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Electric Field-Induced Chaining of Au/Aniline Polymeric Particle Pairs and TEM Characterization**

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The assembly of colloidal particles into functional structures holds promise for potential nanotechnological applications. Among them, one-dimensional structures are currently in the focus of interest due to their unique properties for nanoelectronics, nanophotonics, and energy transfer.^[1–2] Generally, with the development of microelectronics, lithographic microelectrodes are often adopted to produce strongly inhomogeneous fields for driving individual particles into one-dimensional structures, which are copiously reported in the literature.^[3] However, there also remain two mendable aspects. One is the annihilation of Joule heating produced by the strong electric fields needed to overcome Brown motion.^[4] The other is the exclusive characterization by secondary electron microscopy (SEM). In fact, as far as resolution is concerned, TEM may be preferred in many cases, particularly against the background that more complex nanocomposites are emerging. Herein, a free-contact electrode configuration, serving for TEM characterization, is reported with a copper mesh-grid matrix, exploited as one electrode, and a metal probe as counter electrode, which substitute the photolithographic microelectrodes. This novel electrode configuration for colloidal assembly has the advantages of preventing joule heating and allowing direct characterization with TEM, compared to conventional methods.

The probe tip and the copper mesh grid compose a gradient field, not only in the normal direction but also in the tangential direction to the mesh-grid plane due to their extraordinary electrode configuration (see Figure 1 b). The alteration is crucial. In conventional models, the tip and the plane are symmetrically configured, which simplifies the field calculation but lacks a gradient in tangential direction. Chaining is hardly observed by TEM without a tangential gradient.

The dumbbell-like Au/aniline polymeric particle pairs are chosen as building units, because of their characteristic heterostructures, promising perspectives in applications as well as in theoretical investigations, and their superior characterization by TEM, as Au and polymeric aniline show a minor contrast by

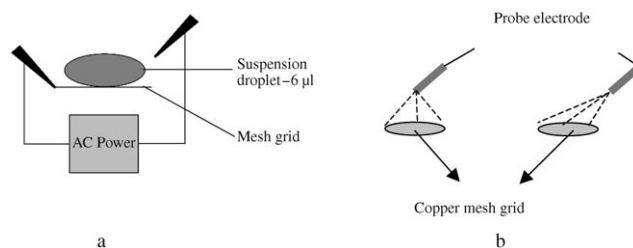


Figure 1. Schematic view of the experimental facility and the electric field distribution. The mesh grid is one electrode, and the probe is the counter electrode: a) improved configuration; b) conventional configuration.

SEM characterization. The synthetic approach is found in the literature.^[5] Briefly, first a 50 mL aqueous solution containing 0.1 wt% HAuCl_4 was prepared and the O_2 in the solution was removed by N_2 bubbling. Then, a fixed amount of distilled aniline, dissolved in 1 mL de-ionized water, was dropped in the above-obtained solution and the mixture was stirred at 90°C for about 1 h. The polymerization of aniline and the reduction of HAuCl_4 occurred synchronously and a Au/aniline polymeric suspension was obtained. The sizes of the Au and the organic spheres are about 20 and 60 nm, respectively. Figure 2 shows the TEM picture of the original sample.

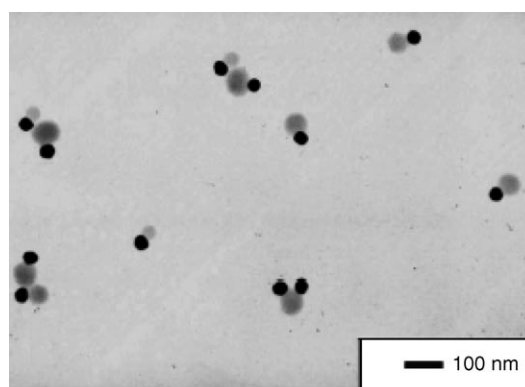


Figure 2. TEM picture of the original Au/aniline polymeric suspension.

Two metal probes were fixed onto a micromanipulator and can be three-dimensionally adjusted. About $6\ \mu\text{L}$ of the suspension was dropped onto the copper mesh grid, which was in a short circuit with one probe, while the other probe was adjacently positioned to the rim of the mesh grid to generate a field gradient. Figure 1 a shows the experimental setup. The voltage was fixed at 50 V to maximize the field strength due to the macroscopic gap between the electrodes. The frequency was tuned from 500 Hz to 100 kHz according to literature data.^[3,6–8] The resultant morphologies confirm the optimal frequency is about 1 kHz. Particle-pair chaining was observed by TEM after the droplet under the alternating-current (AC) field evaporated. Two types of chaining are obtained, depending on whether the particle pair is polarized along the major-axes or the minor-axes direction, as shown in Figure 3. Prompting the

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[**] TEM = Transmission Electron Microscopy.

