Scanning near-field optical microscopy with white-light illumination: nanoscale imaging and spectroscopy of resonant systems.

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We present the realisation of near-field spectroscopic measurements with fibre-tip-based scanning near-field microscopy. It allows simultaneous acquisition of near-field optical images in a broad spectral range (400 nm to 1000 nm), thus recovering local spectroscopic information. The technique is essential for understanding the resonant interaction of light with nanostructured objects as the far-field and near-field spectral response can differ significantly, e.g., in the case of plasmonic nanostructures. By mapping the evanescent fields, the approach also provides spectroscopy technique with nanoscale spatial resolution. Several applications of spectroscopic near-field microscopy are described for visualisation of plasmonic modes in metallic nanostructures and near-field fluorescence spectroscopy.

Keywords near-field optical microscopy, spectroscopy, subwavelength imaging

1. Introduction

Scanning near-field optical microscopy (SNOM) is an important tool in modern nano-optical and nanophotonic studies allowing nanoscale mapping of electromagnetic field in nanostructured environment and in micro- and nanoscale devices [1,2]. Knowledge of local electromagnetic field distributions combined with a simultaneously acquired topography of the surface, as common in SNOM, is imperative to understand light-matter interactions in nanostructures and nanolocal optical characterisation of materials. SNOM applications range from material science and biophotonics to studies of fundamental optical processes. Important breakthroughs have been achieved using SNOM to image the light behaviour in nanostructured environment, such as photonic and plasmonic crystals [3,4], understanding of light flow in photonic circuits [5-7], direct visualisation of the response of optical antennas, imaging of domain structures in ferroelectric and ferromagnetic materials [8,10], investigations of local fluorescence, second-harmonic generation and Raman scattering [11-14].

In most cases, SNOM measurements are restricted to certain fixed wavelengths provided by available laser sources. At the same time, the objects under investigation may exhibit strongly resonant optical behaviour, with optical properties crucially depending on the wavelength of the excitation light. These may be quantum dots, molecules, plasmonic and photonic nanostructures, and metamaterials. Moreover, the resonant wavelength position may be strongly modified due to the electromagnetic interaction between the objects, so it is not always possible and straightforward to predict it even if the resonant optical properties of individual objects are known. In this case during SNOM measurements with a monochromatic illumination, the spectral behaviour and resonant properties of the objects are completely hidden. In turn, if two or more light emitters, e.g., different fluorescent labels, are present in the field of view, conventional SNOM provides convolution of their spectral response, and thus no discrimination between emission at different wavelengths. In the past, even if the spectral dependence of SNOM images has been studied, it was done in a sequential manner by recording several consecutive SNOM images obtained using a different illumination (or detection) wavelength, or by sequentially taking a spectrum at a few specific points of the image. This approach is very time consuming and suffers from system drifts as well as sample and tip deterioration from scan to scan as multiple images are required. This is a reason that near-field spectroscopy has not been successful tool, despite promising access to important information for imaging and understanding of both inorganic materials and biological objects.

In order to overcome these difficulties and introduce real spectroscopic capabilities in scanning near-field optical microscopy, we have recently developed a hyperspectral scanning near-field optical microscope capable of recording, simultaneously, multiple near-field images in 400—1000 nm spectral range during a single scan [15]. This provides access to the near-field spectroscopic properties of nano-objects and enables direct comparison of the images obtained at different wavelengths under exactly the same sample and tip conditions and drift-free. In the following, we will describe the principles of the hyperspectral SNOM imaging and present several application examples. We will show how such a hyperspectral SNOM can be used to image various plasmonic structures for which near-field spectroscopy is imperative in order to access resonant interaction of light and surface plasmons. We will also describe spectroscopic studies of different fluorophores in PVA (Poly-Vinyl Alcohol) matrix, illustrating SNOM capabilities in fluorescence microscopy applications such as cell imaging.
2. Spectroscopic near-field optical microscope

The SNOM instrument used for hyperspectral imaging is based on metal-coated optical fibre probes with a nano-aperture at the tip. This allows measurements in either illumination mode when white light is sent through the SNOM probe, or in collection mode when the probe is collecting the light after its interaction with the sample (Fig. 1). The probe is mounted on a piezotube, for tip-surface distance control (z-direction), which is in turn mounted on a 2D piezostage to raster-scan the probe in the x and y directions parallel to the sample surface. In an alternative configuration, the sample is mounted on the 2D piezo-stage and scanned with respect to the tip.

