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Nanomechanical IR spectroscopy for fast analysis of liquid-dispersed engineered nanomaterials

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ABSTRACT

The proliferated use of engineered nanomaterials (ENMs), e.g. in nanomedicine, calls for novel techniques allowing for fast and sensitive analysis of minute samples. Here we present nanomechanical IR spectroscopy (NAM-IR) for chemical analysis of picograms of ENMs. ENMs are nebulized directly from dispersion and efficiently collected on nanomechanical string resonators through a non-diffusion limited sampling method. Even very small amounts of sample can convert absorbed IR light into a measurable frequency detuning of the string through photothermal heating. An IR absorption spectrum is thus readily obtained by recording this detuning of the resonator over a range of IR wavelengths. Results recorded using NAM-IR agree well with corresponding results obtained through ATR-FTIR, and remarkably, measurement including sample preparation takes only a few minutes, compared to ~2 days sample preparation for ATR-FTIR. Resonator dimensions play an important role in NAM-IR, a relationship which will be elaborated here.

1. Introduction

Nanomaterials are increasingly designed and engineered for specific purposes, especially in nanomedicine, where engineered nanomaterials (ENMs) form the basis of a wide range of novel drug delivery and other therapeutic systems, as well as entities for precision diagnosis [1,2]. Typically, newly designed ENMs are initially synthesized in research labs in relatively small amounts, and go through multiple rounds of adjustment. Therefore, novel tools for fast chemical analysis of minute samples are at high demand.

Infrared (IR) spectroscopy provides information about molecular structures in a sample, by measuring the fraction of incident IR radiation absorbed by a sample at a particular wavelength. Most compounds exhibit peaks in their mid-IR spectrum between 400 and 4000 cm^{-1}. This characteristic set of peaks, with specific positions and relative intensities, is known as the 'chemical fingerprint' of the compound. IR spectroscopy has been a valuable research tool for decades in various fields, such as pharmacy, forensic science and industrial process control [3–6]. However, conventional IR spectroscopy techniques such as attenuated total reflectance-Fourier transform IR (ATR-FTIR) spectroscopy still require relatively large sample amounts and extensive sample preparation. A sample mass of 1–6 mg is typically used for ATR-FTIR [7–9], although samples down to 0.25 mg have been analyzed by this method [10]. Aqueous dispersions of e.g. drugs or colloidal systems are typically dried before measurement, since water is known to disturb IR spectroscopic measurements. Depending on sample concentration, freeze-drying enough material for one measurement can take several days.

In this paper, nanomechanical IR spectroscopy (NAM-IR) is demonstrated to be highly suitable for analysis of ENMs, yielding results similar to those obtained with ATR-FTIR, but in a few minutes, sample preparation included. Samples are collected on nanomechanical string resonators and exposed to monochromatic IR light from a quantum cascade laser (QCL). IR light absorbed by the sample is transferred into a measurable frequency detuning of the string, due to photothermal heating. The resonance frequency shift is directly proportional to the absorbed energy. A NAM-IR spectrum is thus readily obtained by recording this photothermal frequency detuning of the resonator.

NAM-IR has the particular benefit of ultra-fast sample preparation, owing to the non-diffusion limited sampling method used to collect material on the strings. Measurement including sample preparation takes only a few minutes, a significant reduction from

Abbreviations: ENMs, engineered nanomaterials; NAM-IR, nanomechanical IR spectroscopy.

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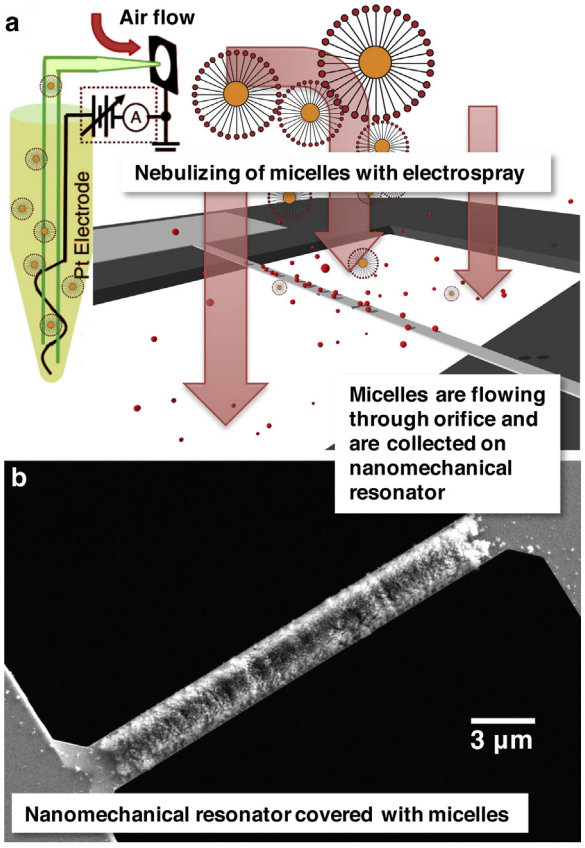

Fig. 1. (a) Schematic drawing of the non-diffusion limited sampling method. The engineered nanoparticles (polymeric micelles in this case) are directly sampled from the liquid dispersion onto the nanomechanical string. An aerosol of the sample is produced by an electrospray. This aerosol is pumped through the orifice in the sensor chip. While passing the nanomechanical string with high velocities, the micelles are collected on the string by inertial impaction with an estimated total sampling efficiency on the order of 10% (number of micelles collected on string vs. number of micelles electrosprayed). (b) SEM image of a silicon nitride resonator coated with micelles.