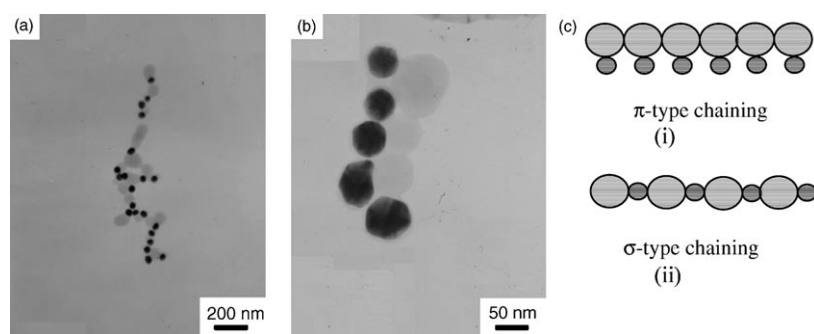


Figure 3. Chaining of different modes at 50 V: a) 1 kHz, showing the σ -type chaining, where the directions of the forces exerted on the Au and organic spheres, are identical; b) the typical π -type chaining at about 900 Hz. As the long axis is perpendicular to the polarizing direction, the dipolar interaction is clearly weaker compared to the σ -type chaining and the chain length is shorter; c) schematic view of the σ - and π -type chaining. Due to the similarity of the $\langle gp \rangle$ -electron bonding, (i) is named after the shoulder-to-shoulder arrangement, and (ii) is named after the head-to-tail arrangement.

morphologic similarity between the particle pairs and π -electron cloud, we may call the two combinations σ - and π -type chaining, respectively (see Figure 3c). In general, the probability for π -type chaining is low due to the following reasons: 1) the interfacial charges with the same polarity prevent the units from conglomeration, and 2) the major axes is perpendicular to the polarizing direction as well as to the assembling direction. Therefore, from any viewpoint of electrodynamics or topology, the formation of π -type chaining is not preferred for the assembly. Accordingly, the chains are short and not stable. However, the mechanism of π -type chaining is not different from the σ -type chaining. They both derive from the mobility and the interaction of particles induced by an AC electric field, namely, the dielectrophoresis (DEP).^[9–10] The morphologies are not ideally chainlike since Brown motion, the evaporation effect and the disturbances during the movement are hardly surmounted.

When the suspension is subjected to an AC field, the Au and the organic section are both polarized and the particle pair can be regarded as a dipole. Here, a particle pair is treated as a bi-spheroid combination with interfacial counteraction. Due to the nonuniformity of the field, there is a DEP force, exerted on the particle pairs. The gold colloid performs as a conductor in electric field, leading to exciting equal-quantity and alien-sign charges on the surface along the field direction, which only depend on the field strength, E . The aniline polymeric colloid behaves as a dielectric in the electric field, with the excited charges depending on the field strength, E , and the polarizability, p . The general average dielectrophoretic force, F_{DEP} is expressed by Equation (1), in dependence on the particle volume, v , and the effective polarizability, p , as well as the root mean square of the electric field gradient, E .^[11]

$$\langle \bar{F}_{DEP} \rangle = \frac{1}{2} p v \nabla \bar{E}_{rms}^2 \quad (1)$$

The colloid particle is composed of two independent spheres. It is inferred that particle pairs are similar to the spherical particles in the dielectric characteristics in addition to some modifications. As far as one homogeneous and spherical

particle are concerned, the effective polarizability, p , as well as thus the particle's dipole effects in an electric field, can be described by the Clausius–Mossotti factor, $K(\omega)$, of Equation (2):

$$K(\omega) = \frac{\tilde{\epsilon}_p - \tilde{\epsilon}_m}{\tilde{\epsilon}_p + 2\tilde{\epsilon}_m} \quad (2)$$

where $\tilde{\epsilon}$, often in the form of $\epsilon - i\sigma/\omega$, is the complex permittivity, dependent on the frequency, ω , and the electrical conductivity, σ , of the medium.

