Microwire formation based on dielectrophoresis of electroless gold plated polystyrene microspheres*

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Microspheres coated with a perfectly conductive surface have many advantages in the applications of biosensors and micro-electromechanical systems. Polystyrene microspheres with the diameter of 10 μm were coated with a 50 nm-thick gold layer using an electroless gold plating approach. Dielectrophoresis (DEP) for bare microspheres and shelled microspheres was theoretically analysed and the real part of the Clausius–Mossotti factor was calculated for the two kinds of microspheres. The experiments on the dielectrophoretic characterisation of the uncoated polystyrene microspheres and gold coated polystyrene microspheres (GCPMs) were carried out. Experimental results showed that the gold coated polystyrene microspheres were only acted by a positive dielectrophoretic force when the frequency was below 40M Hz, while the uncoated polystyrene microspheres were governed by a negative dielectrophoretic force in this frequency range. The gold coated polystyrene microspheres were exploited to form the microwire automatically according to their stable dielectrophoretic and electric characterisations.

Keywords: dielectrophoresis, gold coated polystyrene microspheres, microwire

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1. Introduction

The AC electrokinetic manipulation of microspheres is rapidly becoming a major area of research, with particular applications in biotechnology. Dielectrophoresis (DEP) is a kind of electrokinetic motion of dielectrophoretically polarised materials in non-uniform electric fields. The polarized material is driven toward or away from the high electric field density region according to the complex dielectric permittivity of the material and its surrounding medium.[1−3]

The DEP technique has great potential in many biotechnology applications, such as the characterization, identification and separation of different particles quickly and effectively in solution.[4−7] Recently, these methods have been applied to the submicrometer scale for the detection and separation of latex spheres,[8−11] viruses,[12,13] DNA and proteins.[14−16]

During the research process of DEP, more attention was paid to the dielectric particles.[17,18] However, the particles coated with a perfectly conductive surface (e.g. metal) are still unexplored. According to their stable, conductive and manageable properties, these particles have potential for the research of biosensors and particles tracing. Although the DEP experiments on some gold nanoparticles have been described elsewhere,[19−21] the detailed properties and applications of GCPMs are rarely mentioned. In this paper, native polystyrene microspheres were coated with a gold shell using an electroless gold plating approach. The dielectrophoretic characterizations of the uncoated polystyrene microspheres and GCPMs were measured and compared with each other. Depending on the perfectly conductive surface, the GCPMs were used to form microwires in our experimental system, showing great promising applications in biosensors and other MEMS devices.

2. Materials and methods

2.1. Preparation of gold coated polystyrene microspheres

Preparation of the gold coated polystyrene microspheres (GCPMs) included two processes: first, the microspheres were suspended in the colloidal gold suspension for 12 h and secondly, the gold plating solution and NaOH were used to coat the microspheres. The schematic model of this procedure is shown in Fig. 1.

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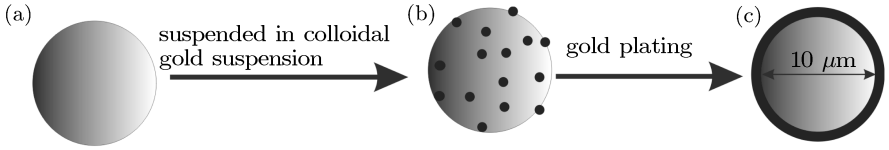


Fig. 1. Electroless gold plating procedure of polystyrene microspheres (a) native polystyrene microspheres, (b) microspheres suspended in colloidal gold suspension so the surface is in contact with some gold nanoparticles, (c) GCPM.

At room temperature, a reducing solution was prepared by adding 12 μL of tetrakis (hydroxymethyl) phosphonium chloride (purchased from Sigma) with 1mL of 1 M KOH (Fisher Scientific) solution to 45-mL deionized water. A gold plating solution of 25mM gold (III) chloride hydrate (Sigma) in 2mL of deionized water was prepared separately. Rapidly inject freshly prepared gold plating solution into the reducing solution and shake it acutely. It will take 12 h for the colloidal gold suspension to become dark brown but translucent, which indicates the size of gold colloids is suitable for gold plating process. Freshly prepared gold plating solution consists of 34 mM (1 mM=10^{-3} mol/dm^3) gold sodium thiosulfate (Alfa Aesar) and 57 mM L-ascorbic acid (Sigma) in 2-mL deionized (DI) water.

