LA MÉTROLOGIE AU CŒUR DES TECHNOLOGIES CONTEMPORAINES

Micro-résonateurs pour l'étude dynamique de la matière molle : De la sédimentation des particules à la stabilité des produits

Micro-resonators for dynamic investigation of soft matter: From particle sedimentation to product stability

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Résumé/Abstract

Ce travail vise à présenter les avancées récentes dans l'analyse de la matière molle à l'aide de la photonique intégrée et de techniques résonantes quasi-surfaciques. Il met en lumière la polyvalence de la structure résonante conçue, composée de micro-résonateurs, en démontrant son application en tant que « Mesureur de vitesse de Sédimentation », « Viscosimètre Optique » et « Zétamètre Optique Résonant » pour l'analyse de solutions transparentes, sombres ou opaques. Ces dispositifs sont développés pour répondre à la problématique de la stabilité de dispersions colloïdales lors d'un stockage à long terme. Des micro-résonateurs organiques UV210, fabriqués par photolithographie en UV profond, sont intégrés dans une plateforme optique permettant un suivi dynamique du processus étudié. Des expériences menées avec des nanoparticules de silice dispersées dans l'eau révèlent une corrélation nette entre l'évolution du signal résonant et la sédimentation de ces nanoparticules. En revanche, l'étude de poudres de noir de carbone dispersées dans de l'eau contenant un tensioactif montre l'absence de sédimentation, ce qui confirme la capacité des structures résonantes à détecter des systèmes colloïdaux stables, même dans des milieux sombres. Ces résultats sont validés et corroborés avec des mesures rhéologiques et de potentiel zêta.

This work aims to thoroughly present recent advancements in soft matter analysis using integrated photonics and quasi-surfacic resonant techniques. Specifically, it highlights the versatility of the designed resonant structure, made of organic micro-resonators, demonstrating their application as a "Sedimentation Rate Meter," "Optical Viscometer," and "Resonant Optical Zetameter" for analyzing transparent, dark, and opaque solutions. These devices are designed to address the challenge of monitoring the long-term stability of colloidal dispersions. Organic UV210 micro-resonators, fabricated via deep UV photolithography, are integrated into an optical test-platform for real-time monitoring and data processing. Experiments on silica nanoparticles into water shows a correlation between resonant signal evolution and sedimentation. The study of black carbon into water with a surfactant shows conversely the absense of sedimentation and then the capability of the structures of detecting stable product even in dark substances. These results are validated through complementary rheological and zeta potential measurements.

1 Introduction

The industrial interest of this research is significant in assessing the dynamic behavior of colloidal dispersions prior to large-scale product production. Stable colloidal dispersions rely on equilibrium between electrostatic forces between dispersed particles, maintaining a stable particle cloud. Perturbation in this equilibrium, arising from changes in particle charge or environmental conditions, can lead to aggregation, sedimentation, and phase changes that compromise product longevity. Identifying stable versus unstable products is critical in pre-industrial applications, such as latex rubber, paints or agro alimentary products [1-3].

This study introduces an integrated photonic platform based on quasi-surfacic resonant micro-resonators to monitor colloidal dispersion behavior in real time. Fabricated from UV210 polymer via deep UV photolithography, these racetrack resonators interact with the surrounding medium through evanescent fields, enabling high-sensitivity detection over hundreds of micrometers [4-6]. Excited by a superluminescent diode, the resonant signal, tracked via Free Spectral Range (FSR) variations, provides insight into dispersion dynamics, including in highly absorbing or opaque solutions. Conventional commercial devices often struggle to analyze dark or opaque substances because their measurement principle is about volumetric light propagation, which is hindered by strong absorption. In contrast, the light circulating within micro-resonators in our approach probes the environment over hundreds of micrometers, even in optically challenging substances.

To this end, the second part of this paper focuses on the principle of resonant measurement. The fabrication process of the micro-resonators is briefly presented, along with the integration of the photonic chip into the optical experimental setup. The third part is dedicated to the behavior of colloidal dispersions with silica nanoparticle suspensions into water and into water plus glycerol and with black carbon dispersions into water and into water plus an anionic surfactant. Initial experiments reveal a correlation between the evolution of the resonant signal and the sedimentation process. Modifying the host medium by adding glycerol introduces the concept of an optical resonant viscometer by changing the sedimentation rate visible by the FSR slope variation. Subsequently, the study of carbon black nanopowder dispersions in aqueous media demonstrates the ability to distinguish between stable and unstable systems through the addition of an anionic surfactant. A clear correlation between the slope of the FSR variation and dispersion stability is thoroughly analyzed. These findings are supported by complementary rheological and zeta potential measurements. Finally, the last section concludes the study.

