Selective and Localized Micro-Assembly of NaCl Crystals by DEP Force

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***Abstract* — This paper reports the experimental results of the micro-assembly of micron-sized NaCl crystals formed between gold microelectrodes using gold colloidal solution by capillary force and dielectrophoresis (DEP). Typical NaCl crystals formed and manipulated are ~40 μm^3 cubes. From experimental results, we have determined the required DEP parameters to manipulate and crystallize NaCl cubes between or near microelectrodes with almost 100% success rate.**

Keywords — ***Dielectrophoresis, NaCl Crystallization, NaCl Sensor, Self-assembly***

I. INTRODUCTION

Since Faraday first studied the optical properties of gold particles in solution in 1857, the optical, electronic and catalytic properties of AuNPs are playing a key role in the development of nano-photonics (e.g., [1]), nanomedicine (e.g., [2]) and biosensors (e.g., [3]). Owing to the quantum-mechanical effects, AuNPs in the diameter size of less than 20nm, which is intermediate between the size of small molecules and bulk metals, possess different physical properties from that of molecular compounds or bulk gold. For instance, the fluorescence [4] and electrochemical characteristics [5] of AuNPs with DNA, sugars and other biological molecules, which can be used potentially in bimolecular manipulations and applications, such as labeling and detection (e.g., [6]). Another unique physical property of AuNPs is their red color in aqueous solutions that reflects the surface plasmon band (SPB), which is due to the collective oscillations of the electron gas at the surface of AuNPs (6s electrons of the conduction band) that is correlated with the electromagnetic field of the incoming light [7]. One of the applications for this unique property is in photonic crystals, which could reflect all incident light at a wavelength in a particular band gap and would transmit almost all the light at other wavelengths [8-9].

Fabrication of gold colloidal crystals can be done by microsphere synthesis and assembly using colloidal solutions. Various methods have been utilized to assemble colloid into crystalline lattices with notable examples such as gravity sedimentation [10], vertical vapour deposition [11], electrostatic force [12]. Among all these methods, crystallization by capillary force has been found to produce good quality crystals and have a much simpler fabrication procedure.

In this paper, we will discuss our ongoing work in micro-assembly of crystals confined between gold microelectrodes on the Si substrate using 2nm gold colloidal solution by combining capillary force and DEP force.

II. EXPERIMENTAL DETAILS

A. Experimental Setup

The Si substrate with fabricated gold microelectrodes was placed on the vacuum pump based stage of a micromanipulator station, which allowed the gold colloidal solution to be injected onto the substrate by microspotting techniques developed by our group [13]. A series resistor of 100Ω was connected to the microelectrodes to prevent short circuit if a crystal was formed between the microelectrodes. Another series capacitor of 1μF was connected to filter the DC component of the voltage for DEP manipulation. Cathode-ray Oscilloscope (CRO) was used to monitor the variation of voltage and current. Schematic diagram of the circuit connecting to the microelectrodes is shown in Fig. 1.

B. Experimental Procedures

The gold microelectrodes were first excited by an AC voltage with frequency of 300 kHz and a specific voltage in each case. A 0.5 μL gold colloidal solution was injected into the gap between microelectrodes. Once the solution was injected, the experiment started and the particles in the solution would be driven to the microelectrode gap by capillary force and DEP force. The voltage was carefully monitored to detect the formation of crystal between microelectrodes. After approximately 20 minutes, the solution was completely evaporated, and a crystal would be observed in between or near the microelectrodes. At this stage, the sample was removed from the AC electric field and was air-dried.

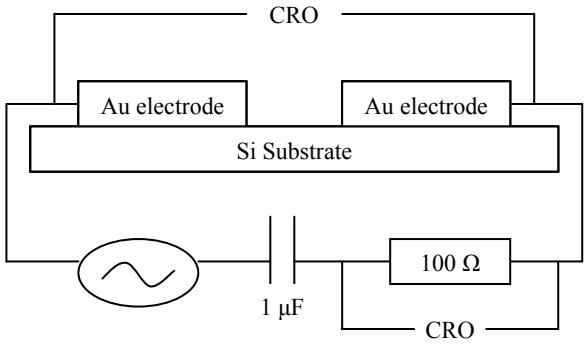

Figure 1 Schematic diagram showing the circuit connecting to the microelectrodes during DEP assembling.

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III. Experimental Results and Discussion

By using the conditions mentioned above, we found that micron-sized crystals were formed between the microelectrodes with different success rate. We then carried out a series of experiments to study the effect of applying DEP force parametrically.

