

Formation of Au Colloidal Crystals for Optical Sensing by DEP-Based Nano-Assembly

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Abstract— We report the observation of photoconductivity in gold colloidal crystal formed based on a dielectrophoresis (DEP) plus self-assembly technique. By using dielectrophoresis and capillary force, we have successfully confined the gold colloidal crystal formation between two electrodes and characterized the electronic properties of the crystal. We have found that the resistance of these crystals (in the M Ω range) has a linear relationship with the intensity of light and hence could serve as optical sensors. We envision that the process developed could be used to potentially fabricate extremely low-cost photo-detector efficiently.

Index Terms—Dielectrophoresis, Colloid Crystal, Self Assembly, Gold nanoparticles, Nano Sensors

I. INTRODUCTION

The study of gold nanoparticles (NPs) or colloid has been drawing much interest in the field of nanotechnology due to its potential applications in nanomedicine and nano photonics. Immense attention is focused on the ability to modify the gold NP surface which allows one to realize unusual cooperative properties that lead to enhanced target binding and introduction of a variety of functional groups [1-5]. This technology has led to the improvement of the sensitivity in medical and biological [6] imaging by site specific labeling of tissues or cells of interest. Medically, due to the biocompatible prosperity of gold NPs, it has also been applied in photo-thermal therapy in preference to the semiconductor quantum dots which is potentially toxic to the cells and consequently humans. Recently, novel methods in gold NP manipulation have been demonstrated such as individual nanoscale device fabrication [7] and size control of the self-assembled gold nanoparticles [8]. On the other hand, sensing technique based on the optical properties of gold NPs or colloid is becoming more promising. For example, localized surface plasmon resonance (LSPR) sensing for optoelectronics and biochemical applications may improve sensor sensitivity while reducing its size significantly [9]. Heat generation upon optical illumination, which becomes especially strong under plasmon resonance, may be used for applications such as drugs delivery [10].

To the best of our knowledge, the photoconductivity of gold colloidal crystal has not been reported. This is possibly because there was no technique to measure directly the resistance change of a Au crystal upon illumination. Here, we present a remarkably simple and low cost method for the fabrication of photonic gold colloidal crystals between metallic electrodes. As a result, we could directly measure the resistance of a Au crystal and hence have observed the photoconductivity in Au colloidal crystals.

II. ELECTRODE FABRICATION

The Au electrodes (Fig. 1) were first fabricated on the Si substrate by a lift-off process. Si wafer was cleaned by immersing it in acetone and followed by isopropanol for 2 minutes, and then were washed thoroughly with deionized (DI) water, and finally dried in an oven at 100 °C. Photoresist was spin-coated on the wafers and the patterns were defined by standard microlithographic method. A 10 nm layer of chromium was deposited on the Si first by thermal evaporation, to provide better gold adhesion to the substrate. A 3000 nm gold layer was then deposited on top of the thin chromium layer. The Au and Cr are etched away to produce the required electrodes with a spacing of approximately 2 μ m. The gold colloidal solution was purchased from British Biocell International, Cardiff, U.K.

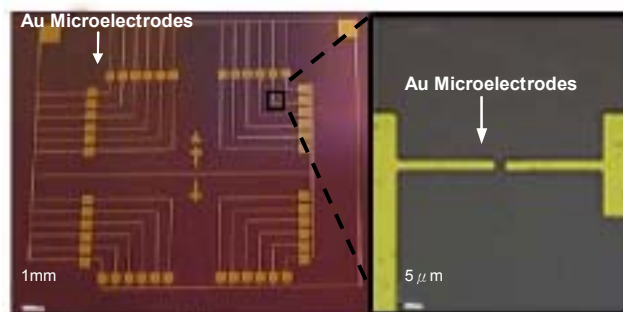


Fig. 1. (a) Photograph of the fabricated array of Au microelectrodes on a Si substrate. (b) Optical image showing a pair of microelectrodes.

