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Nanoelectromechanical System Fourier Transform Infrared Spectroscopy (NEMS-FTIR) for Nanoplastic and Polymer Degradation Analysis

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Summary: We introduce a novel application of photothermal infrared spectroscopy based on nanoelectromechanical systems (NEMS), integrated with a commercially available FTIR spectrometer (NEMS-FTIR). We successfully detected 1 ng of polystyrene (PS) and 1 ng of polypropylene (PP) nanoplastic particles with diameters of 100 nm and 54 nm, respectively. As a case study, we detected small amounts of degradation products originating from plastic tubing. The technique enabled high-resolution spectral identification of samples from microliter to nanoliter volumes on NEMS chips.

Keywords: nanoplastics, trace substances, photothermal sensing, Fourier transform infrared spectroscopy, NEMS-FTIR, degradation

Introduction

The degradation and fragmentation of plastics, driven by various physical and chemical factors, results in the formation of microplastics (MPs) and nanoplastics (NPs), alongside the release of harmful substances and additives into the environment [1]. The growing prevalence of NPs in both the environment and the tissues and cells of living organisms has raised significant concerns regarding their potential biological effects [2].

Analytical techniques such as mass spectrometry-based techniques, surface-enhanced Raman spectroscopy (SERS), and atomic force microscopy-infrared spectroscopy (AFM-IR) offer good sensitivity with detection limits typically in the nanogram to picogram range, depending on the specific method [3]. However, their widespread application for routine environmental monitoring is hindered by factors such as expensive equipment, time-intensive procedures and sample preparation, which limit their practicality in large-scale studies [3].

Nanoelectromechanical infrared (NEMS-IR) spectroscopy, a new analytical approach based on NEMS chips comprising a resonator, has shown very good sensitivity down to the picogram level for the detection of various substances, including polymeric nanoparticles [4], and pharmaceutical compounds [5]. However, the reliance of NEMS-IR on expensive quantum cascade lasers (QCLs), which have a narrow spectral range, limits its applicability for routine nanoparticle monitoring.

In this study, we present NEMS-Fourier transform infrared spectroscopy (NEMS-FTIR) as a novel solution for the chemical analysis of NPs and other trace substances that exhibit IR absorption profiles. Here, in contrast to NEMS-IR, widely available FTIR spectrometers are used as light sources, providing a method with a wide spectral range for IR analysis.

Materials

Polystyrene-based nanoparticles (PS, ⌀100 nm) were purchased from Sigma Aldrich (USA) as a 10%w/v aqueous suspension and polypropylene particles (PP, ⌀54 nm) were obtained from Lab261 (USA) as a 1%w/v suspension. For 50 µg/mL suspensions, UHPLC-MS grade water (Thermo Fisher Scientific, USA) was used for dilution.

Tygon tubing (LMT-55) was used for the plastic degradation experiment. Tubing segments (8 mm long, 3 mm OD, 1 mm ID) were first washed with DI water (18 MΩ·cm; Millipore, USA) to remove potential surface contaminants and then soaked in ethanol (HPLC grade, Sigma Aldrich, USA), with exposure times ranging from 0.5 to 4 minutes. Segments were handled with clean metal tweezers to avoid contamination.

Methods

NEMS chips were fabricated using standard cleanroom lithography. At their center is a 1x1 mm^2 silicon nitride (SiN) membrane whose tensile stress is approximately 50 MPa. Electrical transduction is enabled by two gold electrodes extending along the membrane, each 10 µm wide, allowing the conversion of mechanical vibrations into electrical signals [6, 7].

Due to its robustness, the samples can be applied to the membranes using different sampling techniques [8]. A nanoliter dispenser (BioFluidix-Hamilton, Germany) was used to deposit 20 nL PS and PP suspensions, depositing 1 ng of particles on the membranes. Micropipettes were used to deposit 2 µL of ethanol in which parts of the plastic tubing were soaked.

During the measurement, NEMS chips were positioned at ~10^{-5} mbar inside the nanomechanical IR analyzer (EMILIE™, Invisible-Light Labs GmbH, Austria). When exposed to IR light, the sample absorbs the radiation and heats up, causing thermal expansion and reduced tensile stress in the membrane. The change in oscillation frequency, monitored via a self-sustaining oscillator and a frequency counter [7], correlates with absorbed power. The IR spectrum was generated in the range of 4000 to 400 cm^{-1}, with FTIR settings for resolution, stabilization delay, co-additions, and aperture at 4 cm^{-1}, 30 ms, 200 and 6 mm, respectively.

Results

The NEMS-FTIR spectra of 1 ng of PS and PP NPs are shown in Fig. 1, where characteristic IR peaks of these materials are observed [9] and presented as vertical dashed lines.

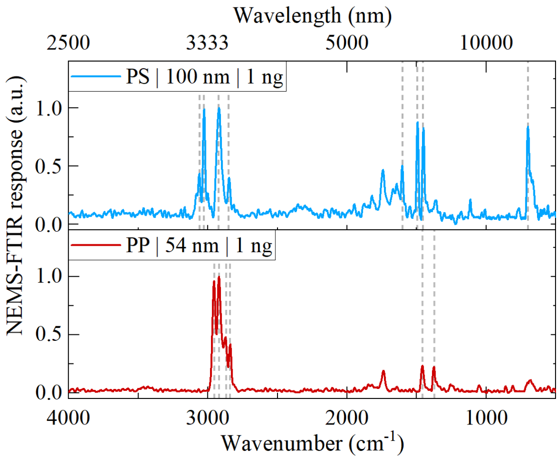

Fig. 1: NEMS-FTIR spectra of 1 ng of PS NPs (top) and PP NPs (bottom). Vertical lines mark the characteristic peaks of each polymer.

Fig. 2 presents NEMS-FTIR spectra of ethanol samples after plastic tubing immersion, showing increasing peak intensity with time, indicating progressive dissolution of the tubing due to its lack of ethanol resistance. IR database analysis identified alkyd varnish and polyurethane, which may originate from tubing additives or coatings dissolving in ethanol.

Summary and outlook

NEMS-FTIR emerges as a promising tool for detecting nanoplastic particles and degradation products of plastics, even from short exposure times, providing a sensitive alternative to more complex methods. The ability to use online available databases further enhances its practicality. While the technique can detect substances down to the low nanogram range, with the potential for detection in the picogram range, extraction from complex environmental matrices may be necessary.

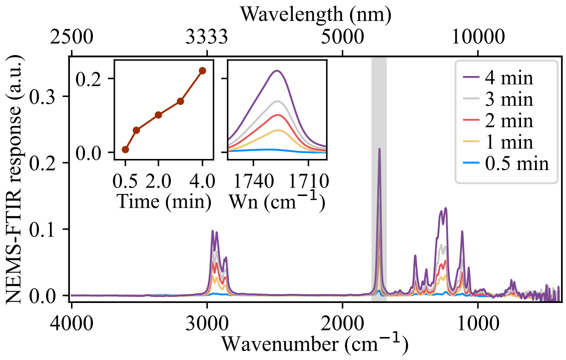

Fig. 2: NEMS-FTIR spectra of degradation products from plastic tubing in ethanol after immersion for different durations. The right inset shows an enlarged view of the 1727 cm^{-1} peak, while the left inset illustrates the change in intensity of this peak over time.

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