Manipulation of nanowires in suspension by ac electric fields

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Nanowires are potential building blocks for nanoscale devices. Manipulation of nanowires in suspension has been a formidable problem. Using ac electric fields applied to strategically designed microelectrodes, nanowires in suspension can be driven to align, to chain, to accelerate in directions parallel and perpendicular to its orientation, to concentrate onto designated places, and to disperse in a controlled manner with high efficiency despite an extremely low Reynolds number at the level of 10^{-5}. The manipulation of nanowires can also be applied to other small elongated entities such as carbon nanotubes. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1812364]

A variety of small entities of low dimensionalities, such as nanospheres, nanodisks, nanowires, and nanotubes, have recently been extensively explored due to their unique attributes and the capabilities to bind chemical and biological entities of interest. Nanowires are one type of small entities with a large aspect ratio. The geometrical shape and the multifunctionalities realized in multicomponent nanowires allow tuning of their physical, chemical, and electrical properties. For example, nanowires have been explored as chemical and biological sensors[1] and nanolasers.[2] Multilayered nanowires have been proposed as barcodes in bioassay,[3] and in gene therapy vessels.[4] Chemical and biological entities, even living cells, have been successfully attached to nanowires.[5]

These attributes notwithstanding, nanowires often need to be transported and assembled in suspension in order to exploit and capture their unique properties. To date, nanowires containing magnetic segments have been manipulated to some degree by applying external magnetic fields using electromagnets or permanent magnets over centimeter length scale.[6] Furthermore, the toxicity of magnetic metals such as Ni, and Co to living systems such as cells,[7] greatly limits the application of magnetic nanowires in biological systems.

In this work, we showed that with the application of ac electric fields with a suitable choice of suspension fluid and electrode geometries, metallic nanowires, regardless of being magnetic or nonmagnetic, can be efficiently driven to align, to chain, to accelerate in directions parallel and perpendicular to its orientation, to concentrate onto designated places, and to disperse on a microscopic scale. This effect is due to the interaction between the polarized charges on the small entities in suspension and the applied electric field, known as dielectrophoresis (DEP).[8,9] We first characterized quantitatively the DEP force on metallic nanowires due to the ac field. This information allows us to design special electrodes to transport nanowires in suspension with high efficiencies despite very low Reynolds number. We have exploited the high polarizability of metallic nanowires, the large aspect ratio of the nanowires that give rise to an enhancement of 380 times, and the low conductivity of the de-ionized (DI) water that further enhances the DEP effect. As a result, we have achieved extremely large DEP forces and been able to transport nanowires to designated places in a direction parallel and perpendicular to its orientation. Our method can also be applied to other small elongated entities such as carbon nanotubes.

We used gold (Au) nanowires made by electrodeposition through a nanoporous template from gold plating solution (Orotemp24, Technic Inc.) at −1 V(Ag/AgCl) with a nominal diameter of 300 nm and lengths between 10 and 15 μm. The Au nanowires were used because Au is conducting, nonmagnetic, chemically inert, adaptable to thiol-chemistry functionalization for biopatterning and biomolecular detection.[10] More importantly, the large aspect ratio of nanowires greatly amplifies the polarization due to the ac electric field by nearly 400 times than spherical particles. The Au nanowires of low concentrations were suspended in DI water with a low conductivity of 2.4 μSiemens/cm and placed in regions of Au electrodes patterned by laser micromachining on quartz substrate. The motion of individual nanowires can be captured by an optical microscope equipped with a video camera operating at 30 frames per second.

The motion of nanowire (NW) of length L and radius a_{NW} in a fluid by an external force F is governed by

$$ma = F - bv, \tag{1}$$

where a and v are, respectively, the acceleration and velocity of the nanowire. The last term in Eq. (1) is the drag force due to viscosity[11] with $b=3\pi\eta LD$, where η is the viscosity and D is the shape factor, which for a nanowire of an aspect ratio of 33 is 0.18. For a constant F or no force, the motion of the nanowire is dictated by $m/b \approx 2a_{\mathrm{NW}}^2\rho_{\mathrm{Au}}/\eta$, where ρ_{Au} is the density of the Au. For a 10 μm Au nanowire of a radius of $a_{\mathrm{NW}}=0.15$ μm, m/b is only $\approx 10^{-6}$ s. In the absence of ex-

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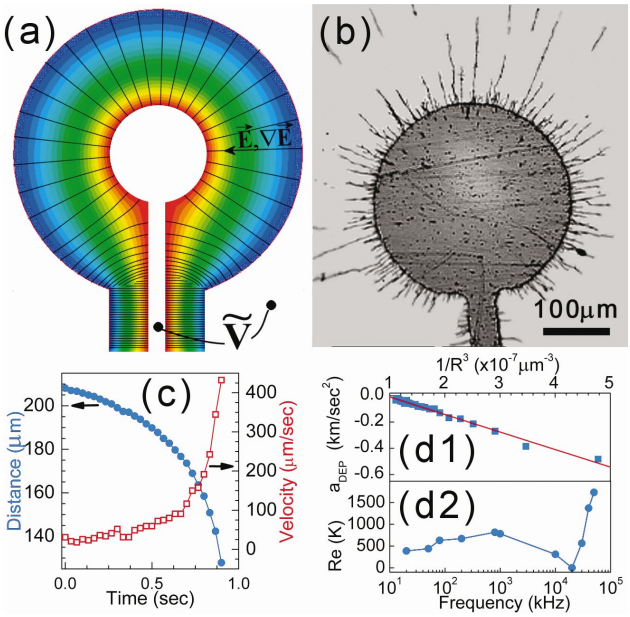

