Dielectrophoretic Self-Assembly of Au Nanorods for Sensing Applications

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Abstract. Anisotropic 1-D metal nanostructures are attractive building block for future optoelectronic nanoscale devices and systems. However, a critical challenge remains the lack of manipulation methods that enable controlled positioning and orientation of metal nanostructures in a fast, reliable and scalable manner. To address this challenge, we explore dielectrophoretic based assembly of discrete gold nanorods and demonstrate site selective assembly and orientation of these rods. The demonstrated optical sensitivity of such large order nanostructures to the local environment opens the way to development of nanoscale sensing devices.

1. Introduction
Colloidal gold nanostructures have received widespread attention in recent years due to both their unusual properties and promising applications.[1-3] Among gold nanostructures, gold nanorods are particularly interesting since their optical properties are tunable throughout the visible and near infrared region of the spectrum as a function of nanostructure size, shape, aggregation state and local environment.[4-6] For nanorods the plasmon band splits in two: the longitudinal plasmon band corresponding to light absorption and scattering along the long axis of the rod, and the transverse plasmon band, corresponding to light absorption and scattering along the short axis of the rod. As result, the light emitted from or scattered off nanorods is strongly polarised along the rod length axis, making them particularly attractive for specialised optoelectronic and bio-chemical sensing applications.[7-10] However, the potential of 1-D metal nanostructures for integration into future nanoscale sensing devices and systems will depend on the availability of new scalable manipulation methods that enable controlled positioning and orientation of nanorods in a fast, reliable and scalable manner. One approach, compatible with these requirements, is the exploitation of electric fields to drive the transport, localization and self-assembly of nanostructures at selected areas on a receptor chip substrate. Self-assembly of a variety of structures ranging in size from microns to nanometres including: GaAs based LEDs [11], biological cells [12], semiconducting and metallic nanoparticles [13], DNA molecules [14] carbon nanotubes [15] metallic and semiconductor nanoparticles [16] using electric fields has been widely reported. By contrast, there have been very few reports of electric field assisted assembly of gold nanorods on substrates suitable for optical sensing applications.[17]

Herein, we report on the dielectrophoretic manipulation and self-assembly of discrete gold nanorods suspended in water solutions at fused silica chip substrates. Dielectrophoresis (DEP) is defined as the
motion of uncharged polarisable particles in a non-uniform electric field [18]. The DEP forces arise from the interaction of the electric field with a dipole induced in the particle which exerts a translational motion on the particle. Depending on the permittivity and conductivity of both the particle and supporting medium, and also on the frequency of the applied electric field, particle motion is directed either towards (positive DEP), or away from (negative DEP) regions of high electric field strength. While DEP occurs under both direct current and alternating current (AC) conditions, AC electric fields are most commonly employed to: suppress electrophoresis of solvent molecules, eliminate motion due to particle surface charge and prevent undesired electrochemical interactions at the electrode surface, such as electrolysis, enabling the application of higher drive voltages. In this work, we demonstrate dielectrophoretic-based self-assembly of gold nanorods 14 nm in diameter and aspect ratio of 3. Nanorods suspended in water, were self-assembled on fused silica substrates, following application of an applied voltage of 20 Vpp at 1 MHz. Typical assembly times were on the order of ca. 30 minutes. Following assembly, nanorod arrays were characterised using scanning electron microscopy (SEM) and optical microscopy. Electric field simulations were undertaken to elucidate the electric field strengths and dielectrophoretic forces resultant on arrays of nanorods. Finally the dependence of assembled nanorod arrays optical properties from the local environment were investigated by darkfield microscopy.

2. Experimental

2.1. Au nanorod synthesis

Seed Solution. CTAB solution (5 mL, 0.20 M) was mixed with 5.0 mL of 0.00050 M H\textsubscript{2}AuCl\textsubscript{4}. To the stirred solution 0.60 mL of ice-cold 0.010 M NaBH\textsubscript{4} was added, which resulted in the formation of a pale brown solution. Vigorous stirring of the seed solution was continued for 2 min. after the solution was stirred, it was kept at 27 °C.

Growth of Nanorods. CTAB (25 mL, 0.20 M) was added to 1 mL of 0.0010 M of AgNO\textsubscript{3} at 27 °C. To this solution, 25 mL of 0.00010 M H\textsubscript{2}AuCl\textsubscript{4} was added, and after gentle mixing of the solution 0.35 mL of 0.0788 M ascorbic acid was added. Ascorbic acid as a mild reducing agent changes the growth solution from orange to colorless. The final step was the addition of 60 μL of the seed solution at 27 °C. The color of the solution gradually changed within 10-20 min. the temperature of the growth solution was kept constant at 27 °C until growth process was complete (90-120 min).