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III. DIELECTROPHORESIS

A. Theory

When a polarizable particle is exposed to an alternating electric field, the Coulomb force on either side will not be equal and there will be a net force on the particle [11]. This is called dielectrophoresis and the general expression is given below.

$$F_{DEP} = 2\pi\epsilon_m \text{Re}\{K(w)\}R^3\nabla|\vec{E}|^2$$

where R is the radius of the particle, ϵ_m is the dielectric permittivity of the medium, E is the electric field intensity, and K is the Clausius-Mossotti factors - the effective polarizability of the particle in media. The equation shows that DEP is strongly dependent on the frequency and the magnitude of the electric field. This was verified experimentally and we found that there is a narrow window for the formation and the rate of formation can be controlled by voltage and frequency [12][13], and the particles will align to the electric field as illustrated in the CAD simulation in Fig. 2. A typical Au NP “nanowire” formed between 2 electrodes by DEP force is shown in Fig. 3.

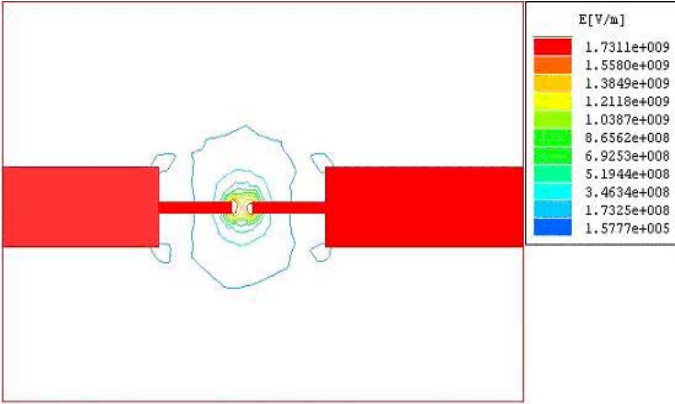


Fig. 2. Simulation of the electric field between the electrodes.

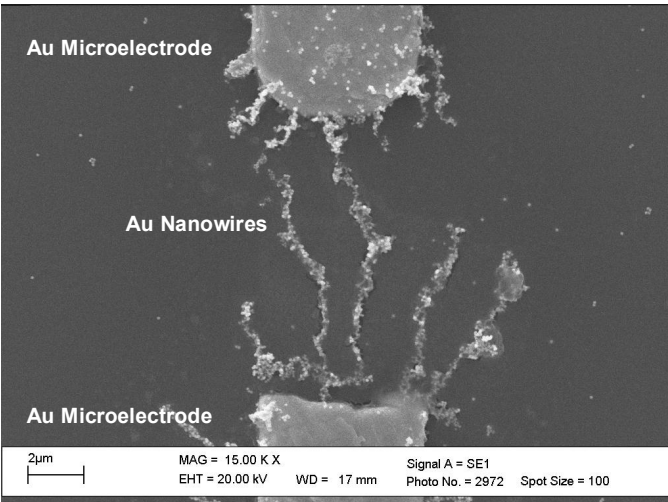


Fig. 3. SEM image of the Au nanowire formed.

B. DEP Condition

A set of experiments were carried out by varying the voltage to investigate its effect on Pearl Chain Formation (PCF). Contrary to the prediction, the size of the particle is weakly independent of the voltage used. The voltage merely determines the rate of PCF and the particle size follows a similar trend and a description of each region in Fig. 4 is given below.

Region 1: This is the region where the gold nanowire formation rate is slower than the evaporation rate hence there is no PCF. A threshold voltage of 3V is needed to complete the formation before the solution evaporates.

Region 2: This is the region where the voltage used is directly proportional to the PCF rate.

Region 3: A higher voltage leads to electrolysis, this leads to corrosion of the electrode and hence the pearl chain formation is slowed down by this effect. Further increase in voltage will damage to the electrodes.

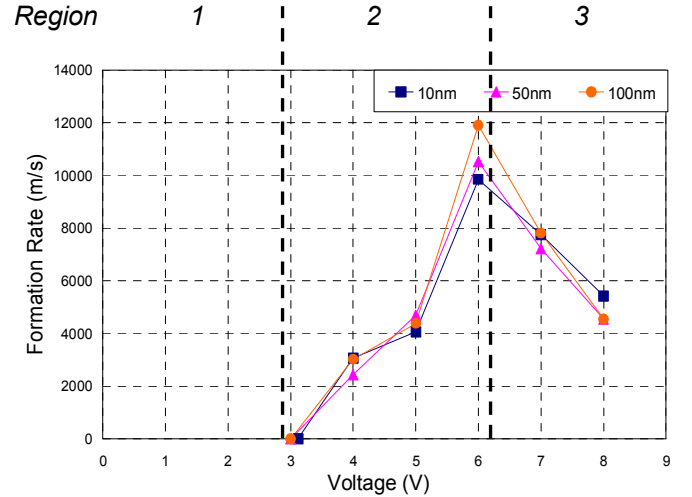


Fig. 4. Parametric plot of voltage relates to the particles size.