FIG. 1. (Color) (a) Simulated electric field distribution between the Au electrodes in white, with electric potential expressed in color contour and electric field in black arrows. Electric field and its gradient are both along the radical direction. (b) Nanowires aligned chained and attached to the inner electrode. (c) Measured displacement and calculated velocity versus time of a nanowire at 10 V and 40 MHz. (d1) DEP acceleration versus $1/r^3$ at 40 MHz, 10 V. (d2) Frequency dependence of Re(K).

ternal force, a nanowire with an initial velocity of $v_i = 100\ \mu$m/s will be stopped within a short distance of $v_i m/b \approx 1$ Å in about 10^{-6} s. This illustrates the fundamental difficulty of moving small entities in suspension with extremely small Reynolds numbers of about 10^{-5}. A small Reynolds number dictates that the drag force due to viscosity will overwhelm the motion of the entity. To efficiently transport nanowires in suspension, one needs not only a large force but also a force that increases in magnitude. This has been accomplished using the ac-driven DEP force with specially designed electrodes.

The current theory of DEP on dielectric materials can be readily extended to metallic spheres. It turns out that both the characteristics of the metallic spheres and the medium in which the spheres are embedded contribute to the DEP effect. Our calculation shows that the electric polarization of metallic nanowires (10 μm in length, 0.3 μm in the diameter), in comparison with spherical metallic particles, is enhanced by a factor of 380 due to its high aspect ratio.[12] The very low conductivity of the DI water also enhances the DEP effect.

In order to determine transport nanowires in suspension quantitatively, we patterned circularly concentric electrodes [shown in white in Fig. 1(a)] with inner and outer radii of 70 and 270 μm, respectively, with an opening for contacting the inner electrode. In this geometry, both the electric field and its gradient are along the radial direction with known dependences of $1/r$ and $1/r^2$, respectively, where r is the distance from the center of the circles. The calculated electric field between the electrodes, also illustrated in Fig. 1(a), shows that the circular symmetry between the electrodes is largely maintained except near the openings of the electrodes. Under an ac voltage with f larger than 10 kHz, the nanowires align radially and accelerate until they are attached and chained to the inner electrode [Fig. 1(b)].

In circularly concentric electrodes, the DEP force on nanowires in DI water is expressed as[8] $(\boldsymbol{p}_{\text{eff}} \cdot \nabla)\boldsymbol{E}$, which is along the radial direction with the magnitude of

$$F_{\text{DEP}} = \frac{V_{\text{rms}}^2}{\left(\ln \frac{r_2}{r_1}\right)^2} V_{\text{NW}} \varepsilon_m \text{Re}(K) \frac{1}{r^3}, \tag{2}$$

where $\boldsymbol{p}_{\text{eff}}$ is the polarization of the nanowires and is proportional to $\boldsymbol{E}$, V_{rms} the rms value of the applied ac voltage, r_1 and r_2 the radii of electrodes, V_{NW} the volume of the nanowires, $\varepsilon_m = 80$ the dielectric constant of the fluid, r is the distance between nanowire and the center of the circular electrode, and Re(K) is the real part of the Clausius-Mossotti factor, which includes the enhancement factor of 380. This form of F_{DEP} enters Eq. (1).

Using circular electrodes, the motion of an individual nanowire can be captured using the video camera by measuring the displacement versus time. One example of the result is shown in Fig. 1(c), from which the velocity v and the acceleration a can be readily determined by differentiation. A nanowire traverses 80 μm in 0.9 s, and acquires a final velocity of 0.43 mm/s and acceleration of 3 mm/s^2 before it reaches the inner electrode. These are very high values for the motion of a small entity and is far more effective than the reported manipulation by magnetic field.[6] The values of F_{DEP} can be determined from Eq. (1) using the value for the drag force. The value of $a_{\text{DEP}} = F_{\text{DEP}}/m$ is plotted as a function of $1/r^3$ in the Fig. 1(d1). The linear relation confirms the predicted $1/r^3$ dependence shown in Eq. (2). Note that at 40 MHz and $V_{\text{ac}} = 10$ V, a_{DEP} as much as 0.5 km/s^2, five orders of magnitude higher than the actual acceleration, has been achieved by the ac electric field alone. This gigantic acceleration is much reduced due to the overwhelmingly large drag force, a result of the extremely small Reynolds number.