The polystyrene microspheres with a diameter of 10 μ m (polysicences) were suspended in the colloidal gold solution and shaken on the vortex for 12 h in order to seed the nano-gold particles on the native polystyrene microspheres surface. After washing a couple of times with DI water, the seeded microspheres were mixed with 600 μL gold plating solution. The GCPMs were obtained directly by adding 300 μL 1 M NaOH.

2.2. Experimental setup

The DEP experiments were observed on quadrupole electrodes, which were fabricated on a square of glass slide using standard photolithography. The materials of the electrodes are platinum and the distance of the two opposite electrodes is 500 μm. A schematic model of the setup for DEP experiments is shown in Fig. 2. The microchip with quadrupole electrodes was placed on the test bed of an inverted microscope (Zeiss Axiovert 40 CFL). A function generator (TTi TGA12104) was used to supply an ac electrical signal to those four electrodes. The electrodes were connected to an AC voltage of angular frequency ω and amplitude V_0 , i.e. $V(t) = V_0 \cos(\omega t)$. The voltage on adjacent electrodes was phase shifted by 180°. A 10× objective lens (numerical aperture of 0.25) was used for the imaging. Diluted GCPMs suspensions were injected in a small cylinder on the surface of electrodes and the experiments was recorded by a high-resolution charge coupled device (CCD) camera (WAT-902H2 Supreme, Watec).

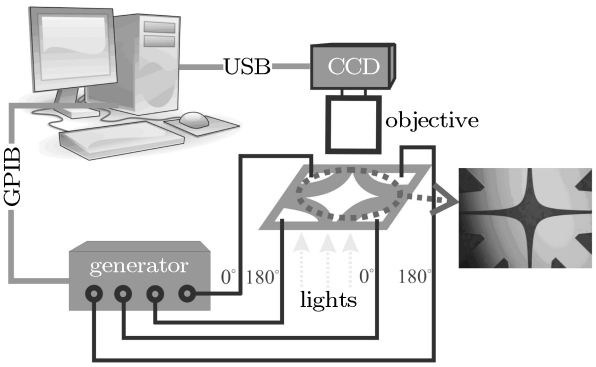


Fig. 2. Schematic model of DEP experimental setup.

3. Results and discussion

3.1. GCPMs

The scanning electron microscope (SEM) image of GCPM is shown in Fig. 3.

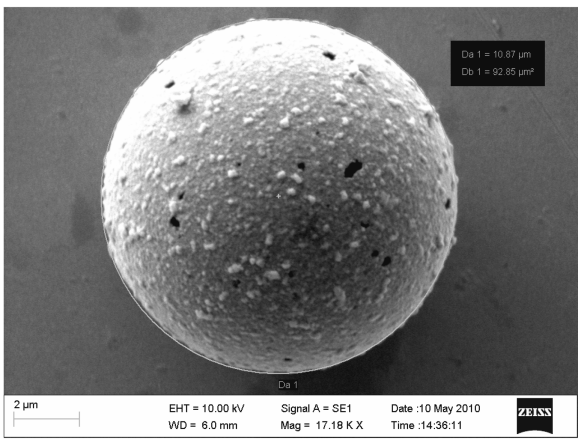


Fig. 3. SEM image of GCPM with the diameter of 10 μm.

The native polystyrene microspheres were coated with a gold shell about 50 nm thick. Due to the gold surface of GCPMs, the light cannot pass through the

GCPMs, leading to a black image under the inverted microscope.

3.2. Dielectrophoresis

Uncharged (neutral) dielectric microspheres in non-uniform electric field experience a time-averaged dielectrophoretic force given by[2]

$$F_{\mathrm{DEP}}(t) = 2\pi\varepsilon_{\mathrm{m}} r^3 \,\mathrm{Re}[K(\omega)]\nabla\left|E_{\mathrm{rms}}\right|^2, \tag{1}$$

where ε_{m} the permittivity of the medium, r the radius of the microsphere, E_{rms} the rms value of the electric field and $K(\omega)$ is the frequency-dependent dipolar Clausius–Mossotti (CM) factor expressed as

$$K(\omega) = \frac{\varepsilon_{\mathrm{p}}^* - \varepsilon_{\mathrm{m}}^*}{\varepsilon_{\mathrm{p}}^* + 2\varepsilon_{\mathrm{m}}^*}, \tag{2}$$

$$\varepsilon_x^* = \varepsilon_x + \frac{\sigma_x}{\mathrm{j}\omega}. \tag{3}$$

Here ε_x^* denotes the complex permittivity which can be rewritten as Eq. (3); σ_x, j and ω are conductivity, $\sqrt{-1}$ and angular field frequency, respectively.

