Surveying colloid sedimentation by coplanar waveguides

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Received 19 December 2015, revised 11 March 2016
Accepted for publication 16 March 2016
Published 26 April 2016

Abstract

By using coplanar waveguides, direct access to the dielectric properties of aqueous solutions of polystyrene beads with different diameters from 330 nm to 10 µm is provided. The relative variation of the transmission parameter with respect to water is monitored, ranging from ~3% obtained for a 9.5% solution with 330 nm diameter beads to ~22% for 10 µm diameter particles at the same concentration. To highlight its applicability in biosensing, the technique was further employed to survey the clustering between biotin and streptavidin-coated beads. The transmission parameter displays a ~50% increase for mixtures containing nine volumes of biotin and one volume of streptavidin-modified beads (4.5 ng µl−1 of streptavidin) and reaches ~400% higher values when equal volumes of biotin and streptavidin-coated beads (22.5 ng µl−1 of streptavidin) were mixed.

Online supplementary data available from stacks.iop.org/nano/27/225502/mmedia

Keywords: coplanar waveguides, colloids, sensors, biomedical applications of nanotechnology, radio-frequency and microwave measurements

(Some figures may appear in colour only in the online journal)

1. Introduction

Designed with targeted properties and combining multiple attributes that allow them to be dynamic, ordered particle assemblies are strong candidates to replace the traditional structures processed with top-down fabrication approaches [1–8]. Self-assembly by gravitational sedimentation is one of the methods largely used to organize particles in desired architectures [9–14]. Understanding the physical phenomena that take place during self-assembly is a crucial step in controlling the structure and properties of the colloid-driven design materials. In this respect, novel approaches to analyze the spatial and temporal information embedded in colloidal systems confined to microfluidic environments are needed.

Interestingly, coplanar waveguides (CPWs) can be used to study the physical phenomena that appear during gravitational sedimentation due to their unique response towards the dielectric properties of the surrounding environment. Microwave measurements using CPWs have been reported for fluidic environments [15–21], with a focus on the dielectric characteristics of liquid samples [16, 20, 22] and biosensing [15, 17–19, 21]. Various other techniques and devices have been designed at microwave frequencies to measure dielectric properties or analyte concentrations in biological systems: coaxial probes [23], microstrip transmission lines [23, 24] or microwave resonators [25, 26]. With few exceptions [23, 25] the majority of these devices are used for the characterization of cells. In this work, we employ CPWs and simple microfluidic structures to study the on-chip sedimentation of polystyrene (PS) nano- and micro-spheres in aqueous solutions. Along with the detection of the solution’s concentration, we monitor the time evolution of the underlying sedimentation processes and we devise a technique applicable to the specific detection of molecular species. The lowest
Figure 1. Schematic view of a microfluidic chamber coupled to a coplanar waveguide fabricated on a fused silica substrate of thickness $h = 400 \ \mu m$ and dielectric permittivity $\varepsilon_r = 3.8 \ \varepsilon_0$. The Al layer, in which the lines are defined, has a thickness $t = 1.2 \ \mu m$, while on the back side of the substrate, the metallic layer has a thickness $t/2$. The coplanar waveguide is defined by the width $w$ of the central conductor and the distance $s$ to the ground planes.

The detected concentration is $4.5 \ ng \ \mu l^{-1}$ of streptavidin, comparable with the sensitivity of transmission methods [23].

