

# Gold Nanoparticle Super Assembly by Dielectrophoresis

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## ABSTRACT

Dielectrophoretic assembly of nanoparticles has great utility in creating intricate designer nanoscale structures. Dielectrophoresis of gold nanoparticles has been used to create nanowires for electronics, high surface area electrodes for sensors, and nanoelectrode nanogaps for molecular electronics. Despite the utility of this technique, little is known about the mechanisms governing different assembly morphologies. This study combines experimental dielectrophoretic capture of gold nanoparticles suspended in water with a theoretical overview of the forces influencing deposit morphology. We used a planar electrode geometry and studied the assembly process using transmission electron microscopy. It appears AC electroosmotic fluid flow and the electrical double layer have a major influence on deposit morphology.

**Keywords:** gold nanoparticles, dielectrophoresis, nanofabrication, nanoelectrodes, AC electroosmosis

## 1 INTRODUCTION

Fabrication of novel nanostructures and their assembly into nanodevices and nanosystems has recently received considerable attention. Dielectrophoresis offers an inexpensive and straightforward means for both the nanofabrication and assembly of nanostructures and systems [1]. Dielectrophoresis describes the force that a nonuniform AC electric field exerts on neutral (uncharged) matter and is widely employed in the manipulation and sorting of biological and synthetic particles. Of particular importance in the fabrication of useful nanodevices is the dielectrophoresis of metallic nanoparticles, such as gold nanoparticles. The utility of highly conductive metallic nanostructures has prompted several investigations into using dielectrophoresis as a means to assemble precision nanostructures to create nanogaps for molecular electronics [2], nanowires and microwires for electrical connection to devices and components [3, 4], and high surface area electrodes for sensor applications.

We examined key forces acting on gold nanoparticles subjected to an AC electric field and describe the effects of these forces. Transmission electron microscopy (TEM) of

gold nanoparticles deposited under the influence of AC electric fields with varying frequencies and magnitudes reveals several key aspects of nanoparticle deposition. AC electroosmosis and double-layer effects at the electrode-solution interface will be shown to have a major influence on nanoparticle motion and the structure that is subsequently deposited. Control over the deposition parameters, particularly the frequency, allows the fabrication of several distinctly different types of technologically interesting nanostructures.

## 2 FORCES ON NANOPARTICLES

Several forces operate on gold nanoparticles and their the suspending medium when an AC electric field is applied. The most influential of these are reviewed here with some theoretical and experimental assessment of their importance. One of the most striking parameters is the frequency of the AC electric field (Figure 1).

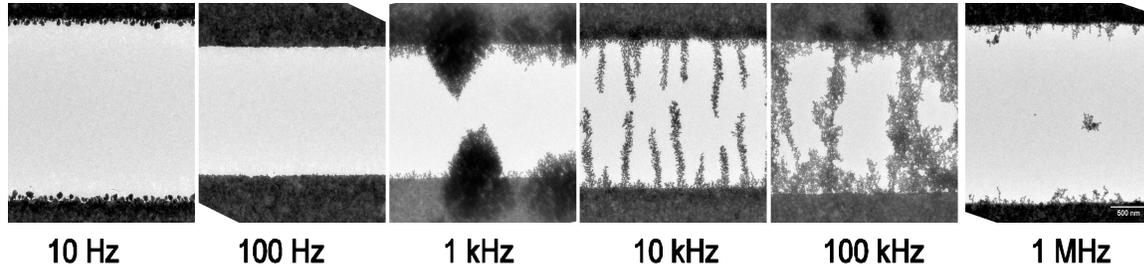
### 2.1 Dielectrophoresis

The primary force driving nanoparticle capture is dielectrophoresis (DEP). Neutral dielectrics in a nonuniform electric field experience a time-averaged dielectrophoretic force given by

$$\langle \vec{F}_{DEP}(t) \rangle = 2\pi\epsilon_m a^3 \text{Re}[K(\omega)] \nabla |\vec{E}_{rms}|^2, \quad (1)$$

where  $\epsilon_m$  is the permittivity of the medium,  $a$  is the radius of the nanoparticle,  $K(\omega)$  is the Clausius-Mosotti factor, and  $E_{rms}$  is the rms value of the electric field. This force is proportional to the volume of the nanoparticle and the gradient of the magnitude of the electric field squared. The Clausius-Mosotti factor,  $K(\omega)$ , represents the complex polarizability of the particle and is given by

$$K(\omega) = \frac{\epsilon_p - \epsilon_m - \frac{j}{\omega}(\sigma_p - \sigma_m)}{\epsilon_p + 2\epsilon_m - \frac{j}{\omega}(\sigma_p - 2\sigma_m)} \quad (2)$$