In Eq. (1), if $\mathrm{Re}[K(\omega)] < 0$, the microspheres move towards the high electric field density region and will be attracted by the electrodes. On the contrary, in $\mathrm{Re}[K(\omega)] < 0$ microspheres move towards the low electric field density region and will be driven away from the electrodes. Therefore, $K(\omega)$ is a key factor to dominate the dielectrophoretic behaviour of the microspheres, which can be rewritten as

$$K(\omega) = \frac{\sigma_{\mathrm{p}} - \sigma_{\mathrm{m}}}{\sigma_{\mathrm{p}} + 2\sigma_{\mathrm{m}}}\left[\frac{\mathrm{j}\omega\tau_0 + 1}{\mathrm{j}\omega\tau_{\mathrm{MW}} + 1}\right], \tag{4}$$

$$\tau_0 = \frac{\varepsilon_{\mathrm{p}} - \varepsilon_{\mathrm{m}}}{\sigma_{\mathrm{p}} - \sigma_{\mathrm{m}}}, \tag{5}$$

$$\tau_{\mathrm{MW}} = \frac{\varepsilon_{\mathrm{p}} + 2\varepsilon_{\mathrm{m}}}{\sigma_{\mathrm{p}} + 2\sigma_{\mathrm{m}}}. \tag{6}$$

In Eq. (6), at low frequencies ($\omega\tau_{\mathrm{MW}} \to 0$), the conductivity terms are dominant, while at high frequencies ($\omega\tau_{\mathrm{MW}} \to \infty$), the permittivity terms are dominant. For conductive microspheres in water, this CM factor typically shows a sharp crossover from +1 at low frequency ($\sigma_{\mathrm{p}} > \sigma_{\mathrm{m}}$) to –0.5 at high frequencies ($\varepsilon_{\mathrm{p}} < \varepsilon_{\mathrm{m}}$). The cross frequency related to the properties of the miacrospheres and medium decreases with the increase of σ_{m} and ε_{p}, while σ_{p} and ε_{m} decrease.

For a signal shelled microsphere, the CM factor can be expressed as[3]

$$K(\omega)' = \frac{\varepsilon_{\mathrm{p}}^{*'} - \varepsilon_{\mathrm{m}}^*}{\varepsilon_{\mathrm{p}}^{*'} + 2\varepsilon_{\mathrm{m}}^*}, \tag{7}$$

$$\varepsilon_{\mathrm{p}}^{*'} = \varepsilon_{\mathrm{layer}}^* \left[\frac{a^3 + 2\left(\dfrac{\varepsilon_{\mathrm{p}}^* - \varepsilon_{\mathrm{layer}}^*}{\varepsilon_{\mathrm{p}}^* + 2\varepsilon_{\mathrm{layer}}^*}\right)}{a^3 - \left(\dfrac{\varepsilon_{\mathrm{p}}^* - \varepsilon_{\mathrm{layer}}^*}{\varepsilon_{\mathrm{p}}^* + 2\varepsilon_{\mathrm{layer}}^*}\right)}\right], \tag{8}$$

where $\varepsilon_{\mathrm{p}}^{*'}$, $\varepsilon_{\mathrm{layer}}^*$ are the equivalent permittivity of the whole spheres and the shell permittivity, respectively. The radii of the outer shell and the core are R_{out} and R_{in}, respectively and the ratio of them is $a = R_{\mathrm{out}}/R_{\mathrm{in}}$.

The real part of the CM factors ($\mathrm{Re}[K(\omega)]$) for native polystyrene microspheres against frequency and GCPMs are shown in Figs. 4(a) and 4(b), respectively. As Fig. 4(a) shows, the cross frequency of the real part of CM factor increases as the medium conductivities increase. However, as the conductivity is very low ($\sim 10^{-16}$ S/m), the native polystyrene microspheres can be exterted only by the negative DEP force, which has relatively larger magnitude of the force at low frequency (< 100 kHz) and smaller at the high frequency (> 100 kHz). Compared with the native polystyrene microspheres, the GCPMs can only be exerted by positive DEP force according to the very high conductivity of gold material ($\sim 10^6$ S/m).[18] Therefore, the amplitude of the force is nearly constant in the frequency range of 0–10^{12} Hz, indicating that in our generator working range (0–40 MHz) only positive DEP can be obtained as shown in Fig. 4(b). In this case, we expect that the GCPMs and native polystyrene microspheres can be separated effectively in the frequency range of the TTi 1244 signal generator supplied.