Frequency was found to be the most important factor in controlling the nanowire formation. The data from experiments performed at different frequencies and particle size with a constant voltage of $6V_{pk-pk}$ are plotted in Fig. 5. Different sizes of particles shows a similar trend but with shifted peak formation rate. A description of each region is given below. The optimum frequency increases as the particle size decreases (Table 1). However, frequency up to 10MHz was applied to 2nm particles but no Au nanowires could be formed. Later experiments show that colloidal crystals were formed in this region and this is described in a later section. We have divided the applied frequencies into 4 regions which are described below.

1. Low frequency region: The gold colloid does not experience any DEP forces in this region and therefore no PCF is detected. Furthermore, the low frequency leads to electrolysis which causes significant corrosion to the electrodes.

2. *Negative DEP region*: The particles in this region are repelled from the electrodes.

3. *Positive DEP region*: This is the ideal region for PCF, the particles are attracted to the highest electric field intensity area. The particles in this region experience a DEP force proportional to the voltage used.

4. *High frequency region*: There is no PCF at high frequency. This is possibly due to the change of the dipole which cannot keep up with the change in frequency, and hence the particles remain stationary. Also, other researchers speculate that this is due to the suppression of the displacement of the counterionic atmosphere around the particles [14].

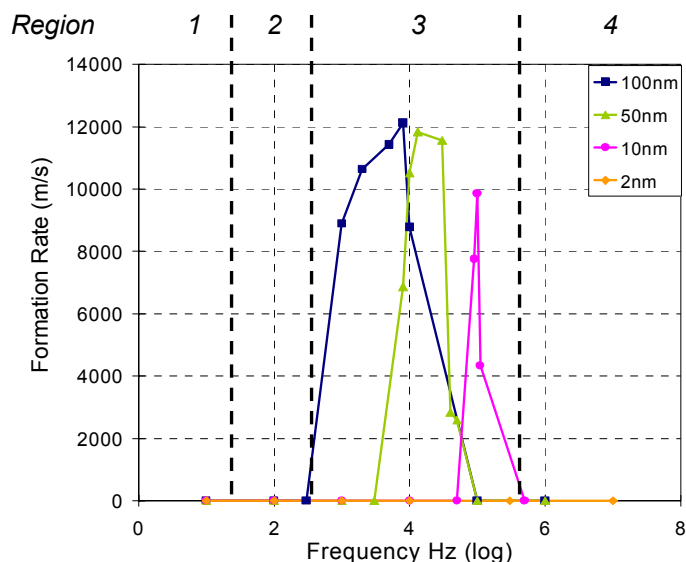


Fig. 5. Parametric plot of frequency relates to the particles size.

Particle Size (nm)	100	50	10
Optimum Frequency (Hz)	8000	40000	100000

Table 1. The optimum frequency for each particle size.

A more profound result in this experiment is that the 2nm particles did not form the desired nanowires. However, a colloidal crystal was observed between the electrodes.

IV. COLLOIDAL CRYSTAL

A. Theory

The formation of natural gemstone opal crystallization by capillary force is a ubiquitous natural phenomenon. Various methods have been utilized to assemble colloid into crystalline lattices with notable example such as gravity sedimentation [15], vertical vapour deposition [16], electrostatic force [17] [18], ultrasound irradiation [19] and self-organization via entropy interaction [20]. Amongst all these methods, crystallization by capillary force has been found to produce good quality crystals and have a much simpler fabrication

procedure. Detailed comparison of each technique can be found in [21][22].

We observed for smaller particles size (2~10nm) the crystal grew preferably in the form of hexagonal or rectangular platelets (Fig. 6a) and for larger particle size (50~100nm) the colloid assemble into strip (Fig. 6b). The general theory of evaporation induced self-assembly of particles on substrate was developed primarily by Nagayama et al. [23] and a comprehensive review of various types of capillary forces on particles has been reported by Kralchevsky and Denkov [24].

