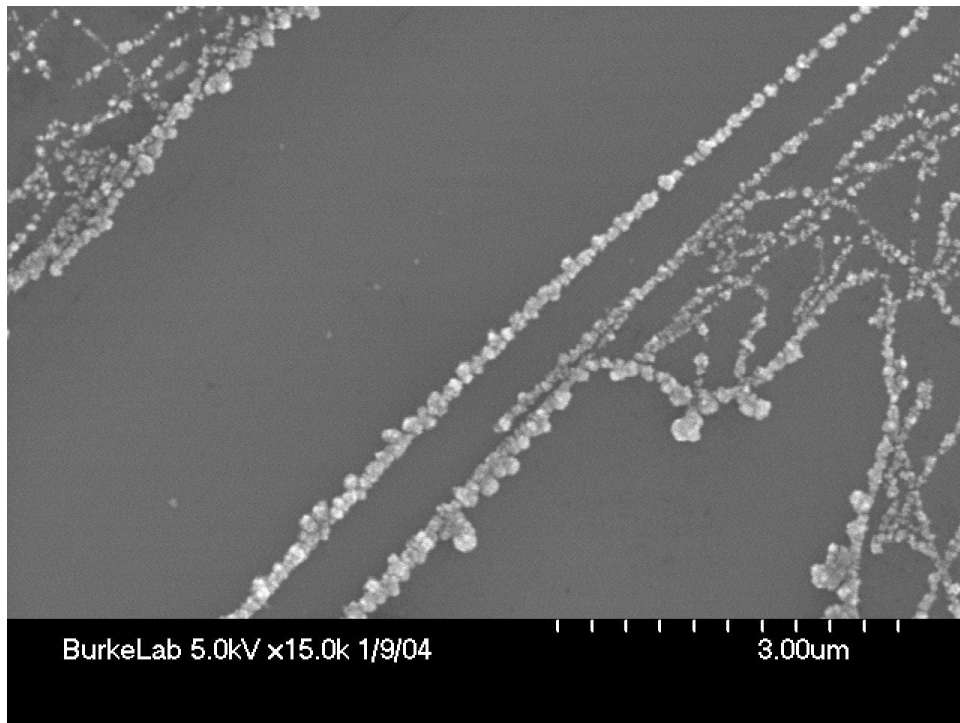


Fig. 4: Higher resolution image of Au nanoparticles on carbon nanotubes.

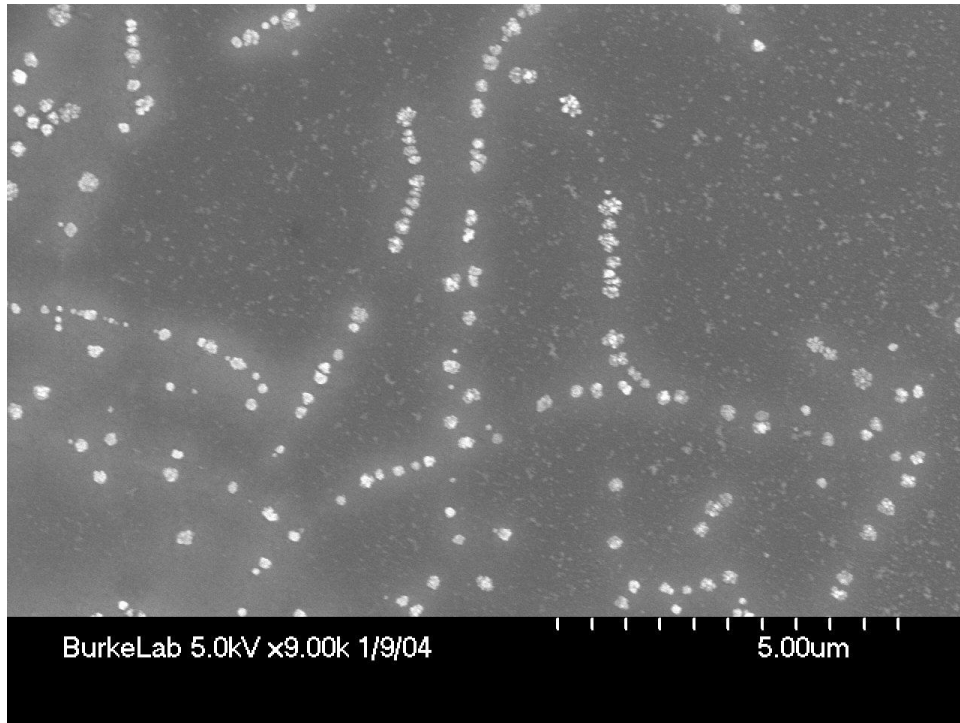


Fig. 5: Carbon nanotubes away from metal electrodes.

