Dielectrophoresis-Raman Spectroscopy System for Analysing Suspended Nanoparticles

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1. Analysing the DEP response of particles

Simulations were performed to determine the dielectrophoretic (DEP) forces on the particles and at what frequency the DEP forces change from positive to negative. Simulations of this nature allow the determination of suitable electric field frequency settings for use during the experiments, which are designed around the crossover frequency.

The suspending medium had a conductivity of 0.01 S.m^{-1} after the addition of X-305 surfactant to DI water, and a relative permittivity of 78. The conductivity of particles was governed by the total surface conductance composed of the contributions of the Stern layer and diffuse layer formed around the particles,[1] and calculated as:[2]

$$\sigma_p = \sigma_{p-Bulk} + \frac{2K_S}{r} \tag{1}$$

where K_s is 10 and 27.5 pS.m^{-1} for WO_3 and polystyrene, respectively.[3,4] The bulk conductivities σ_p of WO_3 and polystyrene are 100 mS.m^{-1} and 19.8 mS.m^{-1} respectively.[5,6] Using equation (1), the conductivity of particles were obtained as 100.5 and 20.3 mS.m^{-1} for WO_3 and polystyrene particles respectively. The permittivity of particles was also taken as 39 and 2.5 respectively for WO_3 and polystyrene particles.[7] Using the above values, the Re[f_{CM}] for polystyrene and WO_3 particles were calculated over a range of frequencies and plotted (Figure 1). According to Figure 1, the polystyrene and WO_3 particles demonstrate crossover frequencies of 3.4 and 22.3 MHz, respectively, below which they show positive dielectrophoretic response.

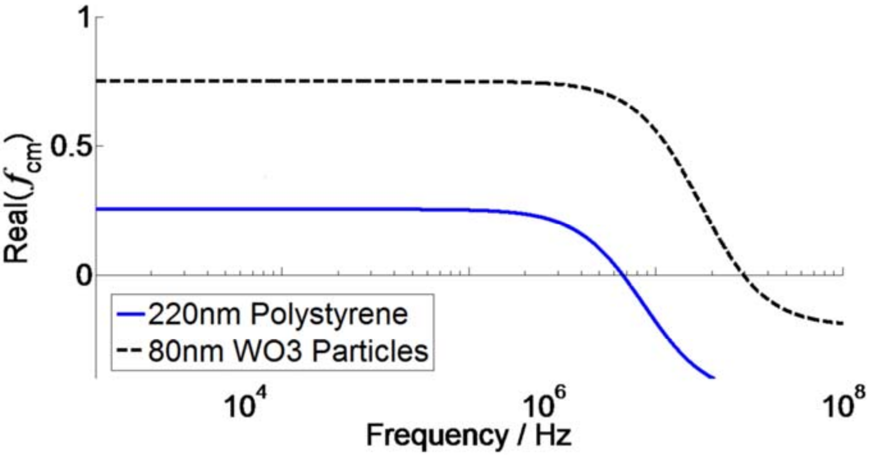

Figure 1 - The variation of Re[f_{CM}] for polystyrene and tungsten trioxide particles at a medium conductivity of 0.01 S.m^{-1} within the frequency range of 1 kHz - 25 MHz

2. Sedimentation force

The sedimentation force, F_{Grav}, which pushes the particles downward, is calculated using equation (2), where ρ is the density (particle ρ_p and medium ρ_m), r is the radius of the particle and g_z is the gravitational acceleration:

$$\vec{F}_{\mathrm{Grav}} = \frac{4}{3}\pi r^3 (\rho_p - \rho_m)\vec{g}_z \tag{2}$$

3. Fabrication

Detailed steps of the fabrication process are included below. These steps are provided for repeatability purposes.

