Dielectrophoretic Assembly of 2 nm Gold Particles for Nano-sensing Applications

Ming Lin Li, Siu Ling Leung, Yan Li Qu, Zai Li Dong, and Wen J. Li*, Senior Member, IEEE

Abstract—This paper describes the assembly of 2 nm gold nanoparticles between micro-fabricated planar electrodes by using dielectrophoresis (DEP). The optimal conditions for effectively dielectrophoretic manipulation have been established through theoretical analysis and experimental validation. In the theoretical analysis, the effect of Brownian motion was taken into consideration, as well as the electrothermal flow and the AC electroosmosis flow. For effective manipulation of nanoparticles using DEP, proper high electric field strength is desired to give rise to dominate DEP effect, since the higher electric field strength increases the Joule heating and the lower strength reduces the DEP force. The current results indicate that the input voltage of 16Vp-p, 150 kHz leads to effective assembly of 2 nm gold nanoparticles. Our study proved that the DEP is capable of consistently assembling gold nanoparticles down to 2 nm in diameter with micro-fabricated electrodes, which was thought to be extremely difficult in the past.

Index Terms—Dielectrophoresis, Gold nanoparticles, Nano-devices, Nanoassembly,

I. INTRODUCTION

METALLIC nanoparticle assemblies into functional structures using DEP are of tremendous significance and has attracted considerable attention [1-9]. For molecular electronics, DEP was employed to trap nanoparticles to bridge nanogap electrodes for the application of electronic transport studies [1-3]. For the self-repairing of broken circuits [4] and electrical connections [5] in liquid or biological environments, gold nanoparticles were assembled into microwires between micrometer gap electrodes using DEP technique. Nanowires with resolution down to several nanometers, which formed with gold nanoparticles of diameter range from 2 to 250 nm, have been demonstrated by several groups [2, 6-9].

However, only a few reports have demonstrated the effective manipulation of 2 nm gold particles using DEP. For instance, Zheng et al. [6] utilized carbon nanotubes as electrodes to generate large electric field gradient to overcome the stochastic thermal Brownian motion of gold nanoparticles and successfully manipulate gold particles with the diameter of 2 nm using DEP technique. Khondaker and Yao [3] employed electrodes with a gap size of sub-10 nm, which are produced by breaking nanowires assembled from gold nanoparticles, to trap a thiol-coated 2-3 nm Au nanoparticle for the measurement of electrical transport, which shows a clear Coulomb staircase at 4.2 K. In addition, with 200 micrometer spaced electrodes, Yuan [10] exhibited the chaining and dendrite formation of gold particles with diameter of 2.5 nm using AC electric field, which ascribed to the combinational operation of DEP and convection. However, in our previous study with several micron electrode gap [9], such desired nanowires formed by 2 nm gold particles had not been achieved using DEP as predicted, which was imputed to the limitations of the Brownian motion and the viscous drag force of fluid motion.

In this paper, we discuss the usage of micro-lithographically patterned electrodes spaced several micrometer apart to manipulate 2 nm gold particles using DEP technique. The optimal conditions for the effective DEP manipulation of such small nanoparticles are investigated by means of simplified theoretical analysis, followed by experimental verification. In the theoretical analysis, the Brownian motion of nanoparticles and the electrothermal flow as well as the electro-osmotic flow are all taken into account.

II. THEORIES

A. Dielectrophoresis

DEP generally refers to the movement of a particle immersed in a liquid with applied non-uniform electric field, arising from the interactions between the polarization of the particle and the non-uniform field surrounded the particle. For particles with nanometer scale, the DEP force must overcome the stochastic thermal Brownian motion to be effective, which is increasingly difficult as the particle size scales down. Therefore, a high strength electric field [2, 6] is indispensable to enable the DEP manipulation. However, a high strength electric field also gives rise to fluid motion such as electrothermal flow and AC...
When exposed to a non-uniform electric field, an uncharged particle will be subjected to a net electrical force, the DEP force. In the special case where the electric field across a particle deviates only slightly from its value at the center of that particle, the point dipole approximation is appropriate to estimate the effective DEP force. For a spherical particle of radius \( a \), suspended in a medium of permittivity \( \varepsilon_m \) and exposed to an electric field \( E \), which will be replaced by the root mean square (rms) value in an alternating electric field, the net DEP force is given by \([12]\)