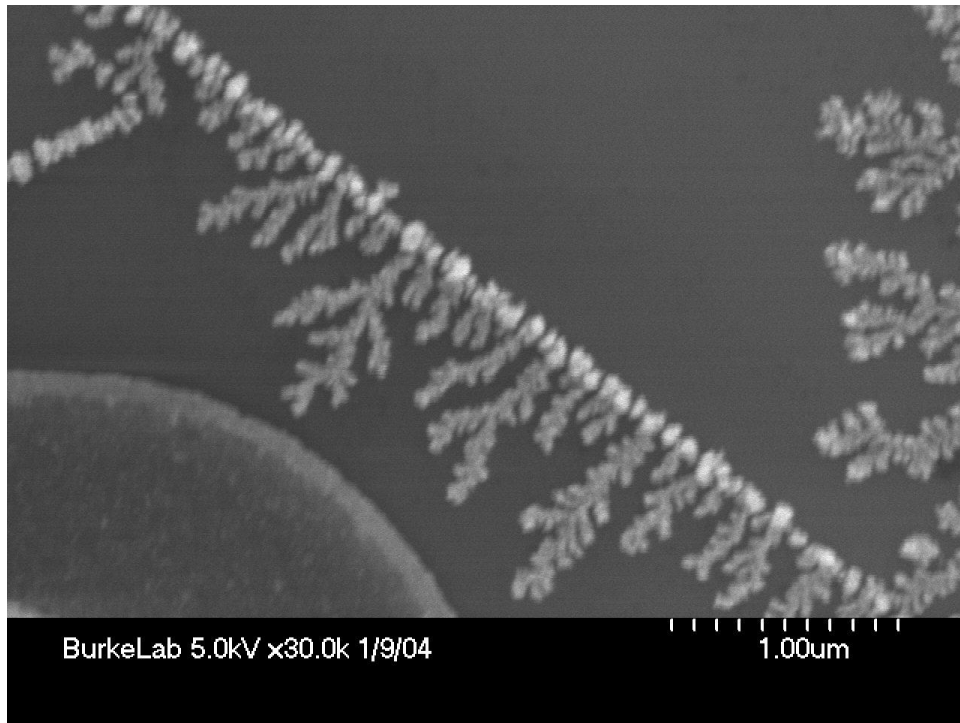


Fig. 6: Dendritic structures grown along a carbon nanotube.

For the sample shown in Figure 3, the resistance between electrodes due to the nanotubes before Au nanowire fabrication was  $\sim 5 \text{ M}\Omega$ . After trapping gold nanoparticles, we have measured the I-V curves at room temperature of the nanowire, and found the I-V curve to be linear to 5 volts, with a resistance of  $780 \text{ k}\Omega$ . This is a conductance about ten times higher than before the Au nanowire growth. While this result clearly demonstrates a significant increase in conductance due to the Au nanowire growth, there is still significant room for improvement, as we discuss next.

Interestingly, we have found that the nanotubes do not need to be in electrical contact with the electrodes in order for our fabrication procedure to work. We have found that, if the nanotubes are close to the Au electrodes but not in contact with them, that Au nanowires still grow on the nanotubes (see figure 4). This is most likely due to the fact that the nanotube significantly bends stray ac electric field lines in its vicinity; this non-uniform ac electric field is strong enough to trap the nano-particles. However, for the carbon nanotubes away from to electrodes, the ability of trapping gold nanoparticles decreases as shown in figure 5. This can be interpreted as the results of low intensity field. The dendritic structures have grown along a carbon nanotube (see figure 6). These Christmas tree-like structures grow only towards the metal electrodes where there is higher intensity field.

Clearly, the surface chemistry of the nanoparticles is of paramount important in this process<sup>16</sup>. In our experiments, we use D.I. water as the solvent, and no special functionalization of the nanoparticles was performed. However, in the future, it may be possible to fabricate custom resistance nanowires by careful chemical treatment of the nanoparticles before the self-assembly process is initiated. Amlani<sup>17</sup> has demonstrated negative differential resistance using  $100 \text{ nm}$  Au particles functionalized with self-assembled monolayers (SAMs). Indeed, in the future, our technique may be engineered to perform as sensitive chemical and biological sensors with chemical specificity, including DNA sensors. For example, chemically functionalized nanoparticles could be formed into nanowires using our technique, with the resistance determined by the surface chemistry of the Au nanoparticles.

## 6. CONCLUSIONS

We have demonstrated the use of nanotube electrodes to manipulate nanoparticles in solution using dielectrophoresis. Our method is robust, reproducible, and extremely simple. As such, it should find broad applicability. While our method relies on carbon nanotubes, in the future it should be possible to apply this technique using other moderately conducting nanostructures, for example biological nanostructures such as DNA and proteins. Since many self-assembled nanostructures have limited capacity to conduct electricity, our technique may be useful for transforming such nanostructures from poor to excellent conductors.

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