Scattering spectroscopy on single plasmonic nanoparticles using a confocal darkfield setup

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Abstract. We demonstrate how to measure scattering spectra of single plasmonic nanoparticles using a confocal darkfield setup. We give an overview of considerations and problems we encountered when employing a darkfield technique based on filtering illumination under low angles instead of the conventional high-angle filtering by darkfield objectives.

1 Introduction

The nanoscale morphology of plasmonic nanoparticles directly defines their optical, catalytic, and electronic properties and even small morphological changes can cause significant property variations [1]. With the emergence of a wide variety of complex [2], highly anisotropic and asymmetric nanoparticles [3], detailed structure–property correlations at the single-particle level become quintessential [4]. A first step would be to distinguish shapes of plasmonic nanoparticles with high accuracy. To this end, a confocal darkfield spectroscopy setup was built which has optimized software for performing such measurements. Here, we present considerations and problems that we encountered in the process of building such a setup and doing measurements on single nanostructures.

2 Optimizing the signal-to-noise ratio

2.1 From brightfield to darkfield

Since plasmonic nanoparticles can scatter into the far field in a large angular range, we chose to use an objective with a high numerical aperture. This restricts the use of dedicated darkfield objectives that separate illumination and collection paths in an angular fashion by blocking signal under high angles. Therefore, we decided to filter out illumination and signal under low angles, inspired by the work of Kukura et al. [5]. They showed that the combination of a collimated illumination beam and a partial reflector in the collection path can significantly increase the extinction contrast of nanoscopic objects. The sizes of the beam and the reflector are crucial to optimize the signal-to-noise ratio and need to be fine-tuned for each specific setup since they are not only correlated to each other, but also to the entrance pupil of the objective and travel distances in the setup.

2.2 Sizes of the beam, reflector, entrance pupil of the objective and travel distance

Ideally, the diameter of the beam matches the entrance pupil of the objective. However, the reflector would have to be at least the same size, blocking (most of) the signal. Underfilling the objective will reduce the spatial resolution, but allows the reflector to be smaller and, hence, block less signal. If resolution is not crucial, one could even think of making the beam diameter as small as possible. However, beams with a smaller diameter diverge faster and one might run into issues if the travel distance in the setup is too long. These examples show that the interplay of these optical components should be considered when optimizing the signal-to-noise ratio.

2.3 Intensity and diffraction

Next to a (close to) darkfield configuration the absolute intensity is important. To obtain interference contrast Kukura et al. used an 82 nm thick Ag partial reflector that has a transmittance of $10^{-3}$–$10^{-8}$ in the visible regime [5, 6]. Since we do not aim for interference contrast, we chose to use 120 nm thick Al, which has an even lower transmittance of $10^{-6}$–$10^{-7}$ in the visible regime (Fig. 1) [7]. This should drastically reduce the laser background intensity.

Finally, reflections in the objective can result in laser signal under high angles. In the setup of Kukura et al. this signal is blocked as well by the partial reflector, by placing it close to the objective [5]. This is not possible in our setup, however, and we resolve this issue with another pinhole, in the collection path (Fig. 1). This pinhole filters any stray light under high angles and can be tuned such that only the zeroth order of the diffraction pattern from nanoscopic objects hits the detector (Fig. 2), which is ideal for spectroscopy.

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Fig. 1 Schematic drawing of the confocal darkfield setup.

Fig. 2 Image of the pinhole plane with the diffraction pattern of a nanoparticle. Making the pinhole, for instance, 10 μm will filter only the zeroth order of the diffraction pattern. M is the magnification on the camera.

3 Measurement considerations

Since we use collimated illumination to underfill the objective, the laser is focused into a near diffraction-limited beam. Any slight misalignment results in both slanted illumination and collection. Depending on the illumination wavelength also the focus of the beam changes, due to chromatic aberrations, and this must be corrected during spectral measurements. Currently, we define the focus as the position where we get the highest signal. By scanning the sample in a spherical fashion around this point we can then find the focus for each wavelength and obtain a scattering spectrum.

The reflectance and transmittance of each optical element are also wavelength dependent, and the combined result is called the instrument response function (IRF). The IRF can usually be obtained by performing a background measurement. However, in darkfield spectroscopy the background signal should be close to zero. Measuring a well-known reference sample is a good alternative to obtain the IRF and we used polystyrene beads with a diameter of 100 nm because of their relatively flat scattering response in the visible regime [5].

Combining this focus-corrected way of measuring with processing raw data using the IRF, it is now possible to measure nanostructures on a single particle level. Fig. 3 exemplifies a scattering spectrum of a Au nanorod with a diameter of 20 nm and length of 75 nm on a SiO₂ substrate.

Fig. 3 Measured, fitted and simulated scattering spectrum of a Au nanorod with a diameter of 20 nm and length on 75 nm on a SiO₂ substrate (normalized).

The next step would be to introduce polarized illumination to distinguish shapes of plasmonic nanoparticles with high accuracy and to correlate these properties to their exact morphology using high resolution transmission electron microscopy.

References