From the slope in Fig. 1(d1) and Eq. (2), we have determined the values of Re(K), which, as expected, is not a constant but depends strongly on frequency as shown in Fig. 1(d2). The value of Re(K) shows a maximum of 781 at 1 MHz, and more interesting, reduces to nearly zero at 20 MHz before increasing rapidly to 1733 at 50 MHz. This strong frequency dependence is due to the fact that the conductivity, the permittivity of the media, the nanowire, and hence the polarizability of the nanowires in the media are all frequency dependent. The small measured value of Re(K) near 20 MHz may be due to circuit absorption. The strong frequency dependence can also be exploited to separate materials with different ac characteristics.

For the circular electrodes described above, the electric field and its gradient are in the same direction. We have designed a quadrupole electrode to accelerate the nanowires in the direction perpendicular to their orientation, capitalizing the fact that the alignment and the acceleration of the nanowires are along the electric field and its gradient direction, respectively. For the quadrupole electrodes shown in Fig. 2(a), electrodes on the opposite sides were electrically connected and between them $V_{\text{ac}} = 10$ V at $f = 1$ MHz was applied. The calculated electrical field (shown by the lines) and the equipotential curves (shown by the color contours) are also shown. Note that the electrical field gradient was designed to be perpendicular to the electric field and be directed away from the center.

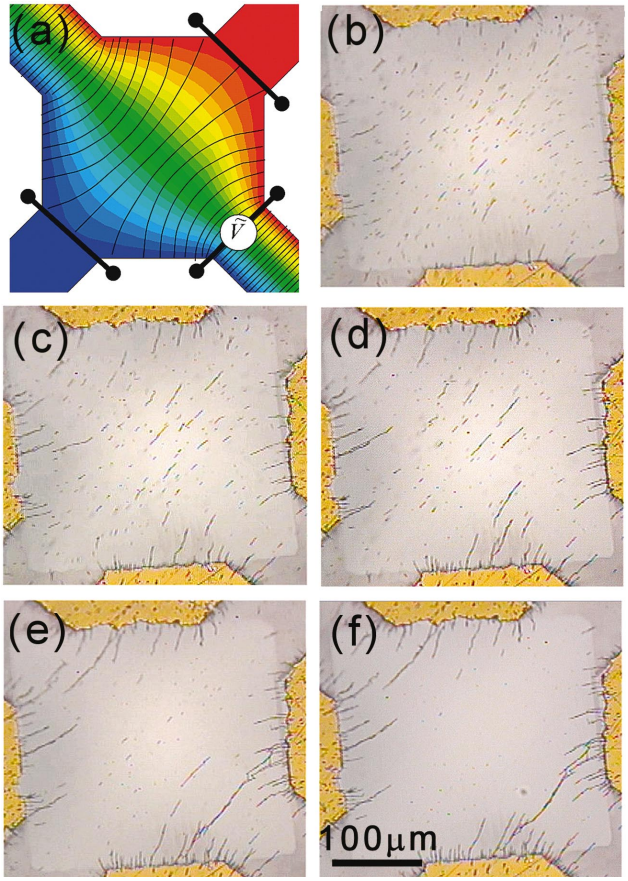

FIG. 2. (Color) (a) Simulated potential (in color contour) and electric field (in black lines) in a quadrupole with connected pairs of electrodes. Images of nanowires at (b) 2, (c) 6, (d) 10, (e) 59, and (f) 180 s after 10 V at 1 MHz has been applied.

After the nanowires were in place, the results shown in Figs. 2(b), 2(c), 2(d), and 2(e) were taken at 2, 6, 10, and 59 s, respectively, after the application of the ac voltage. The aligning of the nanowires along the *E* field direction occurred essentially instantaneously [Fig. 2(b)], with significant chaining at 6 s [Fig. 2(c)]. In this respect, the alignment of the nanowires reveals the actual *E* field. Simultaneously, the nanowires were also being transported towards the high-field regions, moving perpendicular to the alignment direction and thus being depleted from the central region and to congregate at opposite gaps between the electrodes as shown in Figs. 2(d) and 2(e). The alignment and the assembly of nanowires clearly demonstrate the different roles of the electric field and its gradient. The nanowires are essentially completely depleted from the center and collected to the electrodes in 3 min [Fig. 2(f)]. When the ac voltage is turned off at any time during this process, the nanowires immediately stop at their locations.

In summary, we have demonstrated a method for manipulating metallic nanowires, including assembly, chaining, acceleration in a direction parallel or perpendicular to its orientation, concentration onto designated places, and dispersion by designing ac electric field distribution. Our experiments have clearly demonstrated that nanowires align with the electrical field, but accelerate along the field gradient direction. The phenomena can be well described by the DEP theory extended to metallic entities. The transport of nanowires can be used in a wide range of applications involving small entities using special electrode geometries. The lithographically patterned electrodes, compatible with microelectronics, are far more advantageous than manipulation using the external magnetic fields.[6] The method described here also provides a way to study phenomena occurring in systems with very low Reynolds numbers, from transport of small entities to the studies of motion of microorganisms. The manipulation of nanowires shows in this work can also be applied to other small entities with a large aspect ratio, such as carbon nanotubes.

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