2 Resonant principle measurement and experimental set-up

A basic configuration, where the fabrication processes and the geometry is depicted in Figure 1, consists of unidirectional coupling between a racetrack micro-resonator (MR) and a bus waveguide. Resonance occurs when the round-trip phase condition equals *2mπ* (where *m* is an integer), resulting in resonant wavelengths given by [7]:

$$\lambda_{res,m} = n_{eff}\frac{P}{m} \tag{2.1}$$

Here, n_{eff} is the effective refractive index of the propagating mode, *P* the resonator's geometric parameter, and *m* the mode number. Changes in the upper cladding environment, such as migration, sedimentation, or densification, affect n_{eff}, providing insights into soft matter behavior.

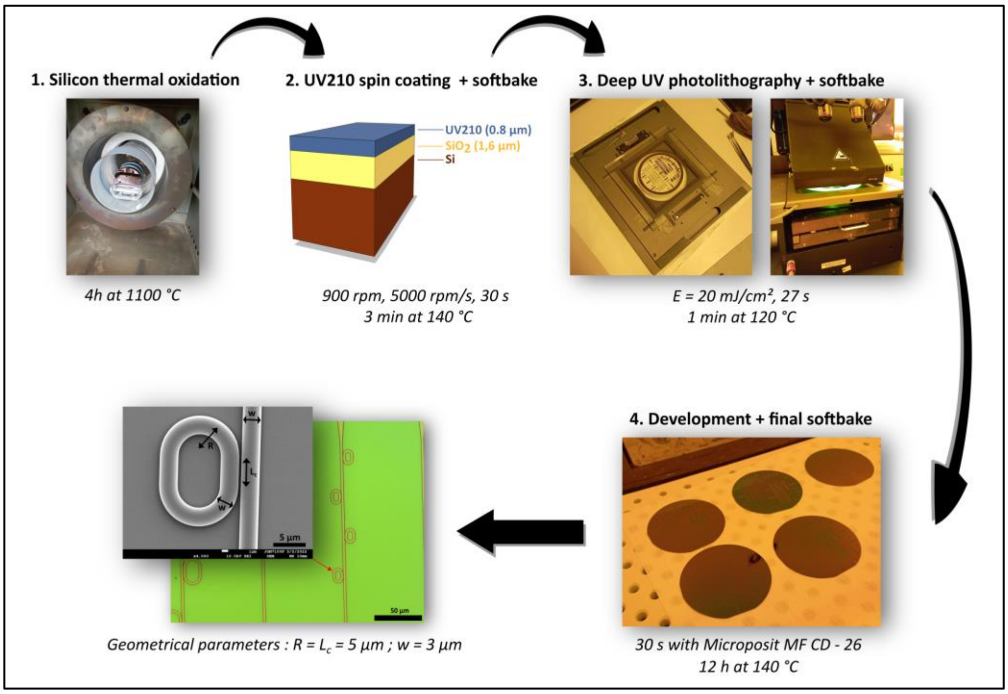


Figure 1: Fabrication process of the resonant structure, along with an SEM image of an MR coupled to an access waveguide, with the geometrical parameters highlighted.

The spectral difference between two successive resonant wavelengths, known as the Free Spectral Range (FSR), is monitored through an optical test platform and is defined by:

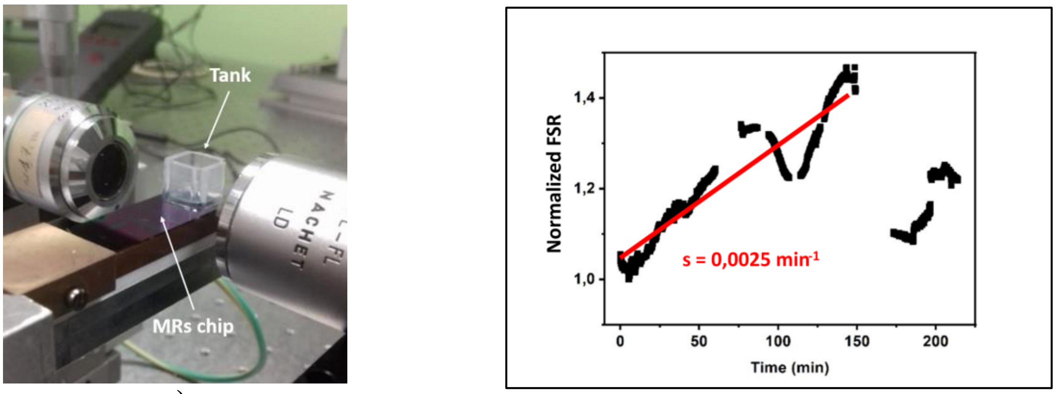
$$FSR = \frac{\lambda_0^2}{P.n_{eff}^{gpe}} \quad (2.2)$$