**Figure 1.** TEM micrographs of 15.5nm nanoparticles deposited with frequencies ranging from 10 Hz to 1 MHz at 7.5 V. Nanoparticles were deposited between parallel electrodes with 3  $\mu\text{m}$  spacing (visible at top and bottom of each micrograph). At low frequencies we saw uniform deposition, while at high frequencies single particle wide pearl chains were formed.

where  $\epsilon_p$  and  $\epsilon_m$  are the permittivities of the particle and medium,  $j$  is  $\sqrt{-1}$ ,  $\omega = 2\pi f$  is the angular frequency, and  $\sigma_p$  and  $\sigma_m$  are the conductivities of the particle and medium. At low frequencies the conductivity terms are dominant, while at high frequencies the permittivity terms are dominant. Positive values of the Clausius-Mossotti factor correspond to a time averaged force pulling the nanoparticle toward regions of high field strength. Negative values of the Clausius-Mossotti factor correspond to time averaged force pushing the nanoparticle toward regions of low field strength. For conductive nanoparticles in water, this factor typically shows a sharp crossover from +1 at low frequencies to -0.5 at high frequencies. The frequency at which this crossover occurs is related to properties of both the nanoparticles and their medium.

A benefit of choosing gold nanoparticles in water for this study is that this  $\text{Re}[K(\omega)]$  crossover occurs at a frequency around  $10^{18}$  Hz, well above any reasonably obtainable electrical excitation frequency. Therefore  $\text{Re}[K(\omega)]$  may be assumed to be +1 under all experimental conditions, i.e. the dielectrophoretic force is always attractive.

## 2.2 Electrode Polarization

Electrodes in solution with an applied voltage attract and repel charged species near the electrode surface, creating image charge in a process known as electrode polarization. This effect screens the electrode potential so the effective field far from the electrode is reduced. If the electrode/solution interface is modeled as a simple capacitance in series with a resistance, the impedance of the interface may be expressed as

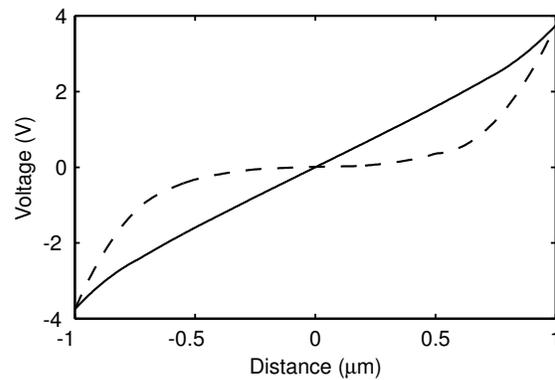
$$Z = 1/(j\omega C_E) + R_S + 1/(j\omega C_E). \quad (3)$$

The effective voltage divided across the bulk of the solution is then

$$V_{\text{eff}}/V_{\text{rms}} = R_S / (R_S + 2/(j\omega C_E)), \quad (4)$$

Graphing equation 4 as a function of frequency shows the majority of the voltage drops across the interface at low frequencies while at high frequencies the solution sees the full applied voltage. The transition between these two regimes occurs at a frequency of 4 kHz for typical values of  $R_S = 120 \text{ k}\Omega$  and  $C_E = 640 \text{ pF}$ .

Interfacial polarization therefore creates different electrical field distributions for low and high frequencies (Figure 2). At low frequencies, the magnitude of the field gradient is large close to the interfacial layer. At high frequencies, the magnitude of the field gradient is smaller but is more evenly distributed across the electrode gap. The planar electrode geometry also causes the gradient to be larger closer to the edge at all frequencies, because of the high radius of curvature at the edge, as seen in the slight curvature of the solid line in Figure 2.



**Figure 2.** Voltage profile inside of a 2  $\mu\text{m}$  electrode gap with 7.5 V applied with no charge in the liquid (solid line) and some charge in the liquid near the electrode surface (dashed line) calculated using finite element analysis

This gradient enhancement leads to two important effects because the dielectrophoretic force is proportional to

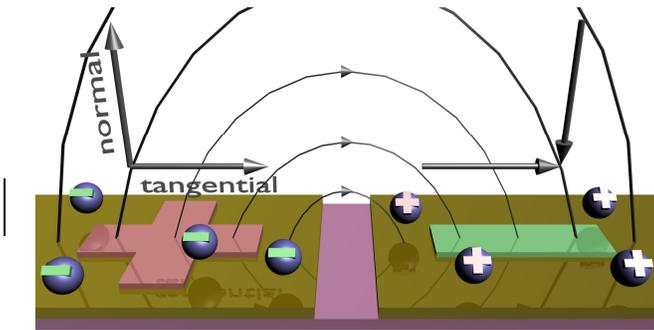
the gradient of the field squared. The force will be larger and spatially concentrated near the interface at low frequencies, and smaller and more evenly distributed across the electrode gap at high frequencies.