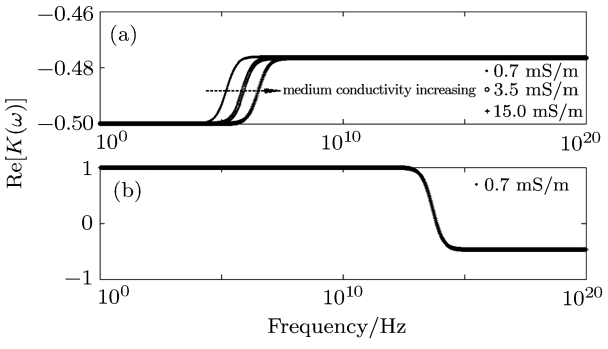


Fig. 4. Real part of the CM factor versus frequency for native polystyrene (dashed) and GCPM (solid line), the dashed circle is partial enlarged detail ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m, $\sigma_{\mathrm{m}} = 0.7$ mS/m, $\varepsilon_{\mathrm{m}} = 78.5 \times \varepsilon_0$, $\sigma_{\mathrm{layer}} = 4.5 \times 10^6$ S/m, $\varepsilon_{\mathrm{layer}} = 6.9 \times \varepsilon_0$, $\sigma_{\mathrm{p}} = 4 \times 10^{-16}$ S/m, $\varepsilon_{\mathrm{p}} = 2.55 \times \varepsilon_0$ and $a = 1.05$).

Figure 5 shows the separation of the two kinds of microspheres with the peak to peak voltage of 10 volts and frequency of 1 MHz. Under this condition,

the GCPM was exerted by positive DEP force while the native polystyrene microspheres by negative DEP force, which is in good agreement with the theoretical prediction. Because the native polystyrene microspheres are driven by negative DEP force, the centers of four electrodes and neighbouring electrodes are in a balanced position, which implies that the force on the native microspheres near the centre is close to zero, so the motion of the native polystyrene microspheres near the centre was not obvious.

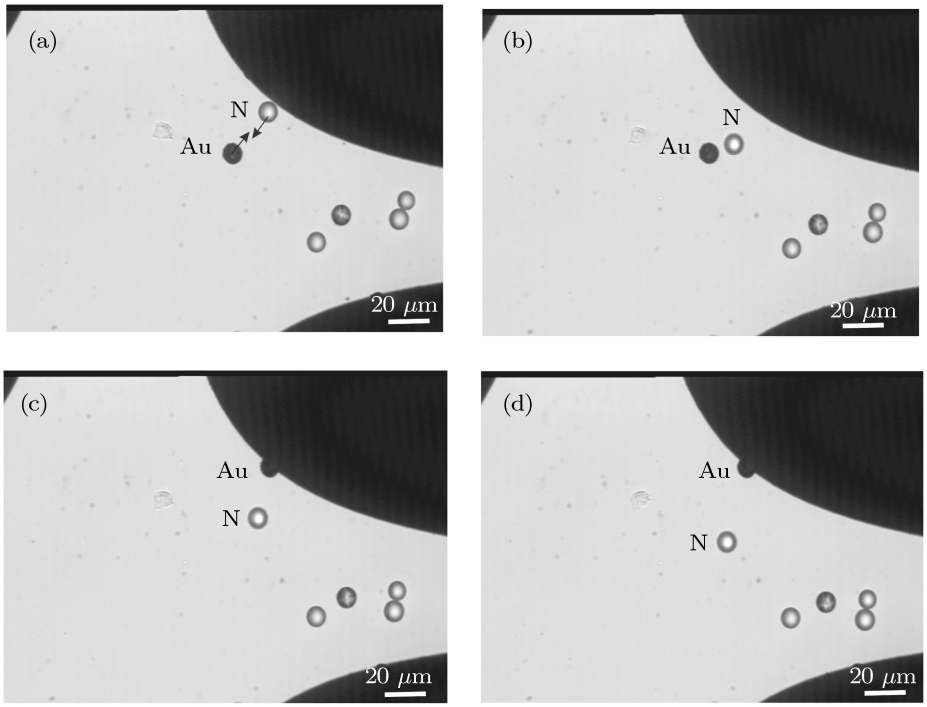


Fig. 5. Dielectrophoresis of gold coated polystyrene(Au) and native polystyrene microspheres (N) at $V_{\rm pp} = 10$ V and $f = 1$ MHz. (a) $t = 0$, (b) $t = 0.6$ s, (c) $t = 1.2$ s, (d) $t = 2.0$ s.