A. Position Control of Crystal Formation

- Effect of Applying DEP Force

To evaluate the effect of the DEP force on the crystal formation, we have performed a set of control experiments by applying capillary force and without DEP force using 2nm gold colloidal solution. As shown in Fig. 2(a), crystals were formed randomly and no pattern of the position of the crystals could be recognized. For Fig. 2(b), a crystal was assembled between a pair of microelectrodes, which was formed by using both capillary force and DEP force. The experimental results verified that DEP force can affect the position of crystals formed on the substrate surface.

- Effect of Applying Different Voltages

Though in the previous section, we verify that by combining the capillary force crystallization with DEP force could alter the position of crystal formed, crystals could possibly be formed at positions other than at the gap between the microelectrodes. Fig. 3 shows three samples which best illustrate the possible positions of crystal formation: (i) at the gap between the microelectrodes; (ii) near the microelectrodes; (iii) other cases.

A series of experiments was conducted by varying the DEP voltage from 0 to 17V peak to peak while keeping frequency constant at 300 kHz to investigate its effect on the position of crystal formation. Table 1 depicts the percentage of position of crystals formed. "At the gap" indicates the crystal is formed between microelectrodes; "Near the electrodes" indicates the crystal is formed around the electrodes; "Other Cases" indicates other positions other than (i) or (ii) or no crystal is formed. Fig.4 summarized the result of Table 1. A brief description of each region of Fig. 4 is given below.

- Region 1:

There is a gradual increase of percentage of crystals formed around the microelectrodes from 0 to 10 V peak to peak. It is a region where the voltage used is directly proportional to the magnitude of DEP force, hence, the larger the effect of DEP force on the particles.

- Region 2:

There is a variation from 10 to 17V peak to peak. High voltage leads to electrolysis, which leads to the corrosion of microelectrodes and effervescence which prevents the formation of the crystals.

From Fig. 4, we can conclude that we can enhance the yield of crystals to be formed around the microelectrodes and obtain 100% success rate by applying the appropriate voltage and frequency.

B. Surface Analysis

In addition to the observation of crystal formation under the microscope, resultant current across the microelectrodes and

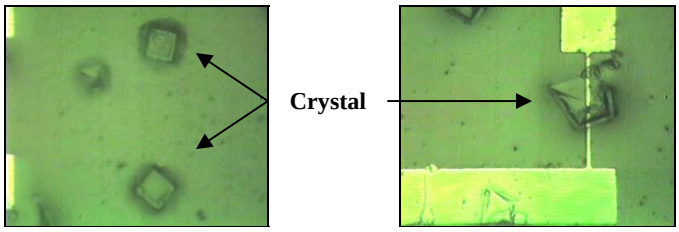


Figure 2. Optical micrograph showing crystals formed by (a) without DEP force; (b) with DEP force.

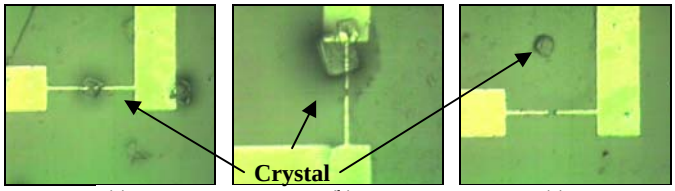


Figure 3. Optical micrograph showing three possibilities of location of crystal to be formed: (a) at the gap between the electrodes; (b) near the microelectrodes; and (c) other cases

TABLE I. Result showing % of Position of Crystals formed

Applied Voltage (V)	At the gap (%)	Near the electrodes (%)	Other Cases (%)
0	0.0	0.0	100.0
2	0.0	10.0	90.0
4	9.1	9.1	81.8
6	33.3	33.3	33.3
8	30.0	60.0	10.0
10	20.0	80.0	0.0
11	20.0	30.0	50.0
12	29.4	35.3	35.3
13	0.0	72.7	27.3
14	20.0	70.0	10.0
15	0.0	45.5	54.6
16	20.0	60.0	20.0
17	21.4	57.1	21.4