At low frequencies, because of its spatial concentration near the electrode edge and consequently shorter range of action, the DEP force may be less sensitive to the geometric field enhancement of protrusions from the electrode surface, promoting more even nanoparticle deposition. Another consequence of this shorter range is separation between the region of high DEP force, where nanoparticles are captured and deposited rapidly, depleting the solution of nanoparticles, and the region of low DEP force where other transport mechanisms such as diffusion and fluid flow dominate.

Qualitatively, the higher collection rate and greater degree of fusion between nanoparticles at low frequencies supports the DEP force being larger. The generally thicker wires and more even depositions observed at low frequencies support the shorter range of the DEP force. We believe the longer range of the DEP force at high frequencies may be responsible for the formation of linear chains of particles.

### 2.3 AC Electroosmosis

For microelectrodes, the electric field at the surface of coplanar electrodes can have a substantial component tangential to the electrode surface. The Coulomb force of this field on the solution interfacial charge (Figure 3) leads to fluid flow along the electrode surface away from the gap in a process termed AC electroosmosis.



**Figure 3.** Surface-bound interfacial charge (spheres) induced by electrodes interacts with the tangential component of the electric field (curved lines) and moves fluid along the electrode surface away from the electrode gap. Negative charge experiences force opposite to the direction of field lines.

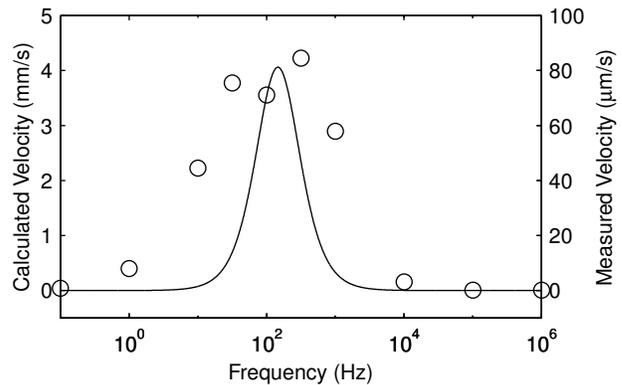
For symmetrical gaps such as those used in this study, fluid velocity near the electrode surface is given by [5]

$$\langle v \rangle = \frac{1}{8} \frac{\epsilon V_0^2 \Omega^2}{\eta x (1 + \Omega^2)^2}, \quad (5)$$

where  $\eta$  is viscosity,  $x$  is the coordinate axis along the electrode surface with its origin at the center of the electrode gap and the dimensionless frequency  $\Omega$  is given by

$$\Omega = \omega x \frac{\epsilon \pi}{\sigma} \kappa, \quad (6)$$

where  $\kappa$  is the Debye-Hückel length. A reasonable estimate for  $\kappa$  from solutions with similar conductivities is about  $(50 \text{ nm})^{-1}$ . For typical DEP conditions, this gives a maximum velocity at the electrode edge of 4.1 mm/s, more than enough to considerably influence nanoparticle transport and deposit morphology. This velocity is small at low frequencies when most of the electric field is inside the interfacial double layer and the tangential field does not extend very far into the solution. The velocity is also small at high frequencies when the charged species in solution are not fast enough to follow the field reversals. However, between these two regimes the velocity can be quite large (Figure 4).



**Figure 4.** Calculated AC electro-osmosis induced fluid velocity (solid line) and measured fluid velocity (circles) versus frequency. Calculations are from equation 5 ( $\kappa = (15 \text{ nm})^{-1}$ ,  $x = r$ ,  $\epsilon$  and  $\sigma$  as above,  $\eta = 0.008904$  poise,  $V_{\text{rms}} = 5 \text{ V}$ ) and measurements are taken from video microscopy observations of  $2 \mu\text{m}$  latex spheres in deionized water ( $V_{\text{rms}} = 7.5 \text{ V}$ ).

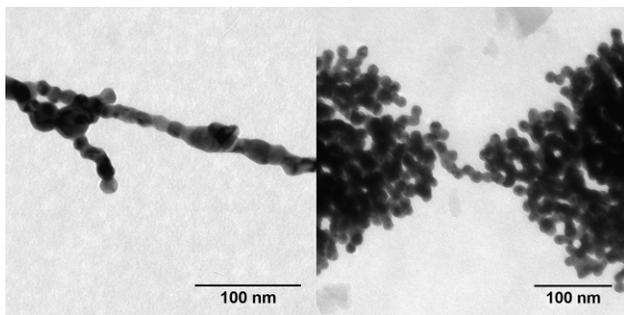
Observation by optical microscopy and TEM shows the deposits formed around high AC electroosmotic flow are very thick (Figure 1) with connections between electrodes consistently forming to the side of the electrode gap (data not shown). Also, deposits formed at frequencies associated with high fluid velocity take longer to electrically bridge the gap.