The tapping-mode distance regulation system is based on the quartz tuning fork to which the probe is attached [16]. The use of a quartz tuning fork allows for a potentially wide variety of probes to be used. A frequency generator is used to excite the tuning fork-fibre system at its resonance frequency, around 32.7 kHz (tuning forks dependent), and the current flowing through the tuning fork is monitored. As the probe is approached to the sample surface, the oscillations of the tuning fork are increasingly damped due to the dissipative forces acting on the tip of the probe. During scanning, this feedback signal is maintained at constant amplitude using the z-distance control, generating the topographic image.

SNOM probes are fabricated using pulled optical fibres which are then bent at around 90° (Fig. 1 (c)) enabling the implementation of tapping mode distance regulation. The SNOM probes used were made using telecom optical fibre with a 9 µm core. The fibre is first stretched in order to taper it at one end and is then bent at 90° by thermal heating using a fibre splicer. The fibre tip can be metal coated if desired. For the metal coated probes, gold or aluminium is sputtered onto a rotating fibre tip; a nano-aperture is then formed by cutting the extremity of the probe at 90° using Focused Ion Beam (FIB). Depending on the position where the SNOM probe is cut, apertures between 50 nm and 500 nm diameter can be reproducibly obtained. An example of such nano-aperture is shown on the SEM image in Fig. 1 (d).

For near-field spectroscopy, coherent broadband light (400 nm to 1000 nm wavelength) from a supercontinuum laser source is used to illuminate the sample (Fig. 1(a)). The light from the laser is first injected into an endlessly monomode photonic crystal fibre in order to localise all the wavelengths in a single Gaussian spot. The sample is then illuminated from the far-field, either in collimated illumination or using a microscope objective, and the near-field signal is locally detected via the SNOM probe. The detected light is spectrally separated by a spectrometer coupled to a high-speed CCD. A full spectrum is acquired at each pixel of the SNOM image, therefore, generating the multispectral near-field optical response of the sample.
The set-up can also be used in illumination configuration where the probe acts as a nano-source of light (Fig. 1(b)). In this configuration, the sample is excited locally using the SNOM probe, and the signal is collected in the far field in transmission or reflection. One can use the broadband light to illuminate the sample through the probe and detect the local spectral response of the sample. Alternatively, for fluorescence microscopy, spectral filters can be positioned in the beam of the white-light laser in order to select the desired excitation wavelengths. In both cases, the signal is collected in transmission or reflection using a microscope objective. That signal is then coupled into an optical fibre and guided to the spectrometer and, similarly to the collection configuration, the full spectrum is acquired on each pixel of the SNOM image, allowing, therefore, for direct correlation with the position of the local excitation.

Independently of the experimental configuration, each image is typically taken at a scan rate of 0.1 Hz (for one trace and retrace cycle) with 256 lines per image and 256 points per line. This means that each image contains 131072 pixels (counting the trace and retrace for one scan), and the same number of spectra are recorded. The acquisition time per pixel is approximately 20 ms which determines the integration time of the spectra. This time was experimentally fine tuned to compensate for the inaccuracy of the various synchronisation devices. After image acquisition, each spectrum is normalised to the reference spectrum (Fig. 1 (d)) taking into account background signal level.

The resulting data set is usually processed to create a false movie describing the evolution of the near-field distribution on the surface of the sample as the wavelength changes (see Ref. [15] for several examples of the movies). Each snap-shot of the movie corresponds to a near-field image at a given wavelength. Since all such images are acquired simultaneously during the same scan, they can be directly compared as there are no drifts or shifts between the individual images. One can also extract the local near-field spectra at any point of the image if desired. As in conventional SNOM, the associated, simultaneously measured topographic image is readily available to compare with the optical images. In the following sections we give application examples of the hyperspectral SNOM set-up in various working configurations.