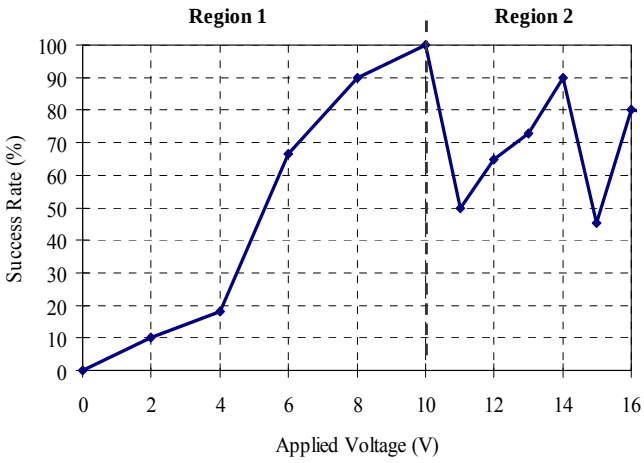


Figure 4. Success Rate of crystals formed around the electrodes at various voltage.

the resistors read by the CRO were also studied. Contrary to the prediction, there was no detectable change of current reading when crystal was formed at the gap between the microelectrodes. It is unexpected for highly conductive gold crystals. Hence, we conducted the surface analysis of the crystals using Scanning Electron Microscope (SEM), Energy-Dispersive X-ray Spectroscopy (EDAX) and Atomic Force Microscope (AFM).

- *Scanning Electron Microscope (SEM) and Energy-Disperse X-ray Spectroscopy(EDAX)*

The crystals fabricated by combination of capillary force and DEP was first examined by an SEM, the result of which is shown in Fig. 5(a). The crystal analyzed in this sample, grew in the form of rectangular platelets in the size of ~40 µm x ~40 µm, but their height could not be observed using SEM at this time, so we cannot confirm that these crystals are 3D cubes.

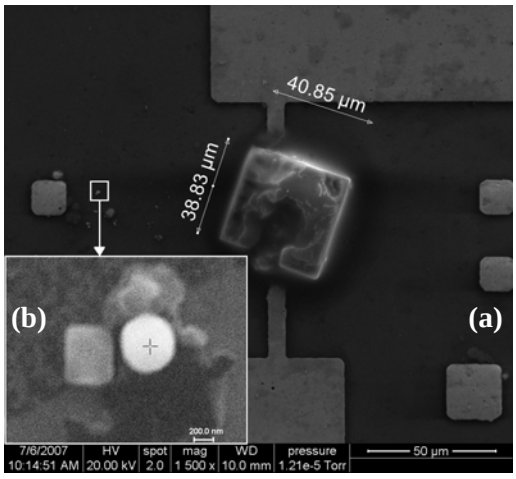
The crystal was also examined using EDAX for chemical characterization, the result of which is shown in Fig. 5(c), with yellow lines indicating the composition peak of gold. Contrary to our prediction, the EDAX result indicates that the crystal formed between the microelectrodes was made of Na and Cl, and not gold crystal. The AuNPs were found around the microelectrodes and coagulated as gold particles in the diameter size of ~500nm (Fig. 5(b)). The EDAX result of the gold particles is also shown in Fig. 5(d), which indicates a high peak composition of gold. The peak Si and O were due to the substrate which was made of silicon dioxide.

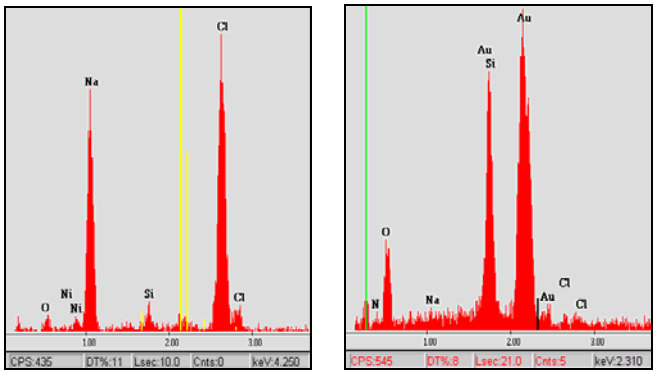
It is an interesting finding which is contrary to our prior results. Previously, we have performed another set of experiments for manipulation of gold nanowire using gold colloidal solution by DEP force [13]. It is extremely possible that the Au crystal reported in that work was actually a NaCl crystal. However, that experimental sample was already destroyed, so no EDAX characteristic could be performed to ascertain the crystal's true chemical composition.