\[
F_{\text{DEP}} = 2\pi\varepsilon_0 a^3 \text{Re}[K] |E|^2
\]

where the italic capital letter \( K \) denotes the Clausius-Mossotti factor,

\[
K = \frac{\tilde{\varepsilon}_p - \tilde{\varepsilon}_m}{\tilde{\varepsilon}_p + 2\tilde{\varepsilon}_m}
\]

Here, the subscripts \( p \) and \( m \) refer to particle and suspending medium respectively, and the tilde indicates the complex phasor of permittivity, which is the function of applied angle frequency \( \omega \), permittivity \( \varepsilon \) and conductivity \( \sigma \)

\[
\tilde{\varepsilon} = \varepsilon - j\frac{\sigma}{\omega}
\]

where \( j = -1 \).

For spherical particles, the real part of complex Clausius-Mossotti factor varies between -0.5 and +1.0. When the sign of \( \text{Re}[K] \) is positive, particles tend to move toward higher electric field regions, termed positive DEP. When the sign is negative, on the contrary, particles move toward smaller electric field regions, termed negative DEP. For assembling gold nanoparticles to bridge the spaced electrodes, positive DEP is primarily desired. On the basis of such requirement, \( \text{Re}[K] \) is assumed to be unity in the following simplified analysis.

To estimate the magnitude of the DEP force, it is necessary to know the electric field distribution, especially the gradient. Here, the electric field is generated by two microfabricated planar strip electrodes. Fig. 1 shows the schematic diagram of the DEP assembling of gold nanoparticles. Using the finite element method, the electric field lines in three-dimensional space can be simulated as shown in Fig. 2. For the sake of simplified analysis, the electric field lines above the electrode surface can be regarded as semicircular arc, especially in the vertical section.

Therefore, the magnitude of the electric field is approximately given by 

\[
E = V/\pi r
\]

where \( V \) is the peak to peak amplitude of the applied voltage and \( r \) is the radial distance measured from the center of the electrode gap. Using Stok’s law, the velocity of a gold spherical nanoparticle induced by the DEP can be consequently estimated by

\[
\mathcal{U}_{\text{DEP}} = \frac{4\varepsilon_0 a^3 V^2}{6\pi \eta a}
\]

where, \( \eta \) denotes the viscosity of the suspending medium.

### B. Electrothermal Flow

When a high intensity electric field is generated to manipulate nanoparticles by DEP, Joule heating will induce a gradient in the conductivity and permittivity of the suspending medium, which results in an electrothermal force acting on the fluid. Using the analytical electric field \( E = V/\pi r \), the electro-thermal body force in two-dimensional system can be described by the following equation \([11]\)

\[
F_{\text{ET}} = -M \left( \frac{\varepsilon_m \sigma_m V^4}{8k\pi r T} \right) \left( 1 - \frac{2\theta}{\pi} \right)
\]

where \( M \) is a dimensionless factor defined by

\[
M = \frac{(T/\sigma_m)(\partial\sigma_m/\partial T) - (T/\varepsilon_m)(\partial\varepsilon_m/\partial T)}{1 + (2\pi f \cdot \varepsilon_m/\sigma_m) + \frac{1}{2} (T/\sigma_m)(\partial\sigma_m/\partial T)}
\]

Here, \( k \) is the thermal conductivity of the liquid, \( T \) the absolute temperature, \( \theta \) the angle between the plane of the electrodes and a radial line from the center of the electrode gap. Based on Eq. (5), the maximum of \( F_{\text{ET}} \) appears at \( \theta = 0 \) and \( \pi \), where radial lines are parallel to the electrodes.