3. Application example: spectroscopy of plasmonic excitations

Periodically nanostructured metal films or surfaces act as plasmonic crystals for surface plasmon polaritons (SPPs) in analogy to 2D photonic crystals [17-20]. The interaction of SPPs with a periodic structure leads to a modification of the SPP dispersion compared to an unstructured metal film, resulting in the formation of forbidden and allowed bands. In the latter, SPP Bloch modes are supported by the periodic structure. These modes determine the optical properties of structured metal films such as transmission, reflection and absorption. Usually, the spectral properties of plasmonic crystals have been studied in the far-field by measuring their far-field transmission or reflection [17,20]. The hyperspectral SNOM described above can be used to study the near-field transmission of the crystal and directly visualise the field distribution of the supported SPP Bloch modes.

3.1 Imaging the Bloch modes on periodically nano-structured surfaces

First, we illustrate the imaging capacities of the hyperspectral SNOM through the study of the spectral behaviour of the Bloch modes of a 1D SPP crystal (SPPC) consisting of an array of slits fabricated using focused-ion beam (FIB) milling in a 300 nm film of gold sputtered onto a glass substrate. An SEM image along with the far-field transmission dispersion of the structure is presented in figure 2. The dispersion of such a periodic structure (Fig. 2) exhibits the typical system of forbidden and allowed SPP bands corresponding to the excitation of the SPP Bloch modes on the metal film interfaces. These have been identified using standard Bragg-scattering considerations of SPPs supported by the smooth film [20].

The hyperspectral SNOM set-up allows us to probe the spectroscopic response of such SPP crystals in the near-field. Fig. 2 (e-j) shows several images of the near field distributions at representative wavelengths extracted from the full spectroscopic data file. For wavelengths shorter than 500 nm, due to optical properties of gold, no SPPs are excited and, thus, solely the direct transmission through the slits is observed, giving rise to a near-field distribution with maxima of intensity positioned on the slits. As the wavelength increases, the near-field distribution remains similar, but the field intensity on the surface increases as coupling to SPPs now enhances the transmission through the slits, and the Bloch modes of the structure resulting from the periodic scattering of the SPPs by the lattice of the plasmonic crystal [17,20,21], are clearly identified as lines perpendicular to the polarisation of the incident light.

As the wavelength increases, the Bloch modes distribution changes. For wavelengths shorter than 600 nm, corresponding to the +/- (1,0) mode for this structure at normal incidence, the Bloch mode intensity has maxima on top of the slits. At the +/- (1,0) resonance wavelength of 600 nm, the field distribution changes to a doublet with a maximum of intensity on the nanostructured slit and a maximum between the slits (Fig. 2 (d,i)). This is a direct observation of the splitting of the two counter-propagating Bloch modes on the nanostructured area. For wavelengths longer than the +/- (1,0) resonance, the field maximum intensity is then localised between the slits. This behaviour is less pronounced at the crystal’s edges where the effects of the finite size of the structure reduce the splitting of +/- (1,0).
3.2 SPPs on finite size plasmonic crystals

Having visualised the SPP Bloch modes within the crystal, it is interesting to see their modifications near the crystal boundary. Strictly speaking, Bloch modes are defined for an infinite periodic structure. The influence of the finite-size crystal lies in the reflection and refraction of the modes on the crystal boundary where periodicity is broken [22,23]. These processes result in the modification of the field distribution both within the crystal due to additional interfering waves after reflection from the crystal boundary inside SPPC as well as outside the crystal boundaries where smooth film SPPs can be excited after the Bloch modes are refracted from the crystal onto the smooth metal surface. Near the crystal boundaries, the conditions for the Bloch mode excitation are broken as the crystal meets the adjacent smooth film. Scattering at the boundaries leads to the SPP Bloch modes transmission from the crystal onto the smooth film at the frequencies matching the smooth film SPPs with no restriction on momentum since in the case under consideration all excited Bloch modes are normally incident on the boundary.

The SPP mode coupling onto the smooth metal film is a consequence of the finite size of plasmonic structures leading to the refraction of the Bloch modes of the structure by the boundary of the crystal, which has a significant influence on the SPP crystal’s optical properties. In particular, it impacts the SPP band-gap formation in periodic crystals. At normal incidence, the conditions for SPP launching on the smooth film correspond exactly to the spectral range of the band-gap in the centre of the Brillouin zone [17]. This is observed in the near-field spectrum measured at point A on the smooth surface (Fig. 2 (c)), where the spectral components absent from the far-field transmission spectrum are instead coupled to SPP modes on the smooth film. As seen above, wavelengths shorter than the lattice period correspond to relatively small near-field intensity and far-field transmission. With increasing wavelength, a clear Bloch mode structure is observed in the centre of the crystal with a characteristic intensity distribution with a period twice that of the crystal lattice characteristic of a (±1,0) mode [24].