2. Materials and methods

Figure 1 shows a schematic of the setup for surveying colloid sedimentation with CPWs. The central strip of the CPW has a width $w$ of $58 \ \mu m$, while the distance $s$ to the ground planes is $36 \ \mu m$. For the measurement of liquid samples, microfluidic containers 3.0 mm wide, 9.0 mm long and $h_{PDMS} = 0.9 \ mm$ high, were fabricated in poly(dimethylsiloxane) (PDMS) using the well known replica molding technique [27]. A layer of SU-8 (Microchem) with thickness $h_{SU-8} = 3 \ \mu m$ was patterned on top of the sensing lines and has the double role of improving the adhesion of the PDMS container and isolating the CPWs during the measurements with liquids. The length $L$ of the CPWs, with pads included, is 8.4 mm. The scattering parameters $S$ of the samples were measured using a probe station and a vector network analyzer in the frequency range from 40 MHz to 40 GHz. A through-line-reflect calibration of the vector network analyzer was performed before the measurements. The calibration of the vector network analyzer moved the reference planes at the end of the coplanar probes. The reference impedance at the end of the coplanar probes corresponds to the impedance of the line standard from the used calibration kit (50 $\Omega$). A first data set was acquired on the calibration standards and the pristine CPWs. Then, the SU-8 film was spin-coated and patterned. This step was followed by an additional set of measurements. Finally, the PDMS containers were aligned and bonded on top of the epoxy layer. Measurements were performed with the empty PDMS containers and with the liquid filled ones.

3. Results and discussion

Colloid sedimentation. Several aqueous solutions of PS beads (microParticles GmbH) were prepared by using three

See supplementary material for experimental methods and analysis.

$D = 330 \ nm$, $2.4 \ \mu m$ and $10 \ \mu m$. For each $D$, seven solutions were prepared with concentrations $c_i$ ($\nu/\nu$) 2.0%, 2.6%, 3.7%, 4.8%, 5.9%, 7.0% and 9.5%. A volume of $60 \ \mu l$ of solution was placed, using a pipette, in the PDMS container and the $S$-parameters of the CPW were obtained. The measured transmission parameters $|S_{21}|$ for the different concentrations and diameters of colloidal particles are presented in figure 2 together with the absolute variation with respect to water, $\Delta |S_{21}|_w = |S_{21}|^D - |S_{21}|^\text{water}$. From these graphs, two important observations can be made: $\Delta |S_{21}|_w$ increases with frequency and, interestingly, the measurements suggest a saturation behavior for the $D = 10 \ \mu m$ polystyrene bead solution, highlighting the sedimentation of the colloids at the bottom of the container. The absolute $\Delta |S_{21}|_w$ and relative $\Delta |S_{21}|_{21w}$ variations, with the water measurement as a reference, are given in table 1 at 35 GHz for three concentration values. Here, $\Delta |S_{21}|_{21w} = - |S_{21}|^D/|S_{21}|^\text{water} + 1$. A relative variation of the transmission parameter of 2.80% was obtained for a 9.5% solution with 330 nm diameter beads, while the same concentration of 10 $\mu m$ diameter particles generates a change of 21.76%. The analysis was made at a frequency of 35 GHz which is high enough to observe significant changes and sufficiently low to avoid the noise-ridden region at the end of the measurement range. While similar results are obtained at different frequencies, a dielectric spectroscopy analysis can be carried out, extended in the supplementary material (see footnote 3). Due to the presence of impedance mismatches between the probes and the CPW, between the bare line sections of the CPW and the sections containing the PDMS walls and between the latter and the probed liquid, the analysis asks for a rather involved mathematical formalism. Indeed, multiple interferences occur between the forward traveling waves and the reflected ones at this interfaces [28]. Compared with a perfectly matched CPW ($S_{11} = S_{22} = 0$), for which the $S$ parameters are given by $S = [0 \ e^{-\gamma L} \ e^{-\gamma L} \ 0]$, with $\gamma$ the propagation constant, the $S$ matrix of the studied device can be obtained by taking in consideration the different impedance transformations (see supplementary material). Yet, the sedimentation of colloids in the present system can be much more simply rationalized by monitoring the time and frequency evolution of $|S_{21}|$.

