Combined far- and near-field chemical nanoscope at ANKA-IR2: applications and detection schemes

Diedrich A. Schmidt\textsuperscript{1,2}, Erik Bründermann\textsuperscript{1}, and Martina Havenith\textsuperscript{1}

\textsuperscript{1} Physical Chemistry II, Ruhr-Universität Bochum, 44780 Bochum, Germany
\textsuperscript{2} Present address: Department of Physics, North Carolina A&T State University, Greensboro, NC 27411, USA

E-mail: Diedrich.Schmidt@rub.de, Erik.Bruendermann@rub.de, Martina.Havenith@rub.de

Abstract. A newly developed microscopy and nanoscopy station that combines far- and near-field microscopy with other microscopy modalities has recently been integrated at the ANKA-IR2 beamline. The various modalities include broadband synchrotron radiation and tunable laser-based near-field microscopy, atomic force microscopy, Raman microspectroscopy, and confocal laser and fluorescence microscopy. This multi-modal nanoscope is designed to combine a broad array of techniques to study the “same” sample at the “same” position. We show some examples that demonstrate several of the available modalities. We also discuss various detection schemes to facilitate sensitive absorption and reaction-kinetic experiments.

1. Introduction

A multi-modal nanoscope, which includes far- and near-field modalities, was recently integrated into the ANKA-IR2 (Karlsruhe, Germany) beamline in 2010. The far-field modalities include various confocal microscopies: optical, laser, Raman, and fluorescence. The near-field modality uses either aperture or aperture-less (scattering) methods in either the optical, infrared (IR), or terahertz (THz) range. By utilizing a metallic nano-finger, the infrared near-field modality can achieve chemical mapping with nanoscale spatial resolution using either currently available tunable laser-based sources or the high brilliance of the ANKA-IR2 beamline in the future. Laser-based infrared scattering-scanning near-field microscopy (s-SNOM) is a powerful chemical nanoscopy technique which has been useful in determining complex dielectric constants at the nanoscale [1], characterizing crystal structure and phonon-plasmon coupling [2, 3], and surface phonon polaritons [4]. Recently, broadband IR [5, 6] and THz [7] nanoscopy has also been shown.

Using laser-based infrared scattering SNOM, we have investigated self-assembled monolayers [8], nanoscale lipid membranes [9], nanografted patches of mixed single- and double-stranded DNA [10], ultra-thin mixed polymer brush films [11, 12], as well as “single” nanoparticles [13], and sub-surface [14] and activated [15] dopants in semiconductors. Utilizing the other modalities available at the ANKA-IR2 nanoscope, we have also investigated the status of mitochondria in UV-irradiated human spermatozoa [16], tracked drug-delivery compounds in live cells [17], and determined variations in surface charge densities of epitaxial graphene by performing a combined confocal Raman and atomic force microscopy study [18]. Here, we report on the status of the instrument at the ANKA-IR2 beamline [19]. We introduce the nanoscope experimental station and present recent examples illustrating the different modalities of the instrument, followed by a discussion on different detection schemes.

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2. Nanoscope station at ANKA

Figure 1. a) Schematic layout of the Nanoscope station at the ANKA-IR2 beamline. The synchrotron radiation passes through a fast feedback system for beam stabilization (FFS) before entering the Fourier transform spectrometer (FTS) and then being focused on a cantilever of an atomic force microscope (AFM). The external tunable CO2 and alignment HeNe lasers, and the spectrum analyzer (SA) for the CO2 laser, are also shown. Arrows represent beam paths. Solid lines represent beam steering optics while dashed lines are movable optics, e.g. flip mirrors, to choose between different radiation sources. The nanoscope also has two fiber-coupled “internal” lasers for Raman or SNOM, a HeNe and frequency-doubled Nd:YAG (532 nm) laser. The SNOM modality can be operated in either scattering mode (s) or transmission mode (t). The Raman and t-SNOM modalities use optical sources, while s-SNOM can use either synchrotron IR and THz, or optical sources. b) Photograph of nanoscope (foreground) in the experimental hutch of ANKA. The FTS can be seen behind the enclosure box of the nanoscope. Photograph courtesy of B. Gasharova.

Figure 2. Flow diagram of the measurement scheme. The modulation of the AFM cantilever is fed to the computer (PC) and is used as feedback for the position of the sample. At each point \((X_i, Y_i)\), a spectrum is acquired. The FTS performs either a continuous scan or a step-scan measurement at two different positions of the interferometer. The detector signal is demodulated at the \(n^{th}\) harmonic, which is set by an external lock-in amplifier.