Where λ_0 is the excited wavelength, and n_{eff}^{gpe} the group refractive index of the structure incorporating modal dispersion. The resonant structures are fabricated from organic resin (UV210) via deep-UV photolithography on oxidized silicon, feature micrometer-scale patterns with 400-nanometer gaps between the access waveguide and MRs. A Superlum diode emitting at 795 nm excites the resonances, with a broad emission spectrum (40 nm) generating multiple resonant peaks. These peaks enable dynamic observation of soft matter processes. Data acquisition is performed with an Ocean Optics spectrometer, controlled via MATLAB, which also performs real-time Fast Fourier Treatment (FFT) to calculate dynamically the FSR evolution. This integrated platform enables dynamic soft matter investigations, specifically colloid dispersion migration and stability assessment, using compact and cost-effective devices.

3 Results

3.1 Toward sedimentation and viscosity measurements

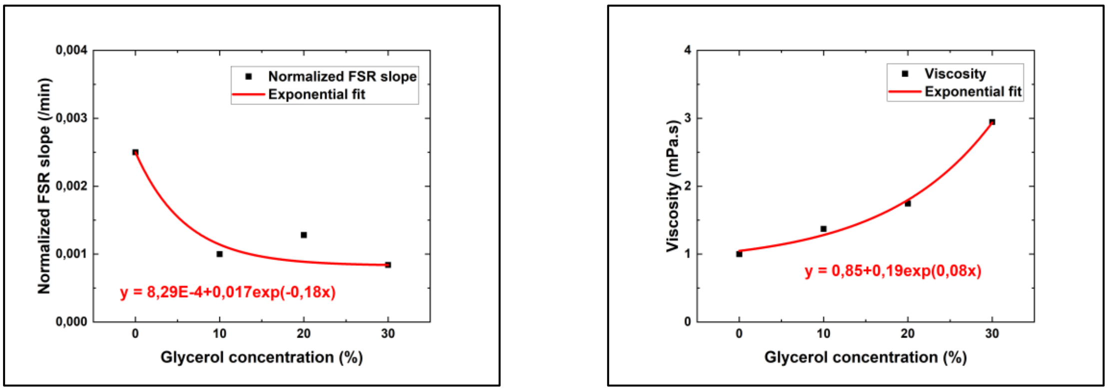
Initial studies were conducted on transparent silica nanoparticles (NPs) migration into water. A tank filled with 168 µL of water was placed in direct contact with the photonic chip, creating a three-layer waveguide structure with the core (UV210) sandwiched between the lower cladding (SiO_2) and the upper cladding (water). Introducing 5 µL with a microlitter pipette of a solution containing silica NPs, at a concentration of 2 mg/mL, altered the upper cladding's refractive index, impacting the global effective refractive index of the structure. The mode's evanescent tail acted as a probe, detecting sedimentation and migration processes. An increase in FSR is a specific signature of the sedimentation process [8,9]. The moment the FSR reaches its peak value marks the end of sedimentation, enabling precise comparison of the experimentally measured sedimentation rate with the theoretical value predicted by the classical Stokes model. During this phase of sedimentation, the nanoparticles (NPs) form a compact layer above the waveguide core, where their density and concentration increase, resulting in a decrease in guiding capacity, mathematically corresponding to a decreased n_{eff}^{gpe} (increased FSR with equation 2.2). In Figure 2.b, the sedimentation process appears to conclude around 145 minutes. After this point, a second phase of rearrangement among the NPs occurs before the FSR stabilizes. This second phase is attributed to a pinning effect caused by the finite dimensions of the tank placed above the chip, leading to curvature at the water/air interface. Evaporation is more pronounced at the center of the tank than at the edges, further increasing the curvature. This increased curvature "sweeps" the NPs across the chip surface, causing their rearrangement and leading to a stabilized FSR appearing at 200 minutes.



a) b)

Figure 2: a) Tank filled with the colloidal dispersion, composed of silica NPs into water, in direct contact with the photonic chip. b) Plot of the normalized FSR evolution over time for silica NPs into water. The first phase of sedimentation associated to a FSR slope end at 145 minutes followed by a rearangement phase with a final stabilized FSR at 225 minutes.

Additional experiments were conducted by adding glycerol to the initial solution in the tank. Silica NPs solutions were also added, and the FSR evolution was recorded. The slope associated with the FSR evolution during the first phase, corresponding to sedimentation, was plotted as a function of the glycerol concentration (Figure 3a). In parallel, viscosity measurements were performed using a mechanical rheometer on four solutions with glycerol concentrations of 0%, 10%, 20%, and 30% (Figure 3.b). From these data, a mathematical relationship between the viscosity and the slope of FSR(t) could be established. Thus, by monitoring the resonant signal of a mixture during the sedimentation process, the viscosity of the mixture can be determined.



a) b)

Figure 3: a) Normalized FSR slope as a function of the glycerol concentration. b) Average viscosity of each sample as a function of the glycerol concentration where the non-linearity clearly appears.

