Novel approach for bottom-illuminated photothermal nanoscale chemical imaging with a flat silicon sample carrier

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Background – Infrared (IR) spectroscopy is the method of choice when it comes to chemical identification within spectroscopic methods, but it has certain drawbacks: First, there is the limited spatial resolution of IR-spectroscopy due to the Abbé limit. Second, many important solvents (especially water) exhibit strong absorption in the mid-IR range. The second issue can be overcome using an attenuated total reflection (ATR) setup, which restricts the interaction between radiation sample to the evanescent field within the first few hundreds of nanometers of the sample. A popular approach to solve the problem of lack of spatial resolution in mid-IR imaging, photothermal scanning probe microscopy is used. This hybrid technique called AFM-IR combines atomic force microscopy with mid-infrared spectroscopy. The working principle is based on a local, short-lived photo-thermal absorption of infrared light induced by a pulsed, tuneable EC-QCL source. This excitation then is measured by the sharp tip of an atomic force cantilever. It has been shown that the oscillation amplitude of the cantilever induced by photothermal expansion is proportional to the optical absorption coefficient [1]. Thus, by tuning the wavelength of the infrared laser an absorption spectrum is generated, by keeping the wavelength fixed and scanning the AFM tip absorption images can be generated. AFM-IR can be combined with ATR type illumination to enable measurements of solid samples in absorbing liquids (e.g., to analyse protein fibrils in aqueous media) [2, 3]. Conventionally, high-refractive index prims (e.g., ZnSe) are used as substrate in these experiments (Fig.1 a.). For AFM-IR experiments these ZnSe prisms unfortunately have several drawbacks: ZnSe is not suitable for every type of sample (e.g., acidic samples or liquids). The handling and sample preparation on those prisms is not easy. Furthermore, ZnSe is a comparatively "exotic" material and there exists comparatively little literature on surface functionalization or micro structuring of ZnSe. Last but not least, the cost of a ZnSe ATR prism for AFM-IR lies in the order of several hundreds of Euros.

a)   b)   c)
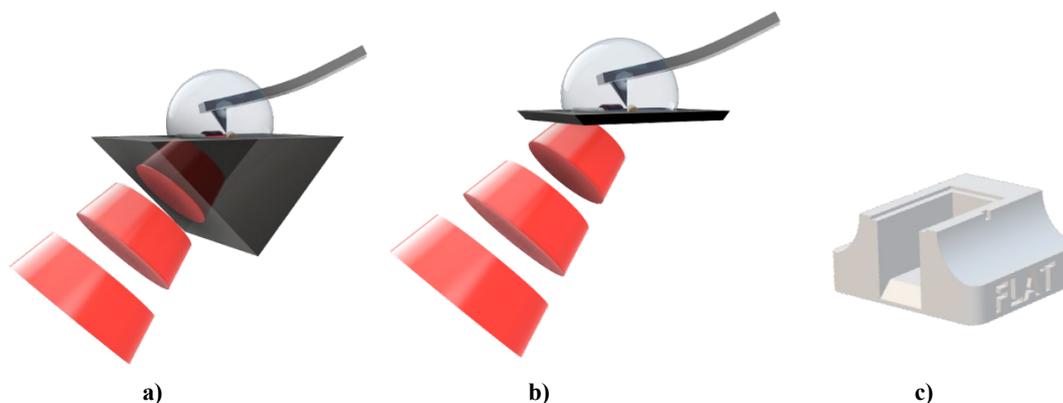
Fig. 1. (a) conventional high-refractive-index prism in AFM-IR liquid measurements; **(b)** the novel flat Si-ATR and **(c)** sample holder fitting the new flat sample carrier designed by rapid prototyping.