Measurements of the CPWs as a function of frequency and time were performed next. The time interval of the entire measurement sequence, for one concentration, was 30 min to avoid the influence of water evaporation on the test concentrations. The $S$-parameters were measured at 2 min intervals, starting from the moment when the solution was placed in the container. The results for the 9.5% solutions are illustrated in figures 3(a)–(c) and reveal that $|S_{21}|$ increases with time $t_i$ for two of the studied systems: 2.4 $\mu m$ and 10 $\mu m$ PS beads. The inset in figure 3(a) shows the time evolution at 35 GHz of $|S_{21}|$ for three measured concentrations of $D = 330 \ nm$ PS colloids. The lowest concentration illustrates the detection limit of the technique. Similarly to the $D = 330 \ nm$ particles, the time evolution at 35 GHz of $|S_{21}|$ is illustrated in the insets of figures 3(b)–(c) for $D = 2.4 \ \mu m$ and 10 $\mu m$ PS spheres. As expected, a fast sedimentation is detected for $D = 10 \mu m$ PS beads. The important differences, observed when
The 330 nm diameter particles with peculiar regimes described in figures 3(d)–(f) are in the non-Brownian regime. The 2.4 μm diameter spheres are in the Brownian regime, while the 10 μm diameter spheres are in the non-Brownian regime. The 2.4 μm diameter particles with Pe ≈ 1 are between these two regimes. Furthermore, for 10 μm diameter colloids, a careful examination of the |S21| time evolution and of its numerical first derivative, which is constant but not equal zero after ~20 min, highlights that |S21| keeps increasing linearly with time (see footnote 3). This suggests that inter-particle interactions are present and slow down the assembly of the spheres at the bottom of the container. In order to limit such effects, especially at high c1, a 7 mM NaCl solution was used to disperse the 2.4 and 10 μm diameter spheres. Note that the particles’ radii are very large compared to the thickness of the Debye diffuse layer.

For both dispersion types, the |S21| time dependence for 10 μm diameter spheres can be fitted as |S21| = A + B[1 − exp(−t/C)]. However, due to the peculiar setup, a limited number of |S21| curves for the 2.4 μm colloids can be fitted as |S21| = A + BCTt − BCT2t2/2, which are the first three terms from the series expansion of the initial exponential. The A Parameters for both 2.4 μm and 10 μm diameter colloids, alongside the |S21| mean values for 330 nm diameter beads were used to calculate the relative variation Δ|S21| (t = 0), plotted as a function of concentration in figures 3(d)–(f). They show a linear dependence and can be used as calibration curves. The coefficients extracted after fitting the data are given in figures 3(g)–(i) for the 2.4 μm diameter colloids and in figures 3(j)–(l) for the 10 μm diameter ones. As it can be seen from figure 3(l), the time constant C−1, relating to the sedimentation rate, has a value of 5.5 min for the 2.0% concentration and slightly decreases to 4.4 min at the 9.5% concentration for the 10 μm diameter beads in water. The dispersions in 7 mM NaCl behave alike, but the mean value for C−1 is 1.3 min lower. A similar analysis can be made for the 2.4 μm diameter beads. The product BC increases with the concentration and it is higher for the saline solutions. For both bead diameters, this behavior can be explained by the fact that the ions present in the saline solutions screen the charge present at the surface of the beads, reducing the inter-particle interactions and increasing the sedimentation rate. The ratio between the time constants of the two types of beads tells us how much faster the 10 μm diameter beads sediment compared with the 2.4 μm ones. At c1 = 9.5%, the 10 μm diameter beads sediment 23 times faster than the 2.4 μm ones.