The quartz slide substrates are first cleaned using 2-propanol (IPA), acetone and de-ionised water (DI water). The slides are then electron-beam (e-beam) coated, first with a 50nm layer of chromium. This layer serves as the adhesion layer. A second layer of 150nm of gold is then deposited on the surface of the chromium. This is the conducting layer for the electrodes. A thin film of AZ1512 photo-resist is spin coated onto the substrate (using a Karl Suss RC8 spinner). The substrate is baked in an oven at 90°C for 20 minutes. Consequently the substrate is exposed to UV light through a chromium mask, which houses the transparency of the electrode design. The exposed substrate is developed in AZ400K developer and a gold etchant (nitro-hydrochloric acid, 1:4 mixture) is used to etch away the unwanted gold. The substrate is rinsed and cleaned using IPA, acetone and DI water. A chromium etchant is then used to remove the excess chromium. The slide is cleaned and ready for the PDMS mould.

The PDMS master mould is created on a cleaned silicon wafer. The clean wafer is spin coated with a 50 μm layer of SU-8 photo resist. The photo-resist is pre baked, exposed to UV light through a microfluidics channel design mask, and finally post baked. The excess photo resist is removed using the SU-8 developer.

In order to obtain a leak proof seal between the quartz substrate and the PDMS microfluidics channel block the following steps are taken:

(i) The PDMS is mixed at a 10:1 ratio following the traditional fabrication techniques using the SU-8 master mould.
(ii) The wet PDMS in the mould is placed on a hotplate at 75°C for 15 minutes. After removal, suitable holes are punched to make reservoirs.
(iii) The sticky PDMS mould is then carefully, under a microscope, placed over the DEP electrodes.
(iv) Finally, the PDMS and quartz are placed in an oven at 80°C for a further 2 hours to allow the PDMS to fully cure.

4. Particles images

Samples of the particle mixtures were placed on glass slides and dehydrated. The samples were then viewed under a FEI Nova Nano SEM (scanning electron microscope). The SEM images help to provide confirmation of the particles configurations and dimensions (Figure 2).

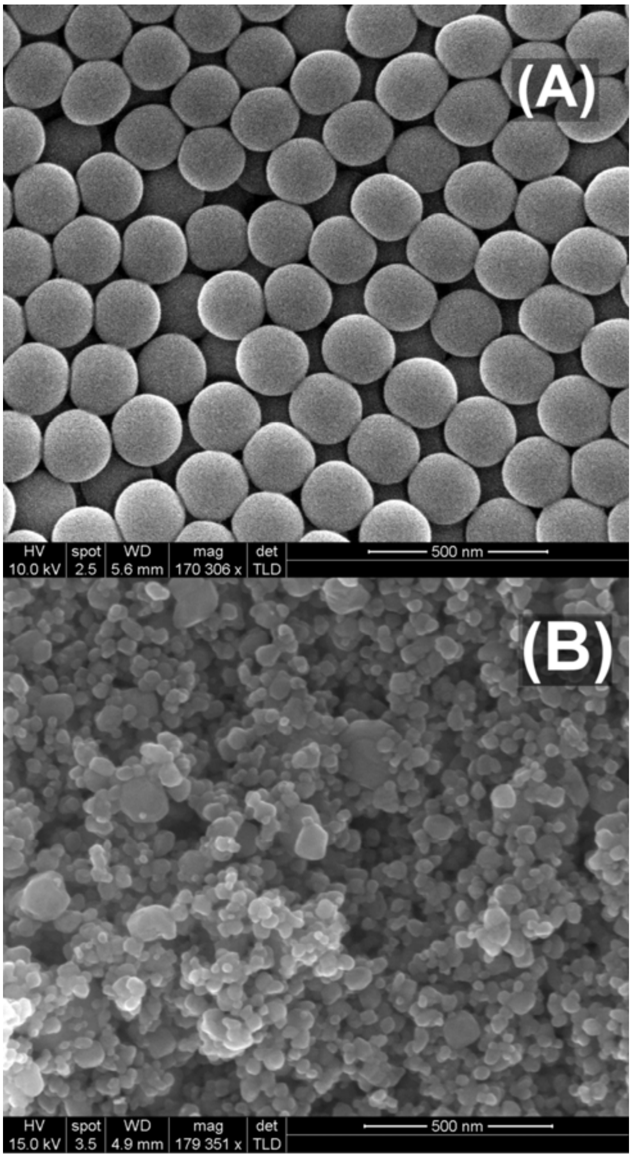

Figure 2 - **(a)** SEM image of polystyrene nanoparticles; **(b)** SEM image of WO_3 nanoparticles