2.2. Au Nanorod characterisation:

Scanning electron microscopy (SEM) images of individual Au nanowires were acquired using a field emission SEM (JSM-6700F, JEOL UK Ltd.) operating at beam voltages of 2 kV. Transmission electron microscopy (TEM) images were acquired using a high resolution TEM (2100, JEOL UK Ltd.) operating at beam voltages of 200 kV. Optical micrographs were acquired using a calibrated microscope (Axioskop II, Carl Zeiss Ltd.) equipped with a charge-coupled detector camera (CCD; DEI-750, Optronics) and with darkfield condenser for darkfield imaging.

2.3. Fused silica assembly chip fabrication:

Transparent fused silica chip substrates comprised two gold comb electrode structures. The electrodes were arrayed such that the electrode fingers (20 μm width, 1000 μm length and 50 μm pitch) were interdigitated and separated by a gap of 10 μm. In this manner, each electrode finger was electrically isolated from its nearest neighbours. Conducting interconnection tracks connected each comb electrode to a unique contact pad. Electrodes, interconnection tracks and contact pads were fabricated by sputtering Au (200 nm) onto a Cr (10 nm) adhesion layer on a four inch fused substrate. Metallisation was patterned using standard photolithography and lift-off techniques.
2.4. Optical characterization Darkfield Polarised Spectroscopy
Brightfield optical images of fabricated electrodes and darkfield optical images of gold nanorod arrays dielectrophoretically self-assembled on electrodes were acquired with an optical microscope (Zeiss axioskop II) equipped with a CCD camera (Optronics DEI-750) using a 100 W halogen lamp as illumination source. Polarised darkfield spectra of linear arrays of gold nanorods were measured with an inverted IX-71 Olympus microscope with an oil immersion darkfield condenser (Olympus U-DCW) and 50X objective. The sample was illuminated with a 100 W halogen lamp. The light collected by the objective was directed into the entrance of slit of a 0.3 monochromator (SP-2356, Acton Research) equipped with a thermoelectrically cooled, back illuminated CCD (Spec10:100B, Princeton Instruments). The experiments were performed by first recording an image of the sample with a mirror in the light path of the spectrometer. Once a suitable linear array was selected, the mirror was switched with a grating (300 groves mm\(^{-1}\)) to disperse the scattered light. The acquisition time for the spectra was one minute. Polarized spectra were obtained by placing a polarizer between the illumination source and the condenser.

2.5. Electric field simulations
Electric field simulations were undertaken to elucidate local electric field magnitudes present at comb electrode structures. Finite element simulations were performed using a partial equation solver (COMSOL Multiphysic) within the electrostatic limit \( \nabla (\varepsilon \nabla \phi) = 0 \). Because the electrode length was much larger than the other dimensions and larger than the gap spacing, the problem could be conveniently reduced to a 2D problem without affect the simulation accuracy. The geometry consisted of two half electrodes 200 nm thick separated by 10 μm on top of 100 μm thick quartz substrate (\( \varepsilon = 5\varepsilon_0 \)) and covered by 100 μm thick water (\( \varepsilon = 30\varepsilon_0 \)) with 20 V\text{pp} across the electrodes.

3. Results and Discussion
3.1. Gold nanorods synthesis and characterization
Gold nanorods were fabricated according to the seed method described in details by El Sayed et al. [19] This method affords high yield of gold nanorods with an intense longitudinal plasmon resonance peak centered at 765 nm and a smaller transversal Plasmon peak centered at 520 nm (see figure 2a). Figure 2b shows a SEM image of gold nanorods deposited on a Si substrate. The average length of gold nanorods measured from statistical analysis on SEM images (image J, 100 nanorods measured) showed an average nanorod length of 41 nm. The diameter of gold nanorods measured from TEM images was calculated to be 14 nm.
3.2. Gold nanorods dielectrophoretic alignment:

Dielectrophoretic self-assembly experiments were undertaken by applying a sinusoidal AC voltage under ambient light conditions to the receptor electrodes at fused silica substrates. The as-prepared nanorod solution (1 ml) was centrifuged three times at 13000 rpm for 5 min and redispersed in 100 μl of DI water (resistivity = 18.2 MOhm cm) in order to minimize the concentration of free ions in solution due to the CTAB excess. A 5 μl drop of the nanorod solution was placed on top of the metal electrodes and left to dry under an applied voltage of 20 V_{pp} at 1 MHz using a function generator (HP8116A Hewlett Packard) via direct probing to contact pads (ca. 30 min). As result of the applied electric field large arrays of gold nanorods aligned perpendicular to the electrodes (and parallel to the
electric field lines) were formed. Figure 3a shows and SEM image of the well separated large nanorod arrays covering the entire electrode area. In contrast, only random gold nanorods between electrodes were observed in absence of applied electric field (Figure 3b). The average diameter and length of formed arrays was estimated to be respectively ca. 100 nm and 10 μm. The extent of nanorod array alignment on the substrate was quantified by determining an orientational parameter, S, defined as

\[ S = \frac{2 \cos^2 \theta - 1}{\langle \cos^2 \theta \rangle} \]

Where \( \theta \) is the angle between an array and the electric field direction, and brackets, \( \langle \rangle \), denote an ensemble average. An order parameter of \( S = 0.98 \), calculated using a sample of greater than 100 separate nanorod arrays, indicated a high degree of alignment (see figure 3c). Closed up examination revealed that gold nanorods within individual arrays were also partially aligned respect to the field direction (see figure 3d). \( S \) values between 0.4 and 0.6 were calculated for individual gold nanorods taken from different array lines.

3.3. Dielectrophoresis-mediated process:
In a neutral prolate ellipsoid nanoparticle (nanorod), an electric field \( \mathbf{E}_n \) parallel to the \( n \) axis induces a dipole moment given by [20]

\[ \mathbf{P}_n = V \varepsilon_m K_n^* \mathbf{E}_n \]

Where \( V \) is the nanorod volume, \( n = L, T \) label the Longitudinal and Transversal axis, \( \varepsilon_m \) the dielectric constant of the medium and \( K_n^* \) the Clausius-Mossotti factor

\[ K_n^* = \left[ \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + A_n(\varepsilon_p^* - \varepsilon_m^*)} \right] \]

in which \( \frac{\varepsilon_p^*}{\varepsilon_m^*} = \frac{\varepsilon_p + \sigma_p}{\varepsilon_m + \sigma_m} \) is the complex dielectric function of the particle and the medium respectively and

\[ A_L = \frac{1 - \varepsilon^2}{2\varepsilon^2} \left[ \ln \left( \frac{1 + \varepsilon}{1 - \varepsilon} \right) - 2\varepsilon \right], \quad A_T = \frac{1 - A_L}{2} \]

is the depolarising factor referred to the longitudinal and transversal axis where \( \varepsilon = \sqrt{1 - \left( \frac{1}{R} \right)^2} \) is the eccentricity and \( R \) the aspect ratio of the particle. When the interaction between the induced dipole and the applied AC electric field is the dominant process in the system, the nanorod experiences a torque \( \mathbf{T} \) which aligned the longitudinal main axis along the field lines

\[ \langle \mathbf{T} \rangle = \frac{1}{2} V \left( A_T - A_L \right) Re(K_L^* K_n^*) E^2 \sin(2\theta) \]

With \( \theta \) the angle between the longitudinal axis and the electric field and a dielectrophoretic force \( \mathbf{F}_{\text{DEP}} \) with the \( n \) axis parallel to the field direction

\[ \langle \mathbf{F}_{\text{DEP}} \rangle = \frac{1}{2} V \varepsilon_m Re(K_n^*) \mathbf{E}^2 \]
Where $\langle \ldots \rangle$ indicates the time average. Metal nanorods are particularly interesting to study due to their conductivity and permittivity much higher than that of the medium. The Clausius-Mossotti factor shows a crossover from positive to negative value well above any reasonable frequency excitation, assuring a positive dielectrophoretic force. For gold rods in water negative dielectrophoresis occurs at frequency as large as $10^{18}$ Hz [21], therefore in the MHz range, the Clausius–Mossotti factor can be approximated with a constant value $K_\alpha \sim A_\alpha^{-1}$ that is only geometry-dependent [22]. Within this approximation, and using an aspect ratio $R=3$, the effective polarisability along the main axis defined by

$$\alpha_L = V\varepsilon_m K_L$$

Can be estimated as $\alpha_L = 5 \times 10^{-32}$ C m²/V. Comparing the dipole energy in electric field with the thermal energy of the particles, we can estimate the minimum electric field strength necessary to overcome the Brownian motion