This crystallization mechanism involves three major steps. Firstly, the monodisperse gold nanoparticles suspended in liquid organize spontaneously by balancing the charge between the substrate and individual particles charge. However the unknown surface chemistry of commercial nanoparticles makes it difficult to unravel the exact electrostatic force involved in this step. Upon raising the concentration in the suspension, capillary forces at a meniscus between the nanoparticles and the surface laterally displace the particles. After complete evaporation in the third stage, an irreversible restructuring of the particle-substrate interface occurs. This fixes the nanoparticles onto the substrate and prevents the displacement of the colloidal crystal when it is resubmerged into the adsorption liquid.

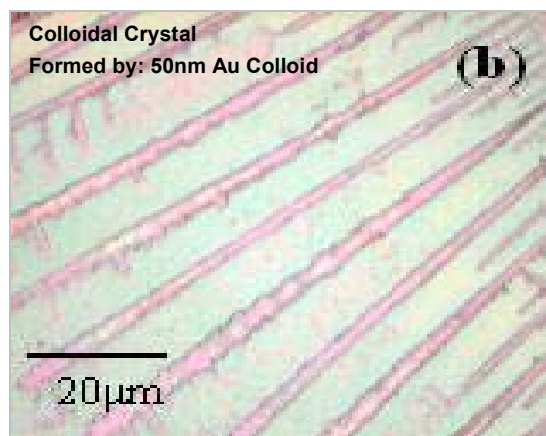


Fig. 6. Optical microscopic image of colloidal crystal: (a) Formed by 2nm Au colloid. (b) Formed by 50nm Au colloid.

Based on these results, we modify the first step of the crystallization mechanism by dielectrophoresis. The first stage controlled by the charge between the substrate and individual particles can be performed by carefully controlling the frequency and voltage. As a result, a stage where the particles are attracted between the electrodes without aggregating was achieved. The combination of the capillary force crystallization and DEP, which affects the position of where the crystallization occurs, can be controlled and the detailed procedures are described below.

B. Experimental Section

The substrate with fabricated gold microelectrodes was placed on the vacuum pump based stage of a micromanipulator station, which allowed the probing of microelectrodes by microprobes. A series resistance of 100Ω was used to limit the current across the colloidal crystal to prevent short-circuit, and a capacitor of $1\mu\text{F}$ was used to filter the DC component. The microelectrodes were then excited by an AC voltage source typically of 7.5 V peak-to-peak with frequency of 300kHz . The voltage was monitored to prevent the Au colloid from bridging the electrodes, because a higher voltage or frequency may cause the colloid to assemble into a wire as reported by [25]. After approximately 15~20 minutes the sample is removed from the probe station and the substrate was air-dried. This is a critical step because if the electric field is removed too early, the Brownian motion would affect the positioning of the gold nanoparticles. On the other hand, if the electric field was applied for too long, the electric field would affect the electrical property of the colloidal crystal. The crystallization was continuously observed using an optical microscope. A SEM image of a crystal formed between a pair of electrodes is shown in Fig. 7.

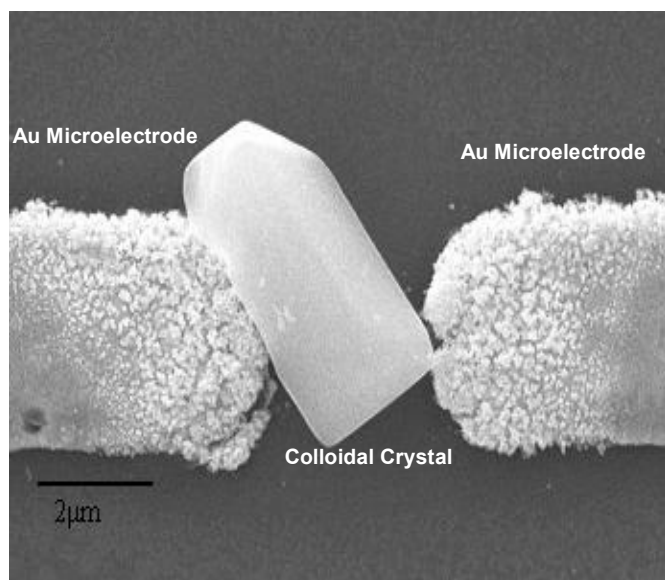


Fig. 7. SEM image of colloidal crystal formed between electrodes by DEP.