3.3. Automatical microwire formation

Based on the above analysis, the most important properties of the GCPMs are their perfect conductance and stable dielectrophoretic characterisation, which can be used in the MEMS devices. There are two kinds of DEP forces exerted on the GCPMs, i.e. one is the traditional DEP force and another is the mutual DEP force.[3] All the analyses of microwires formation in this paper are explained based on the two forces.

When one particle is adsorbed on the edge of the electrodes due to the positive DEP force, the electric field distribution should be disturbed. In order to compare the initial electric field and the one connected with GCPMs, the electric field distributions are simulated using the commercial software: Comsol 3.5a (http://www.comsol.com) and the results are shown in Fig. 6.

The distribution of the initial electric field is demonstrated in Fig. 6(a) when the voltage is energized on the platinum electrodes. Using cross-section function, the norm electric field on line 'ac' has been drawn and the two electric field peaks take place at the edges of the electrodes as Fig. 6(e) shows. Afterwards, the electric field simulation is produced when one GCPM is adsorbed on the edge of electrodes, which shows an obvious variation in the electric field distribution, owing to the perfect conductance of the GCPM. Figure 6(f) shows the norm electric field distribution on a1c1, in which the norm electric field on the surface of the GCPM jumps to the value of 5.5×10^4 V/m, which has a 37.5% increment compared with the smooth electrode edge. Similarly, Figures 6(c) and 6(d) show the electric field distributions for two and three GCPMs absorbed on the edge of the electrodes, respectively. In addition, the norm electric field distributions on a2c2, a3c3, relative to the two and three GCPMs are shown in Figs. 6(g) and 6(h). Obviously, these values of norm electric field on the distal part of the microwires are 2.3 times that and 3.1 times of the initial value on the edge of the electrode, which implies that the electric field is maximum on the distal particles of the microwire,

so the microspheres will be absorbed linearly one by one. According to the simulations and the theory of positive DEP, the GCPMs move towards the high energy density region,[22] leading to a linear connection, which shows a good agreement with the experimental results.