The dimensionless factor \( M \) determines the direction of the fluid flow with respect to the electrode gap. When \( M \) is positive, the liquid moves across the edge of electrodes from the center of electrode gap to the electrode surface. Contrarily, when \( M \) is negative, the flow direction is reversed. To realize the assembly of gold nanoparticles into bridging the spaced electrodes, the factor \( M \) is desirable to be zero or negative. Moreover, the sign of the factor \( M \) varies with the frequency \( f \) of the applied electric field. For a gold nanoparticle solution, the magnitude of factor \( M \) against the frequency of applied electric field at \( T = 300 \text{ K} \) is shown in Fig. 3. The parameters of medium are respectively \( \sigma_m = 5.5 \times 10^{-6} \text{ S/m} \), \( \varepsilon_m = 80 \) \( \varepsilon_0 \), \( \varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m} \), \( 1/\sigma_m \) \( (\partial\sigma/\partial T) = -0.5 \times 10^{-5} \text{ S/m.K}^{-1} \) and \( 1/\varepsilon_m \) \( (\partial\varepsilon/\partial T) = -0.5 \times 10^{-5} \text{ F/m.K}^{-1} \) respectively.
Accordingly, the maximum velocities can be estimated for the frequency limits for electro-osmotic velocity is given by the Smoluchowsky formula:

\[ u_{\text{max}} = \frac{D}{\eta} \cdot \frac{\varepsilon_{m} \sigma_{n} V^{4}}{k T} \cdot \frac{1}{\sigma_{n}} \frac{\partial \sigma_{m}}{\partial T} \]

\[ u_{\text{max}} = \frac{2.5 \times 10^{4} \varepsilon_{m} \sigma_{n} V^{4}}{k T} \cdot \frac{1}{\sigma_{n}} \frac{\partial \sigma_{m}}{\partial T} \]

\[ u_{\text{max}} = \frac{5 \times 10^{4} \varepsilon_{m} \sigma_{n} V^{4}}{k T} \cdot \frac{1}{\sigma_{n}} \frac{\partial \sigma_{m}}{\partial T} \]

\[ u_{\text{max}} = \frac{2.5 \times 10^{4} \varepsilon_{m} \sigma_{n} V^{4}}{k T} \cdot \frac{1}{\sigma_{n}} \frac{\partial \sigma_{m}}{\partial T} \]

Here, \( \sigma_{n} \) is the non-dimensional frequency given by

\[ \Omega = \left( \frac{\omega \cdot \Delta \sigma_{m}}{2 \pi r} \right) / (2 \sigma_{m}) \]

For the gold nanoparticle solution, the frequency dependence of the electro-osmotic velocity is shown in Fig. 4, which reveals that the velocity closes to be zero as the frequency is zero or goes to infinity. The maximum velocity arises at \( \Omega = 1 \), with respect to an angular frequency \( \omega_{0} = 2 \sigma_{m} / (\varepsilon_{m} \varepsilon_{0}) \).

\[ \omega_{0} = 2 \sigma_{m} / (\varepsilon_{m} \varepsilon_{0}) \]

\[ \Omega = \left( \frac{\omega \cdot \Delta \sigma_{m}}{2 \pi r} \right) / (2 \sigma_{m}) \]

\[ \Omega = \left( \frac{\omega \cdot \Delta \sigma_{m}}{2 \pi r} \right) / (2 \sigma_{m}) \]

Fig. 3. Magnitude of the factor \( M \) versus applied frequency \( f \).