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| c1 [%] | Δ|S21| [dB] | Δ|S21| [%] | Δ|S21| [dB] | Δ|S21| [%] | Δ|S21| [dB] | Δ|S21| [%] |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|
| 2.0   | 0.07   | 0.38   | 0.15   | 0.76   | 1.35   | 7.28   |
| 2.6   | 0.08   | 0.43   | 0.17   | 0.87   | 1.88   | 10.12  |
| 3.7   | 0.20   | 1.04   | 0.31   | 1.58   | 2.41   | 12.95  |
| 4.8   | 0.28   | 1.38   | 0.38   | 1.97   | 2.91   | 15.62  |
| 5.9   | 0.33   | 1.73   | 0.52   | 2.68   | 3.34   | 17.96  |
| 7.0   | 0.31   | 1.67   | 0.62   | 3.21   | 3.65   | 19.59  |
| 9.5   | 0.53   | 2.80   | 0.77   | 3.95   | 4.05   | 21.76  |
for solutions of PS beads with different $D$ (a–c). The arrows illustrate the time sequence of the experiments. The insets show the time dependence of $|S_{21}|$, at 35 GHz, for three concentrations $c_i$: 2.0%, 5.9% and 9.5%. Calibration curves, at 35 GHz, showing $|S_{21}|$ dependence as a function of $c_i$ for solutions of PS beads with different $D$ (d–f). $|S_{21}|$ was calculated relative to the water measurement. Note that at $t_0 = 0$, i.e. at equilibrium, the 10 μm diameter sphere dispersions display higher values for $|S_{21}|$ at all investigated concentrations, highlighting the role played by the granularity of the probed colloidal system. Parameters obtained after fitting the time dependence of $|S_{21}|$ for 2.4 μm diameter beads: (j) A, (k) $B$ and (l) $C^{-1}$. Open symbols refer to aqueous solutions, while closed symbols to saline solutions.

Figure 3. Evolution of $|S_{21}|$ as a function of frequency and time for the 9.5% aqueous solutions of PS beads with different $D$ (a–c). The arrows illustrate the time sequence of the experiments. The insets show the time dependence of $|S_{21}|$, at 35 GHz, for three concentrations $c_i$: 2.0%, 5.9% and 9.5%. Calibration curves, at 35 GHz, showing $|S_{21}|$ dependence as a function of $c_i$ for solutions of PS beads with different $D$ (d–f). $|S_{21}|$ was calculated relative to the water measurement. Note that at $t_0 = 0$, i.e. at equilibrium, the 10 μm diameter sphere dispersions display higher values for $|S_{21}|$ at all investigated concentrations, highlighting the role played by the granularity of the probed colloidal system. Parameters obtained after fitting the time dependence of $|S_{21}|$ for 2.4 μm diameter beads: (j) A, (k) $B$ and (l) $C^{-1}$. Open symbols refer to aqueous solutions, while closed symbols to saline solutions.

quicker, in agreement with the ratio of the settling velocities calculated with Stoke’s law [34].

Surveying mixtures of colloids. The above described method can be further applied to study macromolecular association processes [35, 36]. To illustrate this, two solutions containing modified PS beads, 0.95% (v/v) in 50 mM phosphate buffer saline (PBS) and 2 μm in diameter, were used as purchased from Nanocs. One solution contained biotin-coated beads while the other contained streptavidin-labeled ones. Two mixtures, the first 1:1 (v:v) and the second 9:1 (v:v), of biotin and streptavidin-modified PS spheres were prepared. The overall concentration of PS beads remained the same for the two mixtures and equal to 0.95% (v/v). The two solutions and the two references, 50 mM PBS and biotin-coated PS sphere dispersion, were measured using the technique described above. The evolution of $|S_{21}|$ over time at 35 GHz for the four solutions is presented in figure 4(c), while the time dependence of $|S_{21}|$ at the same frequency is displayed in figure 4(d).