$$E_{\text{min}} \cdot P_L \approx kT$$

Using $\alpha_L = 5 \times 10^{-32}$ C m²/V and $T = 300$ K we obtain $E_{\text{min}} \approx 3 \times 10^4$ V/m. Simulation of the electric field across the electrode gap in figure 4a showed that the electric field reached a maximum value of $10^7$ V/m near the electrode edges and never moved below $10^6$ V/m inside the gap, so that dielectrophoretic forces are expected to play a dominant role. This hypothesis was confirmed by the long range self-assembled nanorod arrays obtained experimentally. Formation of linear arrays oriented normal to the electrodes and the alignment of individual nanorods within linear arrays demonstrated that electric field-mediated assembling was the predominant process respect to Brownian motion, electrothermal flow and capillary forces during drying. It is interesting to note that in comparable electric field conditions, gold nanorod alignment has been previously observed in Si/SiO₂ substrates, but no large scale ordering has been reported at the best of our knowledge.[22]

We speculate that the quartz substrate and the large gap length-scale played a determinant role in our observed self-assembly process. It is known that in a Si/SiO₂ substrate the conductive Si-doped layer forms an effective back-gate that cannot be completely screened by the SiO₂ layer with a finite thickness. [23] As result, the modified electric field intensity induces positive dielectrophoretic force near the surface preventing the assembly of nanorods around the centre of the gap [22]. The absence of this effect in quartz substrates used in this work constituted an important advantage during the assembly process. Moreover, the large gap size compared with the nanorod size allowed a long scale assembling mediated by nanorod-nanorod interaction that preserved the axial dipole symmetry, resulting in line-like structure formation. Ongoing experiment are focusing on elucidate how this process take place.

Figure 4: Simulation of the electric field for electrodes spaced 10 μm apart with an applied potential of 20 V pp. (a) Contour plot of a cross section through the electrodes; the color bar indicates the field magnitude.
strength; (b) electric field obtained from the simulation at a distance of 10 nm above the electrode surface.

3.4. Optical properties of Gold nanorod linear arrays:
The optical characteristics of the dielectrophoretic arrays were investigated by optical microscopy under darkfield illumination. Figure 5a shows a scattering image of the self-assembled nanorod arrays aligned normal to the electrodes. Internal alignment of gold nanodots within individual linear arrays was also detected by polarized darkfield microscopy. When nanorod arrays were rotated between crossed polarizers, their intensity varied between maximum brightness when the long axis was at 45° and 135° to the analyzing polarizer (Figure 5b) and minimum brightness (extinction) when at 0° and 90° to the analyzing polarizer (Figure 5c). This change in optical brightness between crossed polarizers indicated a certain degree of uniaxial alignment of gold nanorods within the wires, in agreement with the calculated S value of 0.56.

It is known that the position of the plasmon absorption peak of metal nanorods depends on the dielectric properties of their surrounding media. In particular, recent studies performed on gold nanorods dispersed in various organic solvents, have shown a linear relationship between the square of the peak position of the longitudinal plasmon mode and the square of medium refractive index. [24] In the present study polarized darkfield spectroscopy was used to measure Rayleigh scattering spectra of individual nanorods arrays in media of various refractive index. A transparent substrate with dielectrophoretically self-assembled nanorod arrays was mounted on an inverted microscope equipped with an oil immersion darkfield condenser and was placed in contact with a custom made flow cell. First of all, the scattering spectrum of a selected array was measured in air. Subsequently scattering spectra of the same array in water were also recorded. As shown in Figure 5d a red shift in the longitudinal plasmon peak of the array from 813 nm to 836 nm was observed as the environment changed from air to water, corresponding to a change in refractive index from 1 to 1.33.

4. Conclusions:
In this work, we report the dielectrophoretic self-assembly of discrete gold nanorod suspended in water at receptor electrodes pre-fabricated at fused silica substrates. The approach is a facile nanorod
manipulation method that enables controlled and reliable positioning and orientation of nanorods, resulting in formation of large nanorod linear arrays. Such arrays were aligned parallel to the applied electric field with a high order parameter fit = 0.98. Polarised darkfield microscopy has been used to demonstrate the shift in scattering light observed in individual wires in contact with media of increasing refractive index. As such, the dielectrophoretic method represents a fast, robust and scalable self-assembly approach for manipulation of 1-D metal nanostructures. The sensitivity of such assemblies to the local environment could be potentially important for exploration and development of future sensing devices and systems.

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6. References:
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