5. **Permittivity of the media with suspended WO_3**

The permittivity of the solution can be calculated using equation (3) in the main text. This equation shows how the permittivity of the dispersion system, ε^*, changes with volume fraction, and also changes relative to the applied DEP field frequency. To demonstrate this effect, simulations were performed using the applied DEP frequency range of 100 kHz to 20 MHz and volume fraction from 0 (no WO_3 particles present) to 1 (no suspending medium).

For normal Raman spectroscopy, the applied electric field is provided by the excitation laser source. This source is in the GHz frequency range, where permittivities can be considered to have only real values (as the ω term is very large). However, in this case, the applied electric field can be caused by both DEP electric fields and Raman excitation laser electric fields. For nanoparticles under investigation in this work, the electric field provided by the signal generator via electrodes is much greater in magnitude than that generated by the excitation laser.

Figure 3 shows how the DEP field alters the relative permittivity of the solution. It can be observed that when the frequency of the DEP field reduces below 10 MHz at volume fraction of 0.11, the relative permittivity increases from 73.6 to 91.6. This increase is approximately 125%, and can be used to show how Raman signals from the WO_3 are altered by this change in permittivity.

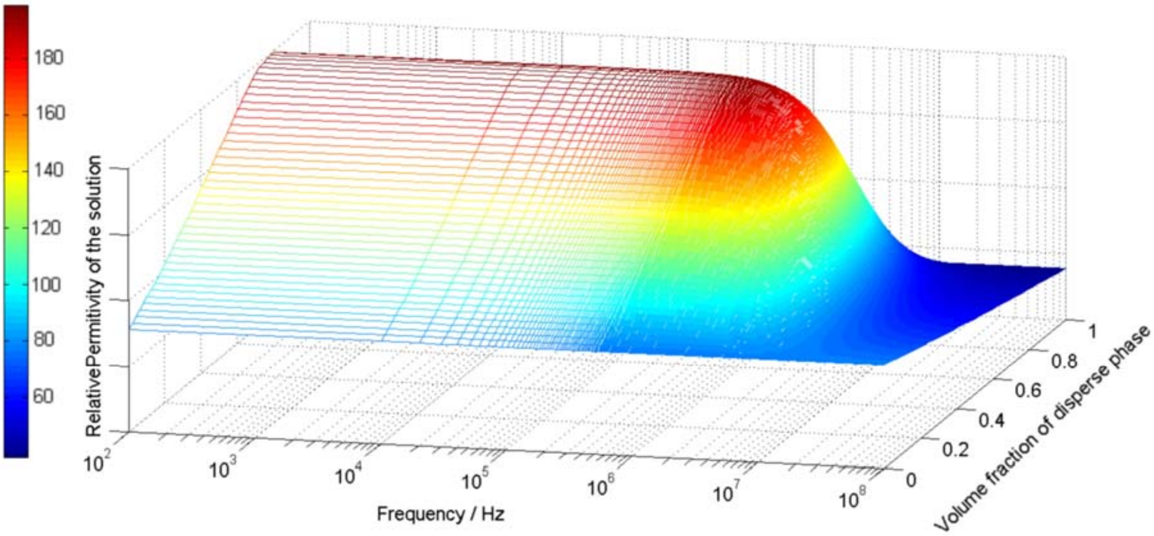

Figure 3 – Relative permittivity of the solution as a function of the dispersed phase volume fraction at different frequencies