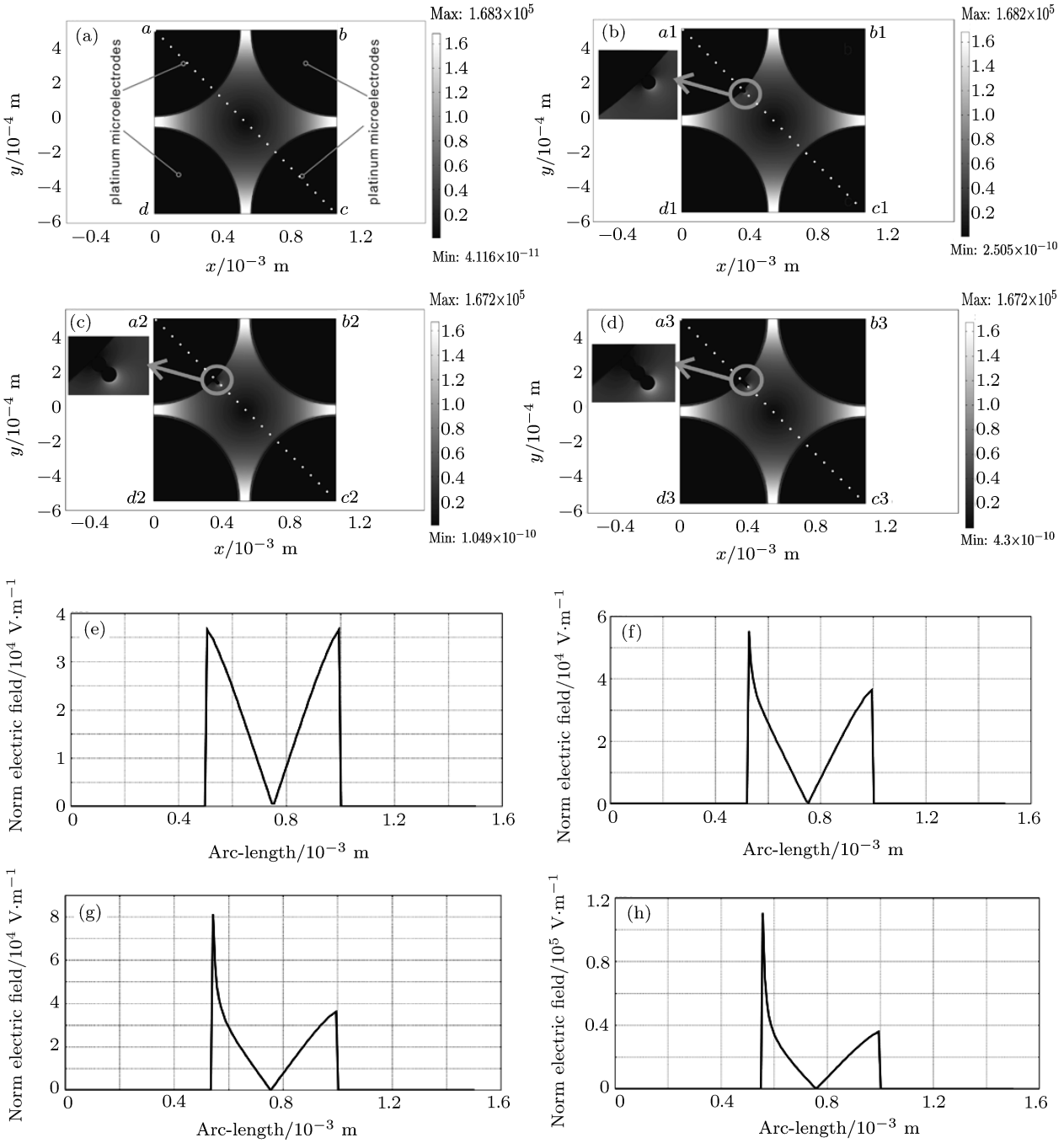


Fig. 6. Electric field simulation results for the microwire formation process: (a) initial electric field distribution, (b) electric field distribution with one GCPM, (c) electric field distribution with two GCPMs, (d) electric field distribution with three GCPMs, (e) norm electric field strength on the line 'ac', (f) norm electric field strength on the line 'a1c1', (g) norm electric field strength on the line 'a2c2', (h) norm electric field strength on the line 'a3c3'.

The above discussions indicate that the microwire based on the GCPMs can be automatically formed by the direct DEP force. However, the mutual dielectrophoresis is still an important factor for the dielectrophoretic manipulation of the microparticles. Depending on the mutual DEP, microspheres dispersed in the electric field attract one another to form a microwire when the electric field strength is higher than

the threshold value.[3] Normally, the mutual DEP is much weaker than direct DEP as a second-order effect. If the microspheres can be contacted together and form a string in the solution, the electrostatic or double layer repulsion must be overcome by dielectrophoretic force. The threshold value of the electric field magnitude can be expressed as[3]

$$|E_{\rm th}| \approx 1.7 \frac{1}{|K(\omega)|} \sqrt{\frac{k_{\rm B}T}{\varepsilon_{\rm p} r^3}}. \tag{9}$$

Equation (9) gives a threshold field magnitude, $|E_{\rm th}|$, which is about 10^5 V/m for the GCPMs (about 10 μm in diameter). In the DEP experimental setup, the maximum distance of the two opposite electrodes is 500 μm, which implies that when the amplitude of the voltage on the electrodes is higher than 10 V, the threshold field strength can be obtained. Therefore, the contribution of the mutual dielectrophoretic force on the formation of the microwire cannot be neglected. Usually, the direct DEP is stronger near the electrodes compared with the mutual DEP, while at the position away from the electrodes, the direct DEP and mutual DEP will compete with each other.[3]

In comparison with the above analysis, an experimental verification for the movements of the GCPMs have been displayed in Fig. 7. Figure 7(a) is the initial state of the GCPMs and the two circles are position symbols of the microwire.