3.2 Toward product stability

This study was extended to dark solutions by replacing silica NPs with carbon black nanopowder. Sedimentation was clearly observed for various concentrations (ranging from 0.1 to 0.5 mg/mL), demonstrating the platform's capability to analyze dark substances. It is noteworthy that the sedimentation process may not begin immediately at the start of the experiment (Figure 4). Indeed, the solution can remain relatively stable for several minutes or even up to an hour before the particles start to aggregate and subsequently begin to sediment irreversibly. Therefore, it is important to conduct measurements over several hours (typically 3 to 4 hours) before concluding whether sedimentation occurs. Replacing the water with an anionic surfactant solution, the sodium dodecyl sulfate (SDS), stabilized the colloid through equilibrium between repulsive and attractive forces, maintaining a constant FSR (Fig. 3). This confirmed the capability to discriminate between stable and unstable colloids dynamically and those results are corroborated by zeta potential measurements (Figure 4). The water and SDS solution successfully surpasses the stability threshold of |30 mV|, a characteristic indicator of colloidal dispersion stability [10-12]. These results demonstrate its suitability for testing industrial pre-products.

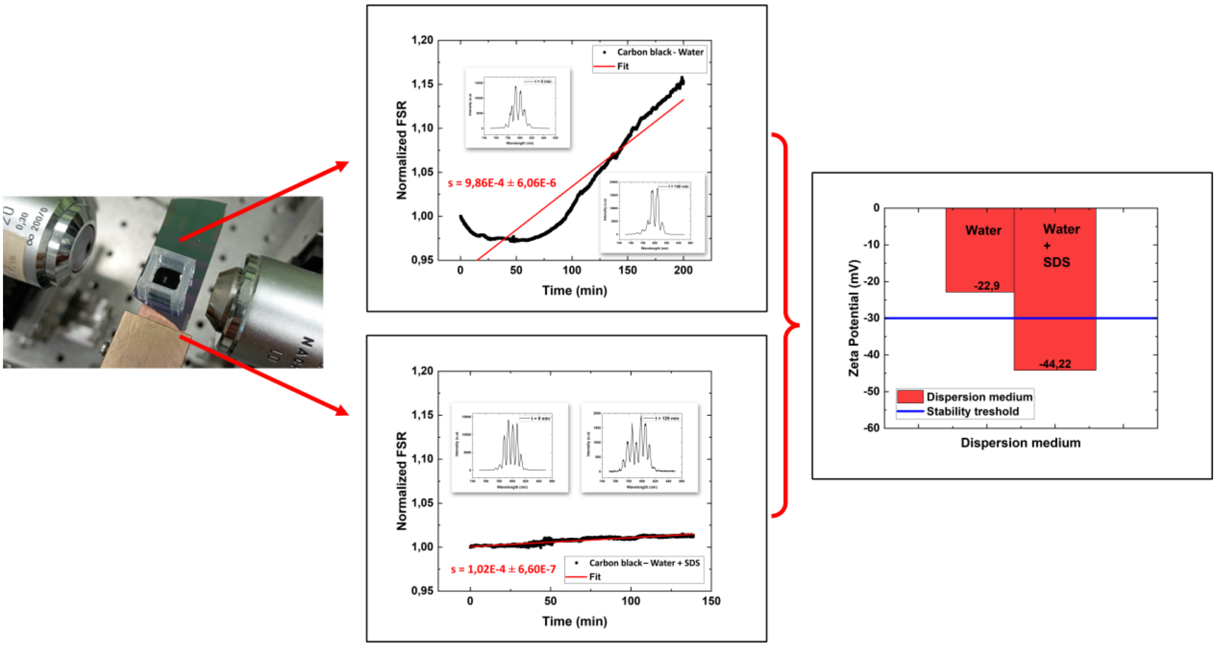


Figure 4: On the left, a tank filled with a carbon black suspension in contact with the photonic chip. In the center, a plot of the normalized FSR over time for carbon black dispersed in water and in water with added SDS. The absence of sedimentation (no FSR slope) observed for the dispersion with SDS is corroborated by zeta potential measurements (shown on the right), where the solution exceeds the stability threshold for colloidal dispersions.

4 Conclusion

Such optronic device developed in cleaning room and incorporated into an optical test platform enable investigation of pre-product stability from industrial. It principle based on a quasi-surfacic resonant signal allow to detect sedimentation and migration in colloidal dispersions. Its ability to probe dark and opaque substances and its capacity for real-time FSR monitoring highlight its potential for cost-effective and efficient stability analyses in various industries.

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