Fig. 4. Frequency dependence of electro-osmotic velocity.

\[ \frac{D}{\eta} \cdot \frac{\varepsilon_{m} \sigma_{n} V^{4}}{k T} \cdot \frac{1}{\sigma_{n}} \frac{\partial \sigma_{m}}{\partial T} \]

\[ \frac{2.5 \times 10^{4} \varepsilon_{m} \sigma_{n} V^{4}}{k T} \cdot \frac{1}{\sigma_{n}} \frac{\partial \sigma_{m}}{\partial T} \]

\[ \frac{5 \times 10^{4} \varepsilon_{m} \sigma_{n} V^{4}}{k T} \cdot \frac{1}{\sigma_{n}} \frac{\partial \sigma_{m}}{\partial T} \]

\[ \frac{2.5 \times 10^{4} \varepsilon_{m} \sigma_{n} V^{4}}{k T} \cdot \frac{1}{\sigma_{n}} \frac{\partial \sigma_{m}}{\partial T} \]

\[ \frac{5 \times 10^{4} \varepsilon_{m} \sigma_{n} V^{4}}{k T} \cdot \frac{1}{\sigma_{n}} \frac{\partial \sigma_{m}}{\partial T} \]

\[ \frac{2.5 \times 10^{4} \varepsilon_{m} \sigma_{n} V^{4}}{k T} \cdot \frac{1}{\sigma_{n}} \frac{\partial \sigma_{m}}{\partial T} \]

\[ \frac{5 \times 10^{4} \varepsilon_{m} \sigma_{n} V^{4}}{k T} \cdot \frac{1}{\sigma_{n}} \frac{\partial \sigma_{m}}{\partial T} \]
four effects, i.e., DEP, electro-thermal flow, AC electro-osmotic flow, and Brownian motion, can be estimated against the applied voltage $V$ using equations (4), (7), (9), and (13). The results are shown in Fig. 5.

The results are shown in Fig. 5. Fig. 5 indicates that the AC electroosmosis at low frequency will induce a fluid flow high enough to obstruct the movement of particles due to DEP regardless of the applied voltage. However, the impact of the AC electro-osmotic flow can be reduced by increasing the applied frequency, i.e., taking 40 kHz as an example as shown in Fig. 5. According to Fig. 3 and Fig. 4, higher frequency is suggested to obtain desired positive factor $M$ and to eliminate the AC electro-osmotic impact. Concerning the frequency, the low frequency also causes an electrothermal flow with negative factor $M$, which will drag particles across the edge of electrodes from the center of the electrode gap. As a result, frequencies higher than 40 kHz were used in our experimental validation, as presented in the next section.

Fig. 5 also shows that a large voltage is essential to provide adequate DEP to offset the Brownian motion. In our experimental conditions, we have found that voltages greater than 15 V $p$-$p$ are sufficient to produce enough DEP force to overcome Brownian effect. Note that voltages larger than 45 V $p$-$p$ will yield higher electrothermal velocity than that of DEP even at higher applied frequencies.

III. EXPERIMENTS

A. Electrode Fabrication and Particle Assembly

Au microelectrodes with a gap separation of 4 $\mu$m were fabricated and patterned on Si/SiO$_2$ substrates with standard micro-fabrication techniques. Si wafers were first cleaned by immersing in acetone, followed by IPA and then DI water. Photoresist AZ5214E was subsequently spin-coated onto the wafers at 3000 rpm for 30 seconds. Using image reversal technique, the photoresist was pre-baked at 90 °C for 40 sec, followed by aligning and exposing under UV light for 30 sec. It was then baked again at 120°C for 6 sec, followed by second exposure for 30 sec. Finally, the resist film was developed by AZ developer for about 30 sec and rinsed by DI water. After that, 50 nm chromium and 300 nm gold films were deposited on the top of the patterned photoresist by electron beam evaporation. Finally, the structures were released by immersing the chip into acetone.