6. **Raman peak intensity concentration relationship for suspended WO_3**

In order to properly calibrate and understand the relationship between Raman peak intensities and solution concentrations, several mixtures of different concentrations were prepared. To mimic the measurement flow conditions, these mixtures were then passed through the device at a flow rate of 4 $\mu l \cdot min^{-1}$, while applying no electric field. Raman spectra for each mixture were taken from the “top surface of the microchannel”, and the Raman peaks of 798 cm^{-1} was normalised and plotted against the mixture concentration.

The relationship between Raman peak intensities and particle concentrations shows a near linear relationship for concentrations below 14 % *w/w* (figure 4). At concentrations above this threshold the relationship changes, possibly due to particle aggregation and sedimentation. We hypothesise that above 14 % *w/w* the medium no longer holds all the WO_3 particles in suspension and excess WO_3 sediments on the bottom of the microchannel.

The intensity measurements from linear concentration estimations were added to figure 4. As can be seen, the two plots follow each other closely for measurements up to 14 % *w/w*. However, at higher concentrations, the DEP focused nanoparticle intensity is almost doubled compared to the highest possible measured concentration in zero electric field condition. This suggests that Raman can reliably measure below 14 % *w/w* concentrations, although above this concentration the readings can be affected by sedimentation, permittivity and electric field issues that have been discussed in the main text and ESI.

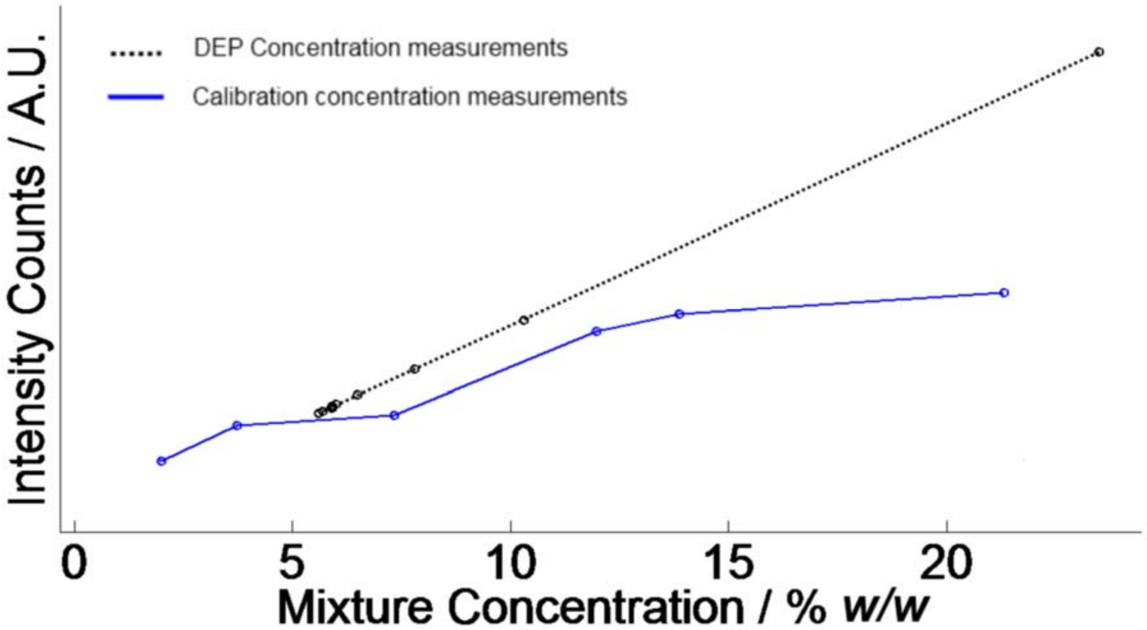

Figure 4 – Raman intensity counts *vs* solution concentrations relationship

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