- *Atomic Force Microscope(AFM)*

We also conduct another surface analysis using AFM to investigate the pattern of AuNPs after applying capillary and DEP force. The gap between the microelectrodes of the substrate was examined by an AFM, the result of which is shown in Fig. 6a. We found that there are Au particles with diameter of ~ 40 to 50nm. This size is 20 times larger than the 2nm AuNPs (Fig. 6b). This phenomenon is due to the coagulation of AuNPs after the gold colloidal solution was evaporated. Electrostatic repulsion introduced in the solution was eliminated and the AuNPs eventually aggregated into larger particles.

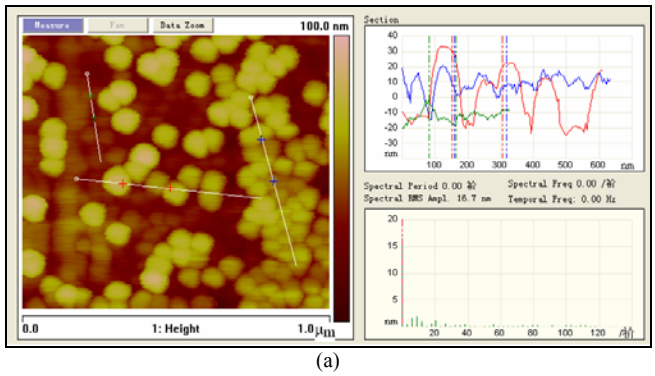
An interesting result from the AFM analysis is that the gold particles aligned in straight lines between the microelectrodes, as shown in Fig. 7. This suggests that there were external forces, other than capillary force and Brownian force, that acted on the AuNPs for alignment. The possible reason for this phenomenon is that the AC electric field applied to generate DEP force, which acts as a pulling force to draw the AuNPs to the microelectrodes. Active investigation in theoretical force analysis is underway by our group to study this occurrence.



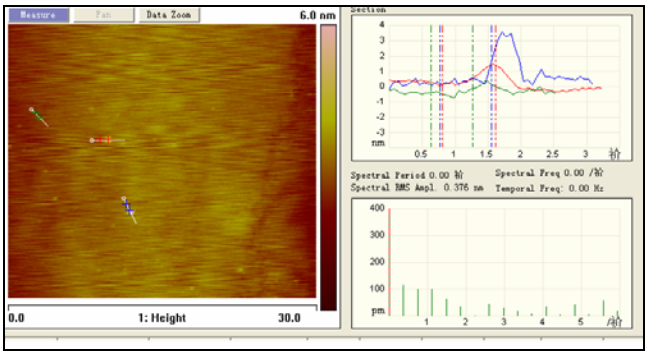


(c) (d)

Figure 5. SEM image showing (a) NaCl crystal formed between microelectrodes; (b) gold coagulation formed around the microelectrodes; EDAX result showing the composition of (c) crystal formed between microelectrodes; (d) coagulation around microelectrodes.

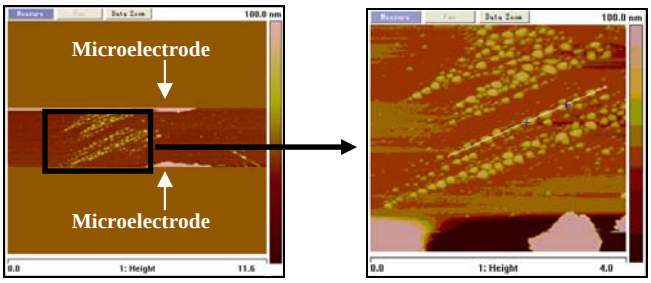


(a)



(b)

Figure 6. AFM image of (a) the gap between a pair of microelectrodes (scanning range = 1µm); (b) 2nm particles from original AuNPs solution.



(a) (b)

Figure 7. AFM image of the gap between a pair of microelectrodes. (a) Scanning range = 11.0 µm; (b) scanning range = 4.0 µm.

C. Theoretical Force Analysis of AuNPs Manipulation

Consider AuNPs suspended in gold colloidal solution in a non-uniform electric field, the AuNPs will experience DEP force, effect of Brownian motion and electric induced flow such as electrothermal flow and AC electro-osmosis. Our group suggests that the formation of gold nano-particle-chains becomes much more difficult to control when the particle size becomes less than 50nm [14]. For small particle size (i.e., in our case 2 nm), the DEP force applied cannot dominate over the effect of electro-osmosis and Brownian motion. Theoretical calculation of DEP force magnitude suggests that higher voltage and higher frequency are needed to overcome the effects of Brownian motion and electric induced flow. However, it is impractical in our AuNPs manipulation owing to the corrosion of the microelectrodes and effervescence. Hence, we can conclude that DEP force has limited control in pulling the AuNPs to the microelectrodes in our experiments.