The 2 nm gold particle suspension used in our experiments is purchased from the BBI International (Cardiff, UK). For the assembly of 2 nm gold particles, a function generator (Hp 8111A, Hewlett Packard Company, USA) is operated at three frequencies of 40 kHz, 100 kHz, and 150 kHz, with a peak to peak voltage of 16V, based on the above-mentioned analysis. A 100 Ohm resistor is connected in series to the microelectrodes for overcurrent protection. During the assembly, a digital real-time oscilloscope (TDS 220, Tektronix Inc, USA) is used to measure both the input control voltage and the voltage between a pair of electrodes. When gold nanoparticles are assembled into bridging the electrode pair, the voltage between the electrodes will drop accordingly. The experimental setup is shown in Fig. 6.

B. Results and Discussion

The voltage across the electrode pair is observed to drop at the frequencies of 100 kHz and 150 kHz respectively, meaning that wires assembled from the gold nanoparticles are formed and connect to the pair of electrodes. Images by scan electron microscopy (SEM) or measured resistances between electrode pairs can be performed to verify such connection. Fig. 7 shows the representative results of the DEP-based assembly of 2 nm gold particles at the frequency of 150 kHz with the control voltage of 16 V $p$-$p$. The measured resistance between electrode pairs is around 160 Ohm, proving that it is not an open circuit.

![Fig. 6. The experimental setup for DEP assembly of gold particles.](image)

![Fig. 7. SEM image of DEP-based assembly of 2 nm gold particles at the frequency of 150 kHz with control voltage of 16 V $p$-$p$.](image)

At the frequency of 40 kHz, no voltage drop across the pair of microelectrodes is observed, meaning that no connections occur
under such control condition. However, further investigation by SEM image in Fig.8 shows that gold nanoparticles were assembled to grow into wires from the edges of electrode pair, which indicates that the DEP is still effective to manipulate these gold particles. The reason of none connection between electrode pairs possibly involves two aspects. On one hand, frequencies higher than 40 kHz will induce the electrothermal flow favorable to the DEP manipulation of gold nanoparticles with the direction from the surface of electrode to the center of electrode gap. The electrothermal flow will provide the central region of DEP with more gold nanoparticles, which is enough to form gold wires to connect the electrode pair. On the other hand, higher frequencies will produce smaller time-vary temperature [15]. In such DEP system, the relative change of temperature is inversely proportional to twice the frequency of the applied field, i.e., $\Delta T/T \propto 1/(2\omega)$.

An interesting phenomenon in these assembly images is that the 2 nm gold particles were driven to form similar dendrite configurations. Exposed to the electric field acting between the electrodes, the wire growth process can be modeled by electrostatics calculations, which was performed by Bhatt and Velev [16]. After bridging the electrode gap, the nanoparticle wires were demonstrated by our group to sense thermal based physical phenomena, e.g. airflow sensing, the same as the previous experimentation with the larger gold nanoparticles (10 nm and 100 nm) [17]. However, the 2 nm gold particles are expected to obtain superior sensitivity and consume lower power in nano-sensing applications, which still under the investigation.

IV. CONCLUSIONS

The assembly of 2 nm gold particles using DEP technique with micrometer spaced electrodes is discussed in this paper. The optimal conditions for the effective DEP manipulation of such small nanoparticles were determined by theoretical analysis and verified by experiments. For a planar electrode pair with a gap of 4μm fabricated on an insulating substrate, voltages higher than 15V are essential to generate high intensity electric field to overcome the Brownian motion. With the voltage of 16 V acting between the electrodes, frequencies higher than 40 kHz are appropriate to manipulate 2 nm gold particles based on DEP. However, higher frequencies, i.e., are required to assemble gold nanoparticles to bridge the electrodes to form useful circuits, e.g., forming nanoparticle sensing elements.

V. ACKNOWLEDGMENTS

The authors acknowledge all the members at the Centre for Micro and Nano Systems, The Chinese University of Hong Kong for their support and encouragement. In particular, the authors would like to thank Dr. W. Y. Cheung, Ms. Winnie W. Y. Chow, Ms. and Mr. Ho Shing Poon for their help on this project and the useful discussions.