In this work we introduce a novel sample carrier for liquid AFM that is more chemically resistant, easier to handle and cheaper than the state of the art ZnSe prisms. Our approach uses micro-machined flat silicon-wafer that can be used for AFM-IR experiments. This opens up new ways for measuring AFM-IR in liquids. The flat shape allows easy handling and spin coating of samples on the carrier. Because the carrier is made of silicon, surface functionalization is well understood. Changing a system build around the use of ATR prisms, of course needs some adjustments to the instrumentation. Using rapid prototyping these new, flat Si-carriers can be made compatible with existing commercial AFM-IR instruments. For highest sensitivity, adjustments to the beam path are required to account for this new substrate's geometry, as there is the change from a high-refractive index prism to a flat ATR holder of different material. This was achieved with an additional, removable collimating lens.

Results – We were able to show the feasibility of this new approach. With our sample carrier it is possible to perform cost effective measurements on the nanoscale in air and in liquids. In Fig. 2. a measurement of a PMMA/PS – polymer blend is shown, where IR-spectra is taken and chemical imaging at two distinct wavelengths is shown.
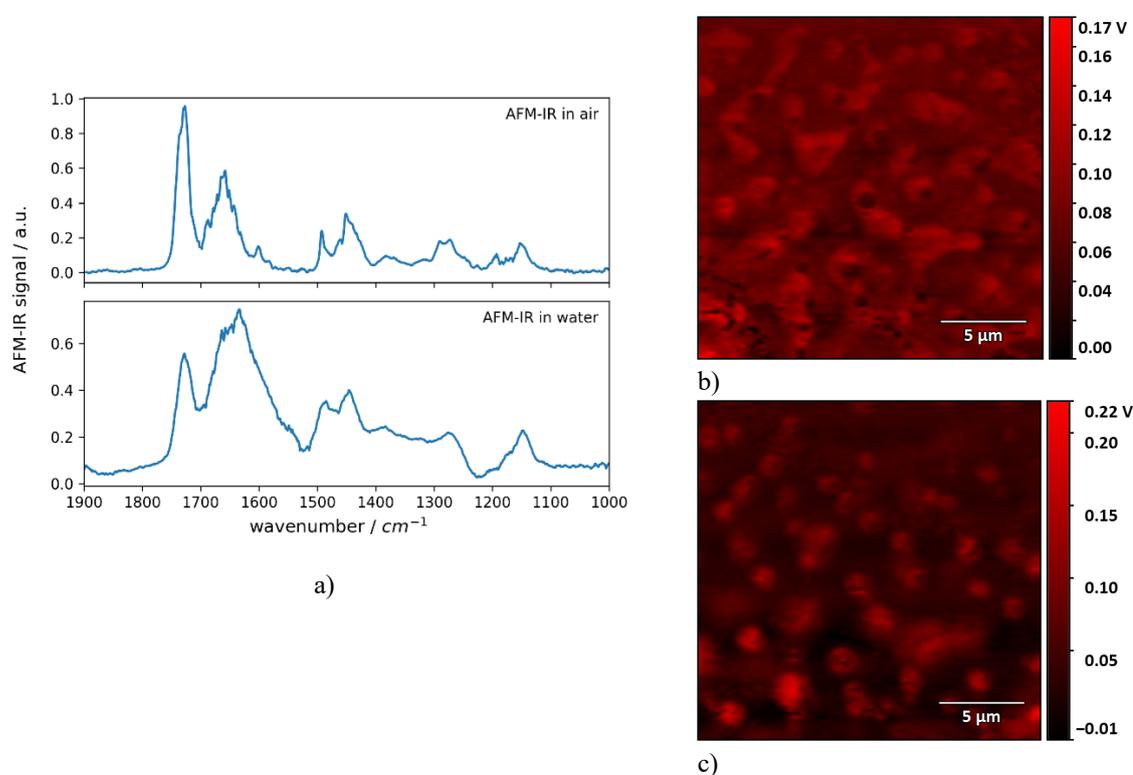
Fig. 2. a) spectra taken on PMMA/PS blend in air & liquid; b) IR imaging at 1732 cm^{-1}; c) IR imaging at 1660 cm^{-1}.

References

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