At the same time, the stabilizing ions such as Na^+ and Cl^- ions in the gold colloidal solution are attracted to the microelectrodes due to the electric field applied. These ions competed with AuNPs to be attracted to the microelectrodes. For the AuNPs size less than 50nm, due to limited control by DEP, the magnitude of velocity of AuNPs to the microelectrodes is less than that of stabilizing ions. Consequently, these ions were attracted to the microelectrodes first and formed the crystal at the gap between the microelectrodes.

IV. CONCLUSION

The micro-assembly of micron-sized crystals formed between gold microelectrodes by DEP force and attractive capillary force caused by solvent evaporation was parametrically studied. Surface analyses on the crystals and the substrate were conducted to understand the results of crystal formation under the influence of capillary and DEP forces. Theoretical force analysis based on particle electro-mechanics was also introduced to interpret the formation of micron-sized NaCl crystals between microelectrodes.

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REFERENCES

[1] D. A. Stuart, C. R. Yonzon, X. Zhang, A.D. McFarland, C. L. Haynes and R. P. Van Duyne, "Towards Advances Chemical and Biological Nanosensors – An Overview," *Talanta*, vol. 67, pp. 438–448, 2005.

[2] N. L. Rosi, D. A. Giljohann, C. S. Thaxton, A. K. R. Lytton-Jean, M. S. Han and C. A. Mirkin, "Oligonucleotide- Modified Gold Nanoparticles for Intracellular Gene Regulation," *Science*, vol. 312, pp. 1027.

[3] H. L. Zhang, S. D. Evans, J. R. Henderson, R. E. Miles and T. H. Shen, "Vapour Sensing Using Surface Functionalized Gold Nanoparicles," *Nanotechnology*, vol. 13, pp. 439-444, 2002.

[4] M. M. Y. Chen and A. Katz, "Steady-State Fluorscence-Based Investigation of the Interaction between Protected Thiols and Gold Nanoparticles," *Langmuir*, vol. 18, pp. 2413-2420, 2002.

[5] S. Chen, R. S. Ingram, M. J. Hostetler, J. J. Pietron, R. W. Murray, T. G. Schaaff, J. T.Khoury, M. M. Alvarez and R. L. Whetten, " Gold Nanoelectrodes of Varied Size: Transition to Molecule-Like Charging," *Science*, vol. 280, pp. 2098-2101, 1998.

[6] Juewen Liu and Yi Lu, "A calorimetric lead biosensor using DNAzyme-directed assembly of gold nanoparticles," *Journal of the American Chemical Society*, vol. 125**,** pp. 6642, 2003.

[7] M. Daniel, and D. Astruc, "Gold Nanoparticles: Assembly, Supermolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis and Nanotechnology," *Chem. Rev. 2004*, vol. 104, pp. 293-346, 2004.

[8] Yablonovitch, E. : *Phys. Rev. Lett*., 58 (1987), 2059.

[9] John, S. : *Phys. Rev. Lett*., 58 (1987), 2486

[10] P. N. Pusey, W. van Megan, "Phase Behaviour of Concentrated Suspensions of Nearly Hard Colloidal Sphere," *Nature*, vol. 320, pp. 340-342, 1986.

[11] Yong-Hong Ye, Franc'ois LeBlanc, Alain Hache' and Vo-Van Truongb, "Self-Assembling Three-Directional Colloidal Photonic Crystal Structure with High Crystalline Quality*," Applied Physics Letters*, vol. 78, no. 1.

[12] M. Trau, D. A. Saville, and I. Aksay, "A Field-Induced Layering of Colloidal Crystals", *Science*, vol. 272, pp. 706-709, 1996.

[13] G. W. Leung, F. T. Lau, S. L. Leung and W. J. Li, "Formation of Au Colloidal Crystals for Optical Sensing by DEP-Based Nano-Assembly," Proc. of the 2nd IEEE International Conference on Nano/Micro Engineered and Molecular Systems (IEEE-NEMS 2007), 2007, pp. 992-996.

[14] M. L. Li, F. Fei, Y. L. Qu, Z. L. Dong, W. J. Li and Y. C. Wang, "Theoretical Analysis based on Particle Electro-Mechanics for Au Pearl Chain Formation," The 7th IEEE International Conference on Nanotechnology, 2007.