As expected, the $|S_{21}|$ and $|S_{12}|$ corresponding to the three PS-based solutions have a linear increase with time, while the 50 mM PBS provides only a weak variation of the transmission coefficients during the measuring interval. The slopes of the $|S_{21}|$ and $|S_{12}|$ linear variations increase by 1.5 times for the 9:1 mixture and 4 times for the 1:1 mixture, compared with the solution containing only biotin-modified PS spheres. The changes are thus consistent with the formation of clusters during sedimentation due to the binding between the streptavidin and biotin-coated colloids. This is corroborated by the SEM analysis, which shows a higher density of particles for the 1:1 mixture (figure 4(a)) compared with the 9:1 mixture (figure 4(b)). The transmission parameters display a ~50% increase for mixtures containing 9:1 biotin:streptavidin volumes (streptavidin concentration $c_s = 4.5$ ng μl$^{-1}$) and reaches ~400% higher values when equal volumes of biotin and streptavidin-coated beads ($c_s = 22.5$ ng μl$^{-1}$) were mixed. The lowest detected $c_s$ is comparable with the sensitivity of transmission methods [23] and the devices can be further calibrated against colloidal solutions of different concentrations in the respective sensing buffer solutions. One salient feature of our experiments is the volume sensitivity of the technique; consequently, the regimes of very low ($< 0.1\%$) and very high ($> 10\%$) particle concentrations are not within the scope of such an approach.
By comparing the behavior of $D = 2.4 \, \mu m$ particles, shown in figures 3(g)–(i), with the behavior of $D = 2 \, \mu m$ biologically-modified beads, the latter sediment slower. The value of $A$ is identical, $-20.1 \, dB$, for the three colloidal solutions displayed in figure 4(c). This is expected since the overall concentration is 0.95% for these solutions. The slope $BC$ inferred for each sedimentation curve has lower values compared with the 2.4 $\mu m$ diameter PS particles. Specifically, $BC$ is 0.12 $dB \cdot h^{-1}$ for the biotin-modified beads, 0.17 $dB \cdot h^{-1}$ for the 9:1 mixture of biotin and streptavidin-modified PS spheres. Thus, the nano- and micro-structural evolution of complex colloidal suspensions can be followed in an effective way in microfluidic environments, contrasting to cumbersome traditional techniques, such as gamma-ray densitometry [35].

4. Conclusions

In summary, we presented the realization of a device integrating coplanar waveguides and simple microfluidic structures, that can be interrogated in the radio-frequency range to study the dynamics of colloidal solutions. Small variations between concentrations of solutions with PS particles of different sizes could be distinguished and the device was used to sense the clustering of streptavidin and biotin-coated PS spheres. The sensitivities of nanoparticle-based biosensors are significantly influenced by small external variations including temperature and operation protocols. Accordingly, the recording and the amplification of the signal from targeted biomolecules in unknown samples by attaching them to specific-size sedimenting beads could be a costly and cumbersome assay technique. For determining analyte presence in a sample, bio-functionalized species of sedimenting colloids could act as reporter particles in conjunction with nano- and micro-engineered traps fabricated on top of the devices. For example, perovskites can be manipulated and used as single particles, due to their unique dielectric properties, not requiring statistical results. The co-integration of photonic structures, possibly as colloid traps, offers another way to diversify and improve the method. The device could be further optimized for quality control in biochip spotting applications at the wafer scale. Our technique could be exploited to study both spatial and temporal resolution colloids in various conditions, like microchannel reactors or droplet microfluidics [37]. Moreover, the devices can be coupled within microfluidic labs-on-chips with other optical sensing platforms for enhanced real-time monitoring of the targeted analytes [38]. For example, by selecting different photonic materials from the variety of existing nano- and micro-particles, this low-cost method can be used in particle-based bioarray strategies. We expect the present method to be pertinent in the study of soft matter self-assembly and dynamics of colloids in complex systems, like semi-solid flow microbatteries [39]—for assessing the passivation of current collectors—or granular matter in microgravity [13, 40]—for surveying crystallization processes.

Acknowledgments

The work was supported by the Belgian FRS–FNRS in the frame of the research conventions no. 2.4510.11, no. T.1004.14—ECOSTOFLEX project, and no. R 50.02.16.F—GRAPHIVITY project and by the Communauté Française de Belgique—TINTIN project, ARC no. 09/14-023.
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