By using the condition mentioned above, crystals can be positioned between the electrodes with high accuracy and a resistance in the $\text{M}\Omega$ range (including contact resistance) indicates the successful fabrication of a Au crystal sensor. One

would expect that the resistance is mainly due to the contact resistance, however we found that only colloidal crystals with $\text{M}\Omega$ range resistance would have optically-sensitive properties. This is unexpected for highly conductive gold colloid. We hypothesize that the $\text{M}\Omega$ resistance is due to the interface and the dislocation and defects in the crystal. However the reason for this is still unclear.

We find the optical sensor fabrication technique described above to be quite reproducible, i.e. we have successfully produced Au colloid sensors from two separate shipments. A better understanding of the crystal formation process could significantly increase the yield of the optical sensors. Active investigation in our group is underway to improve this technology by using the microspotting technique.

C. Sensor Characterisation

Optical absorption spectra of the gold colloids were measured using a spectrometer over the wavelength ranges from 300 to 700 nm. Fig. 8 shows the photonic band gap (PBG) effect on the absorption spectrum of Au colloid. A pronounced dip in the emission spectrum is evidence of inhibited spontaneous emission due to the lack of photon density of states in the spectral region relevant to the pseudo gap. The corresponding absorption spectra of the Si substrate are shown in Fig. 8. This indicates there is no absorption in Si and therefore confirming that the optical properties come from the gold colloids.

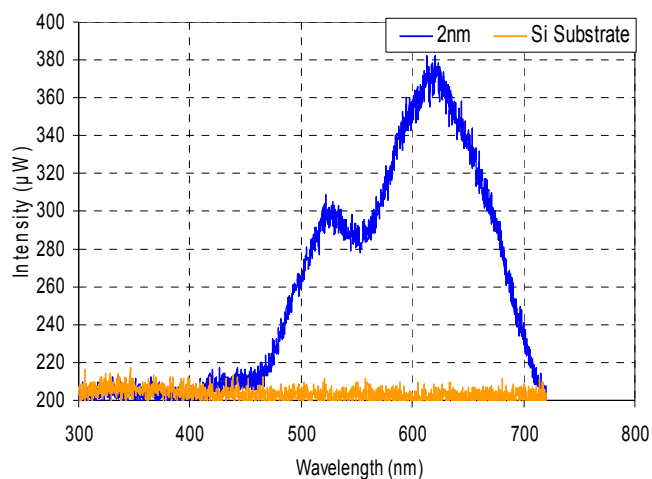


Fig. 8. Photonic band gap effect on absorption spectrum of Au colloid.

Resistance measurements were carried out to investigate how intensity light would affect the resistance of the crystal sensor. The sensor chip was fixed to a PCB and was wire-bonded to enable external electrical connection. Different intensities of light were applied to a Au crystal sensor. The intensity was varied from $1\mu\text{W}$ to $22\mu\text{W}$ and the corresponding resistance of the sensor was monitored. Experimental results showed that resistance across the electrodes decreased with increasing resistance, and the relationship is non-linear as shown in Fig. 9.

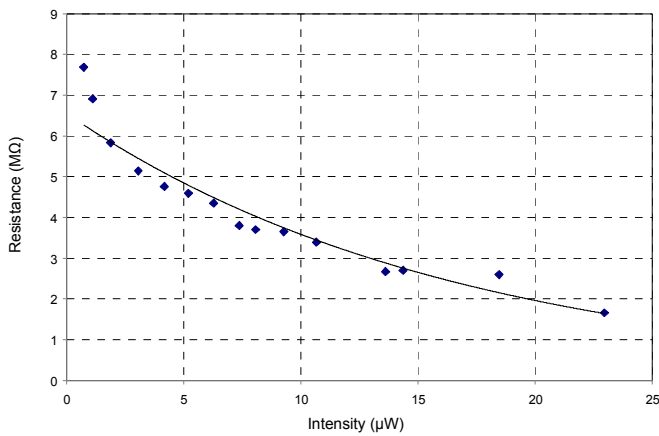


Fig. 9. Magnitude of the resistance of a Au crystal confined between electrodes at different light intensities.

V. CONCLUSION

A mechanism for Au colloidal assembly between electrodes based on DEP and capillary force has been demonstrated. We believed the simplicity of this self-assembly method makes this approach very attractive as a route to economically manufacture optically sensitive nanosensors. The optical properties we observed are still under investigation in our group.

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