![Fig. 2. (a) SEM images of the plasmonic crystal with a period of 600 nm. (b) Experimental far-field dispersion for the plasmonic crystal with period 600 nm. The calculated Bragg scattered SPP modes have been superposed onto the experimental dispersion. (c) Far-field and near-field transmission spectra of the crystal. The near-field spectrum has been measured at point A indicated in the images (e-g). (d) Cross-sections of the near-field intensity distributions measured along the white line in (h)-j). (e-j) Near-field intensity distributions for the 1D plasmonic crystal with a period of 600 nm and a slit width of 100 nm. For all the images, the polarisation is horizontal as indicated on (e). (e-g) SNOM images illustrating the coupling to SPP onto the smooth metal film: the scan size is 40 µm by 40 µm. (h-j) SNOM images illustrating the evolution of the field inside the nanostructured area (Bloch modes): the scan size is 13 µm by 13 µm.](image-url)
The evolution of the near-field intensity distribution on the metal film surface outside the crystal for varying wavelengths of the incident light is shown for selected wavelengths in Fig. 2. At the energy of the +/-(1,0) SPP resonance, corresponding to a wavelength of 600 nm, the SPP waves being launched from the plasmonic crystal boundaries onto the smooth gold film are clearly identified. Once again it should be stressed that all the images are snapshots recovered from the same optical data file and were all acquired simultaneously. One can see that when the smooth film SPPs are excited, the field intensity distribution above the nanostructured area is modified in the same way as when crossing the bandgap. This is related to the fact that the excitation conditions for smooth film SPPs coincide exactly with the band-gap of the SPP crystal [17,23]. At the wavelengths corresponding to the excitation of the SPPs on the smooth gold film, a maximum in the near-field spectrum over the smooth gold film (Fig. 2) and a minimum in the far-field transmission are observed.

3.3 Light harvesting with plasmonic structures

In the photodetector industry, there is currently a high demand to reduce the size of the active area of photodetectors without reducing their efficiency [25]. This may be accomplished by employing plasmonic light gathering structures, consisting of a one dimensional surface grating with a single central aperture or slit commonly termed ‘slit-and-grooves’ structures [26,27]. Such structures, when illuminated at wavelengths near the edge of the band-gap, couple the incident light to SPP Bloch modes which then propagate towards the central slit aperture and thus transmit the incident photon energy through the otherwise opaque metal film. The transmitted light spectrum is determined by the dispersion of the groove grating and transmission of the slit [27]. The resulting far-field transmission exhibits highly selective wavelength dependence and is, therefore, ideally suited for investigation using hyperspectral SNOM imaging.

The structures were studied using the hyperspectral SNOM operating in illumination mode: the incoming light is coupled into the optical fibre of the SNOM probe and the metal coated tip is used to locally illuminate each point of the structure in the near-field and the signal transmitted through the central slit is recorded as a function of the probe position (Fig. 1b). Such local illumination provides information on the spectral contribution of the various parts of the structure to the signal transmitted through the central slit [15].

Notwithstanding the transmission of the slit, the transmission maximum should be expected at the wavelength corresponding to the band edge of the periodic groove array where coupling to SPPs is the most efficient (see section 3.1). This is confirmed by examining the transmitted light spectrum: when only the slit is illuminated, the broad featureless nature of the spectrum demonstrates the absence of slit resonances, such as Fabry-Perot resonances or cut-off of the waveguided modes, in this spectral range (Fig. 3 (b)). When the groove grating is illuminated, a clear spectral
dependence arises due to the light coupling to SPP modes, with the local maximum signal near the same wavelength as in the far-field transmission spectrum. This can be confirmed by the dependence of the transmission spectrum on the position of the illuminating probe: the further the tip from the slit, the more red-shifted the transmission peak. This is due to the decrease of the propagation length of SPPs as the illuminating wavelength decreases, i.e., the further the tip from the slit, the smaller the contribution of shorter wavelengths since their propagation length is smaller. The role of the SPP excitation is also evident from the near-field distributions at different wavelengths corresponding to the different sides of the band-gaps of the groove grating (cf. Fig 3 (d) and (e)). When no SPPs are excited, such as at wavelengths below 550 nm due to the optical properties of Au, only direct transmission through the slit is important (Fig. 3 (c)).

