1 Optical Characterisation of Nanostructures using Hyperspectral Imaging

Hyperspectral imaging encompasses a range of optical techniques in which images are acquired such that each pixel is comprised of a spectrum rather than an RGB colour value. This is advantageous over regular imaging as more quantitative information can be extracted from an image to the extent that hyperspectral imaging techniques have become commonplace in many widely spread fields, including microscopy [**schultz2001hyperspectral**, **leavesley2012hyperspectral**], astrophysics [**hege2004hyperspectral**], remote sensing and geology [**hackwell1996lwir**, **shaw2003spectral**], food standards [**kim2001hyperspectral**, **gowen2007hyperspectral**], and medical imaging [**vo2004hyperspectral**, **martin2006development**, **lu2014medical**]. Within each of these fields, features in an image are more clearly identified by their spectral signatures. In this instance, scanning confocal hyperspectral imaging is applied to optically characterise tips and identify surface plasmon resonances (SPRs) originating from localised surface plasmon (LSP) excitation.

Scanning confocal hyperspectral imaging falls under the category of spatially scanned imaging. Tips are scanned in a grid under the laser spot and the spectral content of the confocal sampling volume is measured at each point using a spectrometer instead of a photodiode or CCD. Images are then formed at a given wavelength or across a wavelength band. In this instance, using the bench-top spectrometer, each image pixel is equally digitised into 1044 bins between 400–1200 nm rather than the conventional 3 RGB colour bands. The 0.8 nm wavelength resolution of spectra classifies this procedure as hyperspectral, as opposed to multi-spectral imaging (images formed using fewer, much broader, wavelength bands) [].

By using this technique, LSPs can be spatially identified with sub-diffraction-limited resolutions below 300 nm. The microscope configuration when applying this technique is shown in Figure 1. This approach to hyperspectral imaging has previously been used to identify plasmonic modes in aggregated AuNP colloids [**herrmann2013**] and to image SPPs [**bashevoy2007hyperspectral**]. In this experiment the technique is used to study the optical response of sharp and nanostructured tips. It is also used with AuNPs to measure the microscope PSF and map aberrations.

Fast image acquisition is made possible by utilising the ultra-high brightness of a supercontinuum laser source and sensitive, TE-cooled, benchtop spectrometers with a 10 ms integration time. Image acquisition is then limited only by the integration time at each pixel and the ∼30 ms movement time between pixels. During this time the focal intensity is $\sim 10^8\,\mathrm{mW\,cm^{-2}}$, which is not sufficiently high enough to damage the 50 nm metallic tip coatings. The illumination and collection configuration is fixed (using the reference intensity) between different samples to maintain comparable scans. Measured spectra are normalised to a spectrum of flat metal of the same material to show geometrical effects only. By using this approach spectral changes between the apex of a tip and its bulk surfaces can be determined.

While not the fastest or most advanced method of acquiring hyperspectral images, the spatial scanning technique is efficient when used with a supercontinuum white-light source, similar to the laser requirement for confocal imaging. Other imaging techniques have been developed to produce hyperspectral images depending on the imaging requirements. These fall under the categories of "spectral scanning", "non-scanning" and "spatio-spectral scanning". Spectral scanning involves wide-field imaging through a range of bandpass filters [**iga2012development**], tuneable liquid crystal filters [**slawson1999hyperspectral**, **gat2000imaging**] or an etalon [**daly2000tunable**]. This is appropriate if studying large areas or when an increased resolution and improved contrast, gained through confocal optical sectioning, are not required. Similarly, if the benefits of sectioning are not necessary and an imaging spectrograph (monochromator with CCD) is available then only a 1d line scan over the sample is required to form an image as opposed to a 2d grid scan whilst measuring pixel spectra [**schultz2001hyperspectral**]. Non-scanning or snapshot hyperspectral imaging techniques are more complex than the previous two categories as both the spatial and spectral information are acquired in a single measurement without the need for any pixel scanning or dynamic filtering. The main method to achieving this is to use a computed tomography imaging spectrometer (CTIS) [**okamoto1991simultaneous**, **bulygin1992spectrotomography**, **okamoto1993simultaneous**, **descour1995computed**]. By using a 2d dispersive grating in the Fourier plane an image can be split into many spectral images, which can be recorded on a CCD array. Advantages of this approach are short exposure times but necessitates a higher computational requirement to disentangle the 2d image into a cube of dimensions (x, y, λ).

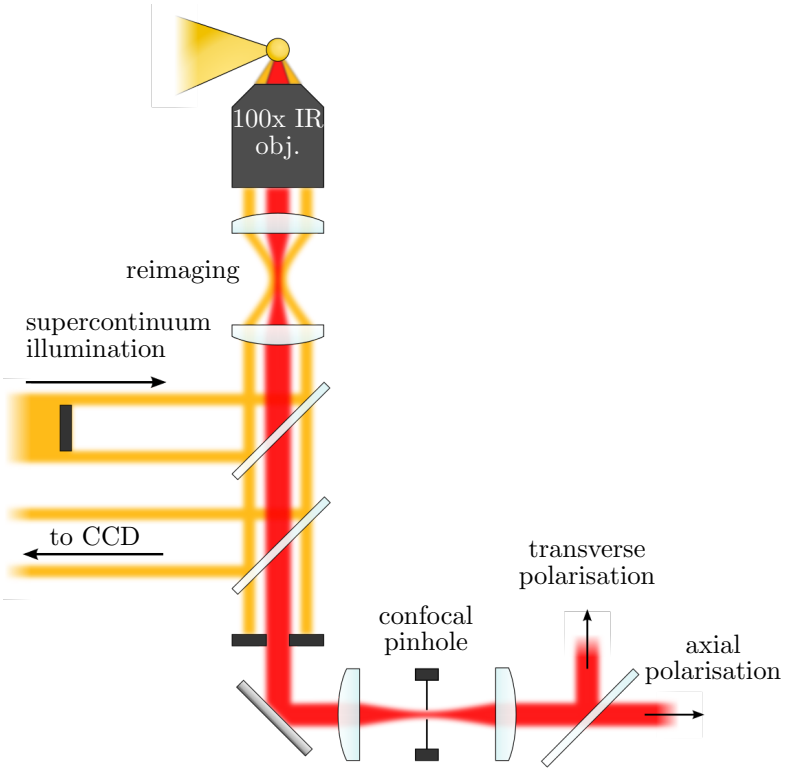

Figure 1: Experiment configuration for hyperspectral imaging. The laser is centered on the tip apex for imaging. The tip is scanned across the beam in a grid with spectra acquired at each position. The resulting image then contains 1044 colours at each pixel instead of the usual 3 (RGB).

Despite the potential improvements gained by using a more advanced hyperspectral imaging technique, spatial point scanning is deemed the most appropriate solution for characterisation. The imaging process is not time-constrained since the microscope platform is stable, resulting in minimal artefacts due to sample motion, and the use of confocal imaging benefits the acquired image quality. Portable bench-top spectrometers are already incorporated into the microscope for use in other experiments and are readily accessible, therefore adapting the microscope to enable use of an imaging spectrograph and line scanning is not a convenient solution. Wide-field imaging is not beneficial at the set magnification due to the small areas of the overall diffraction-limited image that are point scanned and spectrometers have a far superior spectral resolution compared with imaging through bandpass filters. For these reasons, despite its simple and somewhat relatively slow nature, spatial point scanning is used for characterisation.