From the combination of Equations (1) and (2), the dielectric force can now be written as Equation (3):

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

From Equation (3) it follows, when $\text{Re}[K(\omega)]$ is positive, the resulting dipole moment leads to a force towards regions of high electrical field and when $\text{Re}[K(\omega)]$ is negative, the resulting dipole moment leads to a force towards regions of low-field density. Au and organic spheres are both subjected to forces, \vec{F}_{DEP}^{Au} and \vec{F}_{DEP}^{AP} . Thus, the particle pair is subjected to the vector sum of \vec{F}_{DEP}^{Au} and \vec{F}_{DEP}^{AP} . Since the colloid particle is dumbbell-shaped, it shows a geometric anisotropy, with the result that the induced dipole moment is parallel to the imposed electric field only if the particle is aligned with one of its principal axes parallel to the field.^[12] The particle pair will assemble as a σ -type chain by experiencing an alignment torque of the external field. A detailed quantitative description can be found in reference [12]. Just because of the coherent motion of dipoles under an electric field, one-dimensional chains become the prior form of the conglomerates. However, the particle pair is also not in accord with a prolate ellipsoid model. For a lossy ellipsoid, depending on the relative conductivity and permittivity values, all three orientations of the ellipsoid become possible, each in a different frequency regime. In our experiments, no such phenomenon is observed in a broad frequency range. The π -type chaining seems little correlative with the frequency and is determined by the possibility more than by the frequency. If the particle pair is polarized just along the minor-axes direction and the particle pairs congregate into chains before they flip to the major-axes orientation, the π -type chaining will take place.

In Figure 4, Au spheres are sparse, and organic spheres constitute chains, which are prevalent when the frequency is above 1.2 kHz, but below 1.4 kHz. If the frequency exceeds 1.4 kHz, Au and organic spheres link together again. This is reproducible. The above-mentioned theory may account for it. The crucial understanding is the close correlation between $\text{Re}[K(\omega)]$ and the electric field frequency. A further developed expression for $\text{Re}[K(\omega)]$ is obtained in Equation (4):^[13]

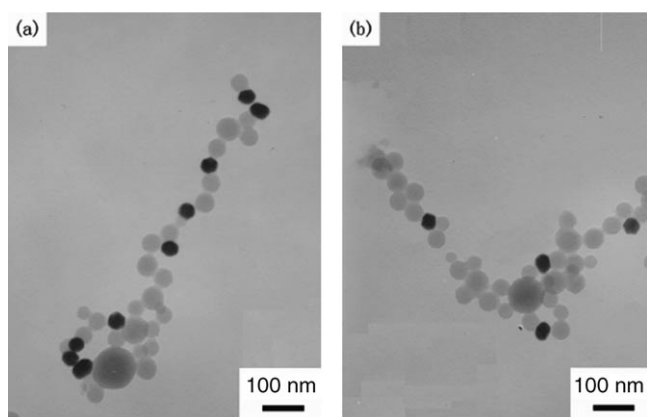


Figure 4. a,b) Microstructures at 1.3 kHz, showing the instance where the direction of the forces, exerted on the Au and organic spheres, are opposite.

$$\operatorname{Re}[K(\omega)] = \frac{(\sigma_p - \sigma_m)}{(\sigma_p + 2\sigma_m)} \left[\frac{\omega^2 \left(\frac{\varepsilon_p - \varepsilon_m}{\sigma_p - \sigma_m} \right) \left(\frac{\varepsilon_p + 2\varepsilon_m}{\sigma_p + 2\sigma_m} \right) + 1}{\omega^2 \left(\frac{\varepsilon_p + 2\varepsilon_m}{\sigma_p + 2\sigma_m} \right)^2 + 1} \right] \quad (4)$$

Equation (4) reveals that when the AC electric fields are employed, both the magnitude and the sign of force can be manipulated by means of changing the frequency. Then, a cross-over frequency, f_0 , is defined to denote the frequency at which the factor $K(\omega)$ changes its sign and therefore the force F_{DEP} reverses. A mathematical representation for f_0 is found by solving Equation (4) for $\operatorname{Re}[K(\omega)] = 0$, yielding Equation (5):

$$f_0 = \frac{1}{2\pi\varepsilon_0} \sqrt{\frac{(\sigma_p + 2\frac{\lambda_s}{R} + 2\sigma_m)(\sigma_p + 2\frac{\lambda_s}{R} - \sigma_m)}{(\varepsilon_p + 2\varepsilon_m)(\varepsilon_m - \varepsilon_p)}} \quad (5)$$

where R is the radius of particles and λ_s is the so-called surface conductance, relevant to charges located on the particle surface, which in turn cause the formation of a diffusion, so-called Debye layer adjacent to the particle surface.^[14]

According to Equation (5), if the particle pair is considered as an aggregate of two individual spheres, the cross-over frequency of the Au part is obviously different from that of the aniline polymeric part, due to their disparate dielectric parameters. When one cross-over frequency is reached, the organic spheres will be subjected to a force opposite to that exerted on the Au spheres. This force detaches the particle pair, whose combination is not strong as anticipated by the reaction approach.^[5] Based on the above-mentioned model, the aniline polymeric and Au particles are independently polarized so that when they are detached, the AC electric field also plays the

DEP role in the particle assembly. As the magnitude of frequency, driving the Au nanoparticles assembly, is far lower than the cross-over frequency, only organic spheres assemble into chains. When another critical frequency is reached, the force on the Au spheres re-consist with that of the organic spheres, which leads to the recombination of Au and organic spheres.