REFERENCES

[1] A. Bezyadgan, C. Dekker, and G. Schmid, “Electrostatic trapping of single conducting nanoparticles between nanoelectrodes,” *Applied Physics Letters*, vol. 71, pp. 1273-1275, 1997.
[2] S. Kumar, S. Yoon, and G. Kim, “Bridging the nanogap electrodes with gold nanoparticles using dielectrophoresis technique,” *Current Applied Physics Letters*, vol. 9, no. 1, pp. 101-103, 2009.
[3] S. I. Khodaker, and Z. Yao, “Fabrication of nanometer-spaced electrodes using gold nanoparticles,” *Applied Physics Letters*, vol. 81, pp. 4613, 2002.
[4] K. D. Hermanson, S. O. Lumsdon, J. P. Williams et al., “Dielectrophoretic assembly of electrically functional microwires from nanoparticle suspensions,” *Science*, vol. 294, pp. 1082-1086, 2001.
[5] S. O. Lumsdon, and D. M. Scott, “Assembly of colloidal particles into microwires using an alternating electric field,” *Langmuir*, vol. 21, no. 11, pp. 4874-4880, 2005.
[6] L. Zheng, S. Li, J. P. Brody et al., “Manipulating nanoparticles in solution with electrically contacted nanotubes using dielectrophoresis,” *Langmuir*, vol. 20, no. 20, pp. 8612-8619, 2004.
[7] X. Xiong, A. Busnaina, S. Selvarasah et al., “Directed assembly of gold nanoparticle nanowires and networks for nanodevices,” *Applied Physics Letters*, vol. 91, pp. 063101, 2007.
[8] R. Kretschmer, and W. Fritzsche, “Pearl chain formation of nanoparticles in microelectrode gaps by dielectrophoresis,” *Langmuir*, vol. 20, no. 20, pp. 11797-11801, 2004.
[9] G. W. Leung, F. T. Lau, S. L. Leung et al., “Formation of Au colloidal crystals for optical sensing by DEP-based nano-assembly,” in *Proc. of The 2nd IEEE International Conference on Nano/Micro Engineered and Molecular Systems (IEEE-NEMS 2007)*, Bangkok, Thailand, 2007.
[10] Y. J. Yuan, M. K. Andrews, and B. K. Marlow, “Chaining and dendrite formation of gold particles,” *Applied Physics Letters*, vol. 85, no. 1, pp. 130-132, 2004.
[11] A. Castellanos, A. Ramos, A. González et al., “Electrohydrodynamics and dielectrophoresis in microsystems: scaling laws,” *J. Phys. D: Appl. Phys.*, vol. 36, pp. 2584-2597, 2003.
[12] T. B. Jones, *Electromechanics of Particles*, Cambridge; New York: Cambridge University Press, 1995.
[13] N. G. Green, A. Ramos, A. González et al., “Fluid flow induced by nonuniform ac electric fields in electrolytes on microelectrodes. III. Observation of streamlines and numerical simulation,” *Physical Review E*, vol. 66, no. 2, pp. 26305, 2002.
[14] M. Li, Y. Qi, Z. Dong et al., “Limitations of Au particle nanassembly using dielectrophoretic force -- a parametric experimental and theoretical study,” *IEEE Transactions on Nanotechnology*, vol. 7, no. 4, pp. 477-479, 2008.
[15] A. Ramos, H. Morgan, N. G. Green et al., “AC electrokinetcs: a review of forces in microelectrode structures,” *J. Phys. D: Appl. Phys.*, vol. 31, pp. 2338-2353, 1998.
[16] K. H. Bhatt, and O. D. Velev, “Control and modeling of the dielectrophoretic assembly of on-chip nanoparticle wires,” *Langmuir*, vol. 20, no. 2, pp. 467-476, 2004.
[17] S. Leung, M. Li, F. Lau et al., “Fabrication of gold nano-particle based sensors using microspotting and DEP technologies,” *Proc. of SICE Annual Conference 2008: International Conference on Instrumentation, Control and Information Technology*, August 22, 2008.