The nanoscope experimental station is coupled to the broadband synchrotron radiation of the ANKA-IR2 beamline via a fast feedback system for beam stabilization and a vacuum Fourier-transform spectrometer (FTS, Bruker Optik, model VERTEX 80v), with a far-infrared/THz spectral extension to \(\sim 10 \text{ cm}^{-1}\) (see Fig. 1). After the light passes through the Fourier transform spectrometer, it is coupled to the microscope using broadband mirror optics to access both the THz and IR radiation from the beamline. The microscope (WTec, model alpha300ASR) is already equipped for three measurement techniques: atomic force microscopy, scanning near-field optical microscopy, and confocal Raman microscopy. The fourth technique, infrared scattering...
SNOM, utilizes a metallic probe of an atomic force microscope (AFM) in combination with the IR radiation from the beamline or, when used off-line for pre-alignment or preparatory studies, a tunable CO2 laser. The SNOM modality in transmission uses specialized aperture tips for top illumination, and can be performed with either a 532 nm or 633 nm laser, while scattering SNOM can be performed with a separate 633 nm laser. The confocal Raman microscopy (cRM) modality can be operated with either the 532 nm or 633 nm laser, with diffraction-limited lateral resolution that depends on the laser source. For scattering SNOM, we operate the nanoscope in a non-contact mode of the AFM in order to modulate the near-field signal and use higher-order harmonic demodulation \([20-22]\) to eliminate background radiation and enhance the near-field contrast \([23]\). Figure 2 shows the flow diagram for the measurement scheme with a broadband radiation source.

3. Modalities
In the following, we present recent examples highlighting the optical and IR near-field (SNOM), far-field confocal Raman, and atomic force microscope (AFM) modalities of the ANKA-IR2 nanoscope.

![Figure 3](image)

**Figure 3.** a) Topography of a metallic nano-structured test sample. b) Transmission SNOM image measured with a photomultiplier. c) line profile of the photomultiplier signal in b) along the dashed white line showing an optical resolution of \(<90\) nm at \(\lambda = 532\) nm, corresponding to \(\sim \lambda/6\); the inset is a schematic of the nano-structured sample. Scale bars in a) and b) are 200 nm.

For near-field imaging in the optical regime, we use a metallic nano-structured test pattern made from silver. The light from the 532 nm laser is focused onto the apex of the specially designed nanocone. In transmission SNOM, we achieved simultaneous optical and spatial resolution of less than 90 nm. Figure 3a) shows the topography of the metallic nanostructures measured by the specialized aperture tips, while Fig. 3b) shows the simultaneously acquired transmission SNOM image recorded by a photomultiplier.

For scattering SNOM, we use a “soft” matter test sample of a microcontact-printed line pattern on a gold coated substrate consisting of double stranded DNA. Figure 4a) shows the topography of the DNA (bright vertical stripes in Fig. 4a)) surrounded by a self assembled monolayer of octadecanethiol (ODT), which fills the open space in-between the DNA stripes by binding to the gold surface of the substrate. The simultaneously acquired near-field image is shown in Fig. 4b). The wavelength of \(\lambda = 9.5\) \(\mu m\) (from a CO2 laser), coincides with an absorption maximum of DNA. The dark vertical stripes correspond to DNA, while ODT has no absorption bands near 9.5 \(\mu m\), resulting in a clear contrast between the two materials. The subtle variations in intensity of the near-field image are due to interference with the background signal. More complex nanostructures can be made with the available nanolithography software using
Figure 4. a) Topography of a microcontact-printed structured monolayer of double-stranded DNA separated by octadecanethiol (ODT); the DNA self-assembles in a monolayer which is \(\sim 20\) nm higher (bright, narrow stripes) than the ODT (darker, wider stripes). b) Simultaneously measured near-field image of the sample at \(\lambda = 9.5\) \(\mu\)m with a resolution of \(< \lambda/100\), near the absorption maximum of DNA. The dark bands in the image correspond to the DNA stripes, while the ODT has no absorption near 9.5 \(\mu\)m. Scale bar is 2 \(\mu\)m in both images.

nanografting with the tip of an atomic force microscope cantilever in a liquid environment. For more details that demonstrate the complex nanografting of mixed, single- and double-stranded DNA patches, and their subsequent spectral read-out by scattering SNOM, we refer the reader to Ref. [10].

Figure 5. a) Optical image of an onion cell showing the scan area in red. b) False-color chemical map of the onion cell in a) showing the cell walls (red), primary water content (blue), and the amino acid tyrosine (green). c) Representative Raman spectrum showing the three primary bands used to create the image in b): tyrosine band at 852 cm\(^{-1}\), C-H stretch corresponding to the cell walls (red box), and the O-H stretch of water (blue box). Scale bars in a) and b) are 40 \(\mu\)m and 10 \(\mu\)m, respectively.

One of the highly versatile modalities of the nanoscope is confocal Raman microscopy, as it offers a non-invasive, quantitative, and non-destructive method to examine living cells. In addition, it can be used to investigate liquid samples or samples containing a high water content. As an example, we looked at a fresh sample of onion cells prepared by peeling a single layer of onion skin and mounting it on a CaF\(_2\) window. Figure 5a) shows the optical image of a fresh onion cell. Figure 5b) shows a false-color overlay image that highlights the large water content of the onion cell (blue), the cell walls (red), and the amino acid tyrosine (green). The individual chemical images used to create Fig. 5b) were made by integrating over the corresponding bands of interest and are shown in Fig. 5c): O-H stretch of water (blue box), C-H stretch which shows the structure of the cell walls (red box), and the amino acid tyrosine at 852 cm\(^{-1}\). The ANKA-IR2 confocal Raman microscope included in the nanoscope system was also used to monitor the status of mitochondria in UV-irradiated human spermatozoa [16] and in tracking drug-delivery compounds [17] in living human cells. The system can be equipped with additional lasers in the future, such as 488 nm and 785 nm, to widen Raman applications in the analysis of living cells.
or tissue, semiconductor devices, or in materials analysis.