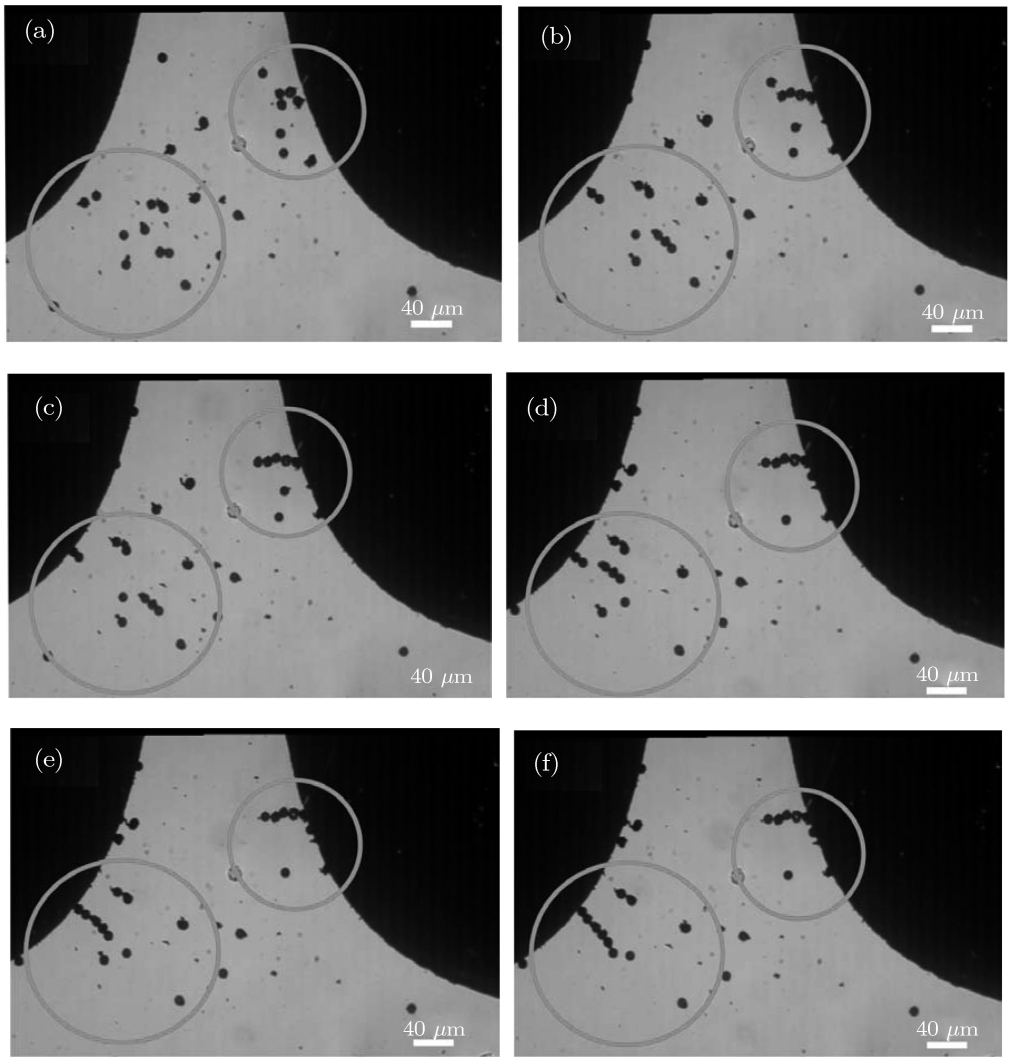


Fig. 7. GCPMs distribution due to the positive DEP force: (a) Initial distribution of GCPMs, (b) t (time)=0.4 s after energising the electric potential, (c) $t = 1.2$ s, (d) $t = 2.0$ s, (e) $t = 2.8$ s, (f) $t = 3.2$ s.

When the 10 Volts (peak to peak) electric potential is energized on the electrodes, the microspheres near the electrodes are absorbed at the edge of the electrodes directly due to the positive DEP force, being the start of the microwire. However, the microspheres far from the electrodes are domained by the mutual DEP to form short microwires and then driven by the stronger positive DEP force to move towards

the microspheres absorbed on the edges of the electrodes. (The DEP force is propotional to the cube of the characteristic size of the particles based on Eq. (3)). Therefore, the microwires formed by GCPMs are governed by both direct positive DEP force and mutual DEP force. Figures 7(b) to 7(f) show the formation procedures of the microwire, verifying the above theoretical analysis. In Fig. 7, the two connected microspheres in the upper part of the big circle, are stuck at the bottom and they have no motion.

Since the electric field strength is higher near the electrodes, the narrow gap between the adjacent electrodes is easier to connect with the microwire. The microwire formed at the narrow gap to connect two electrodes are shown in Fig. 8. Figure 8(a) is the initial state of the GCPMs and Figs. 8(b) to 8(d) are the separated frames of the experimental video. The microwire formed rapidly after energizing the electric potential on the electrodes. An interesting point is that GCPMs at the centre are absorbed together due to mutual DEP force and then move towards the electrodes due to the direct DEP force.