The increased density of deposits and corresponding increase in time taken to bridge the gap under high flow

conditions is likely caused by a combination of mutual attraction between particles due to hydrodynamic forces, replacement of diffusion by fluid flow as the primary long-range transport mechanism for fresh nanoparticles, and replacement of medium-range dielectrophoretic forces by fluid flow, preventing the formation of pearl chains.

### 3 APPLICATIONS

Two regimes of nanoparticle deposition are of particular technological interest (Figure 5). When two wires meet and make electrical contact, the voltage difference becomes very small and deposition stops, often leaving a chain a single nanoparticle wide at their meeting. At 10kHz, the AC electroosmotic flow causes most of the wire to be dense and several hundred nanometers thick, except at the meeting point where a pearl chain of a few nanoparticles makes the connection. Stereomicroscopic investigation of this connection shows it is very close to the substrate surface. The low resistance of thick connecting wires combined with a nanoscale constriction makes this structure suitable for the formation of a nanogap for molecular electronics. At 1 MHz, there is virtually no AC electroosmotic fluid flow, allowing the dielectrophoretic force to dominate. Single nanoparticle wide pearl chains frequently bridge the entire gap and electrically connect both electrodes. These bridges can be fragile over distances of several microns and frequently break with sample preparation. TEM stereomicroscopy again shows these structures to be very close to the underlying substrate. This type of one dimensional nanostructure is suitable for large-scale preservation of quantum effects associated with constituent nanostructures, such as optical and electrical properties for light emission or detection [4].



**Figure 5.** Meeting point of deposits at 1 MHz (left) and 10 kHz (right) (7.5 V, 3 micron gap, 15.5 nm nanoparticles).

An additional physical parameter in the formation of nanostructured connections their electrical resistance and this is controlled by the degree to and mechanism by which the nanoparticles fuse together. Particle fusion is energetically favorable because of the reduction in surface area, but repulsive inter-particle forces must first be

overcome by the dielectrophoretic force. For most microelectrode applications, a low resistance is desirable. For sensor applications, a high surface area may be desirable. The resistance of our nanowires ranged from less than 100  $\Omega$  to greater than 1 k $\Omega$ . The current which flows through the nanostructure at completion, set by a choice of series resistance, seems to be inversely proportional to the post-formation resistance of the completed nanostructure, probably because the nanostructure is annealed by Joule heating.

### 4 CONCLUSIONS

Dielectrophoretic capture of gold nanoparticles provides a powerful means of creating unique and useful nanostructures. The morphology of nanoparticle deposits formed in this way is highly sensitive to the frequency of the applied field, primarily because of AC electroosmotic fluid flow and interfacial layer effects. Knowledge of these frequency dependent mechanisms should enable a wider variety of more precise nanostructures to be formed and assembled using dielectrophoresis, particularly nanogap electrodes and one dimensional nanowires.

### ACKNOWLEDGEMENTS

This study was supported by grants from the National Institutes of Health (NIH/NHGRI Grant 1R01HG003565) and the David and Lucille Packard Foundation. We thank Dwight Howard for assistance with experimental setup, and Prof. Wayne Current and Kelvin Yuk for helpful comments. Fabrication work was carried out at the Northern California Nanotechnology Center and TEM at Materials Science Central Facilities, both of the University of California, Davis.

### REFERENCES

- [1] M. P. Hughes, *Nanoelectromechanics in engineering and biology*. Boca Raton, FL: CRC Press, 2003.
- [2] S. I. Khondaker, Z. Yao, L. Cheng, J. C. Henderson, Y. X. Yao, and J. M. Tour, *Applied Physics Letters*, vol. 85, pp. 645-647, 2004.
- [3] K. D. Hermanson, S. O. Lumsdon, J. P. Williams, E. W. Kaler, and O. D. Velev, *Science*, vol. 294, pp. 1082-1086, 2001.
- [4] B. Ozturk, I. Talukdar, and B. N. Flanders, *Applied Physics Letters*, vol. 86, pp. 183105, 2005.
- [5] N. G. Green, A. Ramos, A. Gonzalez, H. Morgan, and A. Castellanos, *Physical Review E*, vol. 61, pp. 4011-4018, 2000.