![Atomic force microscope image of a partially graphitized SiC(0001) substrate](image)

**Figure 6.** a) Atomic force microscope image of a partially graphitized SiC(0001) substrate. The bright region is SiC and the dark region is single layer graphene. b) Line scan along dotted line in a) showing the vertical resolution of ~1 nm. Scale bar in a) is 400 nm.

As a final example that illustrates the sensitivity of the atomic force microscope modality, we studied a partially graphitized silicon carbide (SiC(0001)) sample. One of the growth modes of graphene on 6H-SiC(0001) is the conversion of three Si-C bilayers into a single sheet of graphene [24–26] by evaporation of the Si. Figure 6a) shows how the atomic force microscope resolves partially graphitized SiC(0001). The bright areas are SiC while the dark areas are single layer graphene. A line scan (dashed line in Fig. 6a) across the growth front, with a step height of ~1 nm, is shown in Fig. 6b).

4. Detection schemes

In many applications, time-dependent processes at the nanoscale, such as dynamics in chemical reactions, kinetics at interfaces, energy level transitions in semiconductors and solid state materials, are of prime importance. For such applications, we study the pulse structure of the ANKA storage ring in the visible, IR, and THz spectral range [27] to be able to exploit the short pulses emitted by the storage ring. Figure 7 shows a measurement of a regular fill pattern during user operation. The 1 GHz avalanche photo diode used here resolves individual pulses that correspond to individual bunches (Fig. 7a,b). The structure, although not the intensity distribution (due to THz-field and electron bunch coherence effects), is similar to the THz pulse trains resolved with a hot electron bolometer [28]. The room temperature IR detector with a bandwidth of 200 MHz is not fast enough to resolve the individual pulses, but allows for the separation of the pulses originating from the three bunch trains in the ring (Fig. 7c). A room temperature IR detector (VIGO PVI-4TE-4, DoroTEK GmbH, Strausberg, Germany) with an increased bandwidth and risetime of ~0.5 ns partially resolves the separate IR pulses of each bunch (Fig. 7d). In the future, infrared hot electron bolometers could provide sufficient speed to resolve the 2 ns spaced single pulses in more detail.

Using the visible light, a trigger can be derived to detect the IR or THz radiation synchronous with the roundtrip time in the storage ring. One possibility to improve the signal-to-noise ratio in normal imaging modes is to use boxcar techniques to arm the detection branch only when the signal is present while removing excess noise during the time between pulses. The typical decay of the ring current with time or fluctuations from pulse to pulse can be compensated by a second, nearly identical detector monitoring the signal, or by using a balanced detection scheme. These methods can improve the image quality while at the same time learning more about the necessary conditions to obtain stable intensity and timing in storage rings.

5. Outlook

In a recent work [15], we have shown that it is possible to gain new insights in nanofabrication by studying the “same” sample at the “same” location, and using a multimodal approach with
far-field synchrotron IR microscopy, confocal Raman microscopy, atomic force microscopy, and scattering near-field IR microscopy. The available multi-modal ANKA-IR2 nanoscope station provides the unique possibility of studying the same sample location using a “single” instrument with different modalities. The high brilliance and broadband synchrotron radiation of the ANKA-IR2 beamline, in combination with various laser sources, covers the optical, mid-IR, far-IR, and THz regions of the electromagnetic spectrum. The far-field confocal microscopy techniques are all diffraction limited, however the near-field methods approach resolutions of $\sim \lambda/1000$ [29], and are essentially limited by the size of the probe used for SNOM [30]. Improvements in spatial resolution of near-field imaging can be made by utilizing designer metallic waveguides [31, 32], which enhance the coupling and localize the electromagnetic field to smaller volumes.

6. Summary
In summary, we outlined the new nanoscope station that was recently installed at the ANKA-IR2 beamline. The multi-modal nanoscope, which incorporates far-field, near-field, and tactile methods, such as confocal microscopy (laser, optical, and Raman), SNOM in different modalities, and atomic force microscopy, offers the ability to gain new insights as the various methods can examine the “same” sample and “same” location without the need of moving to different instruments. We presented several examples of the possible measurement modalities of this instrument, including metal nano-structures for transmission SNOM, microcontact-printed DNA for scattering SNOM, fresh and wet onion cells for Raman microscopy, and partially graphitized SiC for atomic force microscopy. The emission pulse structure of the ANKA storage ring was examined and resolved in the visible and IR to investigate the possibility of measuring kinetics and dynamics, and we discussed different detection schemes for improving the signal-to-noise ratio and the imaging quality for future applications.
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