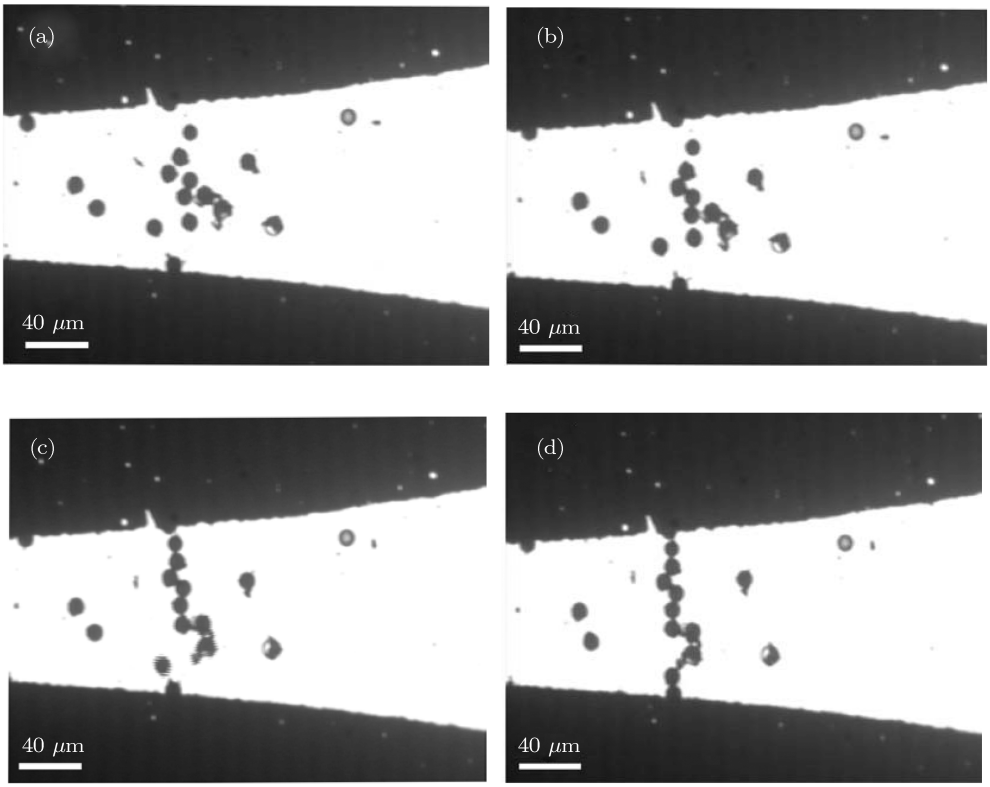


Fig. 8. Microwire formation at the narrow gap of the electrodes: (a) initial state time t=0, (b) $t = 0.12$ s, (c) $t = 0.24$ s, (d) $t = 0.3$ s.

In order to check the conductance of the microwire formed between the electrodes, impedance spectra of the microwires in the dry state were measured. When the microwire was formed, the solution was heated by the electrothermal and microscopy light until it was dried. Then the impedance spectra were measured using impedance analyser (inovol dielectric analyser). There were 13 successful connections in all our 20 experiments, which means that 65% of the connection by the microwire was in the conducting state. One example of the impedance spectrum of the microwire is shown in Fig. 9, where the electrodes gap is 60 μm. Figure 9 shows that the phase and the amplitude of the impedance spectrum are all nearly constant, where the phase of zero implies the microwire is a pure resistance. Therefore, we expect that the microwire could affect the normal DEP experiments and should be analysed.

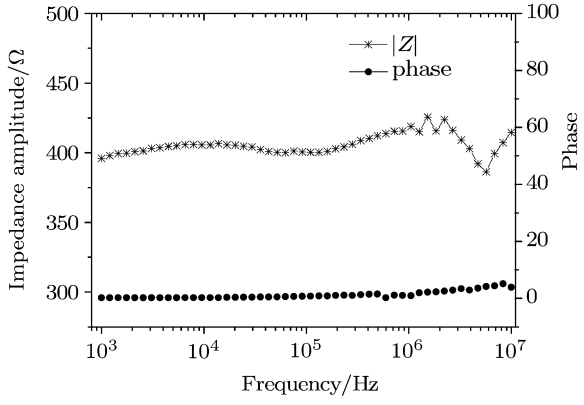


Fig. 9. Spectrum of a microwire with the length of 60 μm.

4. Conclusion

The GCPMs were prepared using the electroless gold plating approach. Theoretical analysis on the dielectrophoretic characterisation of the GCPMs was carried out and the results showed that the GCPMs were only exerted by positive DEP force in the frequency range of 10 Hz to 40 MHz. The DEP experiments were conducted and the experimental results showed a good agreement with the theoretical predictions. According to their stable dielectrophoretic characterisation and electric properties, GCPMs were used to form microwires between the adjacent electrodes. The impedance spectra of the microwires were measured and the results showed that the microwires formed by GCPMs were approximately pure resistors. Therefore, GCPMs can be used to produce mircrowires in the microfluidic systems, showing a great potential for bisensors, photonic crystal, microelectronic device and catalysis.

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