4. Application example: spectroscopic imaging of fluorescence

A number of far-field fluorescence imaging techniques have been developed in recent years to achieve super-resolution optical imaging in biophotonics and cell imaging, achieving resolution beyond the diffraction limit down to 50 nm and better [28-31]. These methods include techniques involving point-spread function engineering, such as STED microscopy, and single molecule imaging approaches such as PALM and STORM. However, all these techniques place significant restrictions on the choice and range of fluorophore, thereby limiting the scope for spectrally multiplexed imaging of a number of different fluorescently labelled biomolecules. On the other hand, no such restriction applies in principle to scanning near-field optical microscopy (SNOM) which also offers resolutions down to tens of nanometres. SNOM also provides the additional benefits of a direct comparison of the optical imaging with surface topography, while its near-field nature ensures measurements are surface specific, enabling, for example, measurement solely sensitive to biological cell membranes.

Here we demonstrate the capability of hyperspectral SNOM to simultaneously detect and directly identify fluorophores in the near-field. In order to illustrate this, a sample consisting of fluorophores with two different emission wavelengths (570 nm and 595 nm) in a thin film matrix of PVA (Poly-Vinyl Alcohol) were studied.

A PVA-water solution doped with two different types of conjugated polymer nanoparticles (F8BT and EXP2), emitting at two different wavelengths, was used to spin-coat a thin layer of 250 nm on a glass cover slip substrate. Due to both their water solubility and low toxicity, conjugated polymer nanoparticles offer an attractive alternative to quantum dots for use in life sciences. Their applications in biological imaging has already been successfully demonstrated [32,33].

For this application, the SNOM set-up is used in excitation mode, as illustrated on figure 1 (b) and described above. The sample is excited locally using a coated SNOM probe, and the resulting fluorescence is collected in the far field. This configuration avoids unnecessary bleaching of the fluorophores caused by far-field illumination. For the excitation of the fluorophores, a short pass filter was positioned in the beam of the broadband continuum laser in order to select only the wavelengths between 450 nm (the shortest wavelength of the laser) and the cut-off wavelength of the filter, 500 nm. The resulting fluorescence is collected in transmission using a microscope objective with a numerical aperture of 0.75. The signal is then coupled into an optical fibre and guided to the spectrometer and, just as for the other configurations, the full spectrum is acquired on each pixel of the SNOM image, therefore allowing for direct correlation between the position of the local excitation and the near-field fluorescence spectrum.

In figure 4, selected hyperspectral SNOM images are presented for three different collection wavelengths. By separating the wavelengths, one can clearly identify the two different fluorophores present on the surface. The fluorescence spots observed at locations A and B of the image can be identified through their emission spectra as the EXP2 and F8BT polymer nanoparticles, respectively, while in location C both polymer nanoparticles are present. In conventional SNOM imaging, one would see both ensembles of molecules simultaneously without any possibility to differentiate between the different nanoparticles present in the sample. The corresponding near-field spectrum is also available and allows for an even better discrimination.
Access to the full near-field spectrum is of great importance when studying the interactions between fluorophores and their immediate local environment, as this can lead to very large spectral shifts that would not be distinguishable in a far-field spectrum averaged over a large number of fluorophores.

5. Conclusions

We have described the implementation of near-field spectroscopic measurements using a SNOM set-up combined with white-light illumination and spectrally sensitive detection. It allows investigation of the spectral optical properties at every point of the SNOM image, therefore enabling reconstruction of resonant near-field optical properties of the object under consideration, which can significantly differ from the far-field optical properties. We have presented several application examples addressing different properties of plasmonic structures and nanoscale fluorescence imaging. Comparison of the near- and far-field spectral responses and spectral dependence of the near-field distributions provide important insights into the underlying physics and details of the interaction of light with nanostructured surfaces can be unambiguously identified. Hyperspectral SNOM is an important tool for the study of resonant optical systems in material science, photonics, cell imaging and biophotonics.

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