The optimum frequency is the result of reconciling Equation (4) and some external electromagnetic field-induced effects. Based on Equation (4), in the higher- and low-frequency regime, $\operatorname{Re}[K(\omega)]$ trends towards constants with the quantities $\frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m}$ and $\frac{\sigma_p - \sigma_m}{\sigma_p + 2\sigma_m}$, respectively, so that the curve of the $\operatorname{Re}[K(\omega)]$ -frequency function is flat in the low-frequency range as well as the high-frequency range and monotonously changing in intermediate frequency range. Therefore, when the frequency is tuning higher and higher, the F_{DEP} has less influence in the assembly while the oscillation of the dipole moment, induced by the external electromagnetic field, plays an increasingly dominant role, which will influence the chaining stability (see Figures 5a and 5b). But if the frequency is too low to ignore the

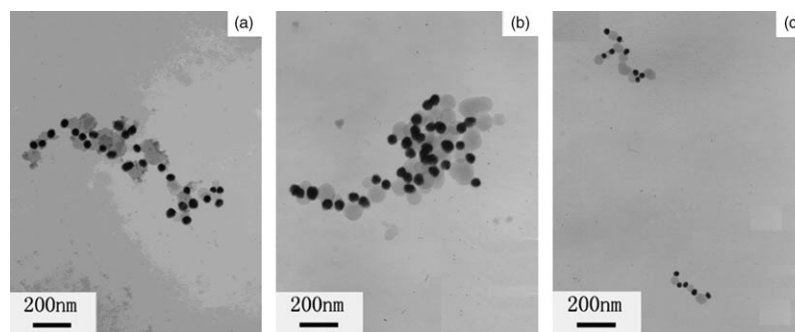


Figure 5. Imperfect chaining at 50 V at different frequencies. a,b) Microstructures obtained at 2 kHz and higher frequency. Conglomeration is observed, which can be ascribed to the instability, induced by oscillations of the dipolar moments. c) Microstructure obtained at 500 Hz, showing short chains. This is due to the insufficient polarizability caused by the “shielding effect” of the solvent molecules.

“shielding effect” of the solvent, the particles will fail to form chains because the surrounding H_2O molecules weaken the dipole interactions (see Figure 5c). So, excessively high or low frequency is inadvisable. According to our experiment, approximately 1 kHz maximizes the effects. The average chain lengths at different frequencies are plotted in Figure 6. Finally, the assembly, which does not finish until the suspension is evaporated within approximately 1 h, implicates the existence of a ripening process, which is responsible for the stability of the chains after the electric field is removed. It is also confirmed by the fact that in TEM, large conglomerates of dissociated Au and aniline polymeric particles are often found, but no small dissociated particles are observed.

In conclusion, chaining of inhomogeneous particle pairs can simply be obtained and predicted by the use of dielectrophoresis, in combination with some novel and interesting phenomena. The works reported here further develop the assembling approaches both in the electrode configuration and the characterization. The theoretic interpretation indicates that as far as particle-pair-like nanostructures are concerned, the inte-

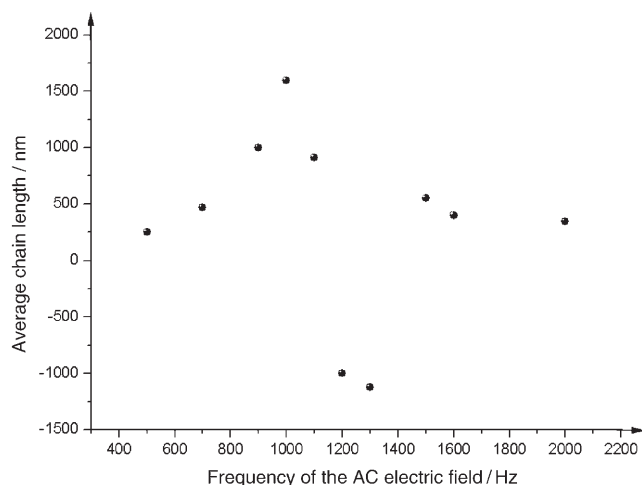


Figure 6. The average chain length varies with the frequency of the AC electric field. The negative length values mean that the DEP forces, exerted on Au and aniline polymeric particles, are reversed and these particles are detached.

gration of two individual spheroid models is also valid. With the development of nanotechnology, more complex nanostructures are emerging and the demand for high-resolution characterization increases. Even at this exploratory stage, our method and conclusions will play quite important roles.

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Keywords: colloids · dielectrophoresis · electrochemistry · particle pairs · self-assembly

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