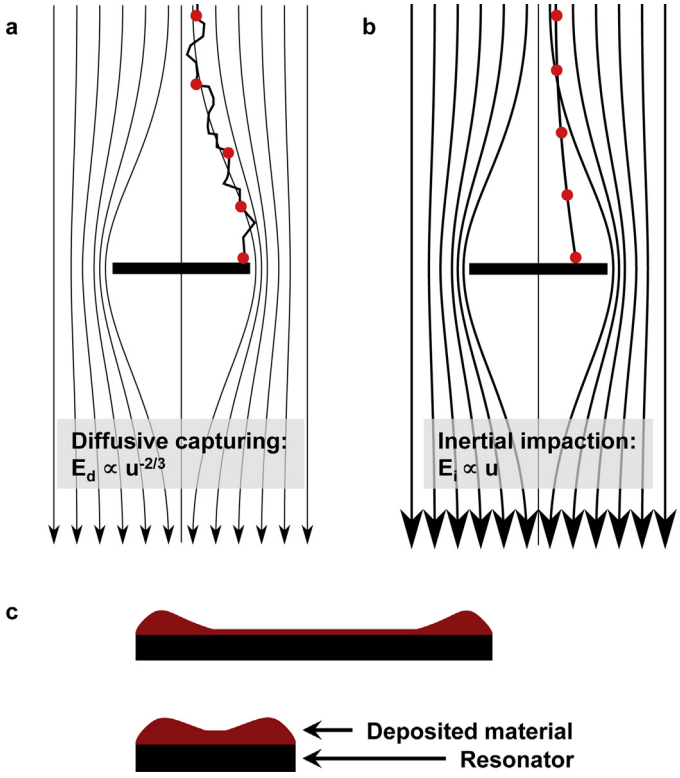

Fig. 2. Particle collection on strings. (a) Diffusive capturing (with collection efficiency E_d) occurs when thermal wiggling of a particle causes it to leave the streamline around the string and deposit on the fiber. (b) Inertial impaction (with collection efficiency E_i) happens, when a particle has a large enough momentum to continue its travel towards the string instead of following the streamlines that bend around the string. If the particle velocity u is sufficiently increased (as indicated by the thick flow lines), the dominant collection mechanism becomes inertial impaction. (c) Particles leaving the streamlines due to either collection mechanism are most likely to hit the string near the edges. Collection on narrow strings is more efficient because of this 'edge effect'.

that required for conventional methods. Sampling on strings is done by nebulizing ENMs directly from dispersion using an electrospray or jet nebulizer setup. The aerosol containing the material to be analyzed flows through an orifice in the sensor chip, over which the resonator is spanned. In this way, the nanomechanical resonator functions as a single filter-fiber (Fig. 1) [11,12].

The main mechanisms by which nebulized materials are captured on the resonators are diffusion and inertial impaction (Fig. 2a and b). When a particle is deposited due to diffusion, it is the Brownian motion of the particle that causes it to wiggle out of its trajectory and impact on the fiber, when passing on an adjacent streamline. If a particle has a large enough momentum, it can get deposited by inertial impaction. In this type of deposition, the large particle velocity and/or mass causes it to leave the streamline that bends abruptly around the string and hit the fiber. Inertial impaction can be efficiently exploited for sampling of ENMs on strings, by using high velocities. The small orifice in the sensor chip, featured by the NAM-IR sampling setup, can accelerate the ENM aerosol to velocities in the inertial impaction sampling regime.

The collection efficiency of a single filter-fiber is defined as the fraction of particles collected to the total number of particles that would have passed through the fiber if they had moved on straight lines. The total collection efficiency E_c can be defined as the sum of the collection efficiencies due to diffusion (E_d) and inertial impaction (E_i) [11]:

$$E_c = E_d + E_i = a_1(d_f u)^{-2/3} + a_2 u/d_f, \quad (1)$$

where d_f is the fiber diameter and u the aerosol velocity. a_1 and a_2 are constants depending on the particle and the fluid in which it is suspended.

At high velocities, collection can be assumed to take place by inertial impaction alone, and Brownian diffusion is thus ignored. In this case, the collection efficiency is

$$E_c = a_2 \frac{u}{d_f}, \quad (2)$$

The collection efficiency is thus directly proportional to particle velocity. Eq. (2) also shows that the collection efficiency increases for narrow fibers. This makes sense, as particles leaving the streamlines are more likely to hit the string near the edges (Fig. 2c).

In order to further appreciate the importance of particle velocity on collection efficiency, we can write the number of particles collected per time as

$$N_t = d_f L C_p E_c u = L C_p a_2 u^2, \quad (3)$$

with the particle number concentration C_p and the fiber length L [11].

The non-diffusion limited sampling method has an up to 100% collection efficiency of the particles flowing in the projection of the string resonator, which means that only very small volumes of dilute sample solutions are necessary to coat the resonator.

Eqs. (1)–(3) demonstrate the importance of geometrical aspects when materials are deposited onto mechanical string resonators by non-diffusion limited sampling. The geometry of the resonators is equally important for their sensitivity, when measuring