Photothermal circular dichroism studies of single nanoparticles

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Conclusion and outlook

In this thesis we focus on the design of an optical setup based on photothermal imaging to measure the circular dichroism (CD) of single nanoparticles. Chapters 2 and 3 describe the development of the optical technique and how to avoid pitfalls that may create artefact signals. We show by performing proof-of-principle experiments that the technique is indeed sensitive to CD of single nanoparticles, with sensitivities down to g-factors of 3×10^{-4}, and can in principle be extended for spectral measurements. In the following chapter we apply photothermal circular dichroism (PT CD) to study the CD of chiral plasmonic nanoparticles and try to find a relation between the chiral geometric features and the measured CD signal. In chapter 5 we show that PT CD facilitates optical studies of magneto-optic phenomena at the single-particle level.

Photothermal circular dichroism When we perform a modulation of polarization to study the minute dichroism effects of a nanoparticle residing in a focused laser beam, we are prone to artefacts due to even the slightest beam misalignments, because of the strong focusing conditions. To avoid these artefacts it therefore judicious to use weakly focused light. On the other hand when we are interested in imaging applications of nanometer-sized objects we seek for diffraction-limited optical resolution and therefore require a tightly focused beam. Photothermal imaging provides a simple solution to that problem as it is a two-laser technique. We can use a strongly focused probe laser, which provides diffraction-limited resolution, and we can choose to focus the heating beam only weakly to avoid artefacts linked to strongly focused polarized light. Photothermal imaging comes with another benefit for the measurement of the CD of single nanoparticles as it measures, to first approximation, the effect of a thermal lens and is therefore a true absorption signal free from scattering contributions. We show, by employing a simple square-wave modulation of the polarization, that we can indeed tell apart the two enantiomers of lithographically manufactured chiral nanostructures. However, such a simple square-wave modulation scheme has severe restrictions when it comes to measurements of either weak CD g-factors or particles with substantially larger linear dichroism (LD) compared to their CD values. This restrictions are linked to the polarization modulator itself as it gives rise to a residual intensity modulation on top of the polarization modulation and, additionally, the single-modulation scheme may lead to

leakage of LD into the CD signal. We show that this leakage of LD into CD and the effect of residual intensity modulation can drastically be reduced when performing a polarization modulation based on two polarization modulators in series. This dual-modulation scheme allows us to perform reliable CD measurements even on rod-like nanoparticles which naturally exhibit strong LD effects. We achieved measurements of small CD g-factors of only a few 10^{-4} on single gold nanoparticles, which are only one order-of-magnitude away from ensemble techniques that average the signal over millions of particles. On the other hand, single-particle measurements of such high sensitivity require large heating powers and might lead to thermally-induced reshaping effects that alter the particles' shape and properties. Better contrast mechanisms such as fluorescence-detected PT or measurements performed in super-critical xenon could allow for comparable sensitivity at much reduced heating powers. We envisage that, when augmented with a suitable tunable heating laser, PT CD would also facilitate studies of the spectral chiroptical properties of plasmonic nanoparticles on the single-nanoparticle level.

Plasmon-coupled circular dichroism PCCD Circular birefringence (CB) is the refractive counterpart of CD and can occur in molecules even at wavelength where they do not absorb. A liquid exhibiting CB has different refractive indices for left- and right-circularly polarized light. Consequently, when a plasmonic nanoparticle is placed in this liquid, as its resonance condition is dependent on the surrounding liquid's refractive index, we expect to observe two shifted plasmon resonances depending on whether we shine left- or right-circular polarized light on the particle. The shifted resonance gives rise to a circular polarization-dependent differential absorption - i.e. to CD. So in a sense the liquid's CB gets transferred to CD in the presence of the plasmonic nanoparticle. Our measurements on the PCCD of a $100\,\mathrm{nm}$ gold nanoparticle immersed in the chiral molecule carvone, despite our good sensitivity of g-factors down to 3×10^{-4}, did not deliver any measurable CD signal. We conclude that spherical nanoparticles, due to their broad plasmon resonance, are not ideal to measure PCCD induced by differences in refractive index $n_{LCP} - n_{RCP} = \Delta n$ which are typically on the order of 10^{-4}. We propose to use plasmonic particles which are more sensitive to minute refractive index changes. Such a system could for example be a nanorod or a pair of nanospheres at close distance. The near field at the tip of the nanorod, or in the gap in between the nanoparticles should be much more sensitive to minute changes of the refractive index. However, in this case great care must be taken to avoid heat induced reshaping that would result in a broadened resonance and therefore in a loss of sensitivity.

Correlation of shape chirality and CD In chapter 4 we looked at the chiroptical response of wet chemically synthesized particles and found that the single-particle measurements display a striking difference in the chiroptical behaviour compared to the ensemble measurements. Not only did we find that the strength of the CD signal varies strongly between the particles, we also find CD signals of opposite sign. The wet chemical synthesis process of chiral nanoparticles, assisted by chiral molecules, aims at creating geometric chiral features of a certain handedness. However, when we look at the geometric chirality (here the helicity) on the single-particle level, by performing electron tomography measurements, we find regions of opposite handedness even within one particle. When we compare the single-particle optical signal to the geometric chirality we find a weak correlation between the average helicity and the chiroptical signal. That means that the shape alone does not allow for a straightforward prediction of the chiroptical signal. To investigate the influence

of plasmonic resonances and wavelength dependence, we perform similar measurements on quasi-achiral gold nanoparticles and found that even if we take into account plasmonic effects and simulate the optical response, based on the shape of the particle, we find no clear link between the measured optical signal and the one retrieved from BEM simulations. We therefore conclude that there must be other contributions as for example surface ligands on the particles or the presence of the substrate, that induce an additional symmetry-breaking and therefore affect the particles' chiroptical response. Additionally, the ensemble measurements are performed with the particles in solution, allowing for arbitrary orientations and therefore the ensemble measurement not only averages different particles it also averages different particle orientations. One possible way to test the influence of substrate and the different orientations in our single-particle measurements would be to trap the particles optically with an NIR beam and then perform a CD measurements. Trapping the particles by a third NIR beam inside a liquid, by for example using two microscope objectives facing each other like in 4Pi microscopy, would allow the particle to freely rotate and also remove the substrate-induced symmetry break and maybe allow for a better comparison of ensemble and single-particle measurements.

Measuring the magnetization of single nanoparticles Circular dichroism occurs in chiral molecules or nanoparticles due to a lack of mirror symmetry. However, CD also occurs in magnetic materials irrespective of shape due to Faraday or Kerr effects. Magnetic moments on nano-sized objects are typically measured by MFM or scanning SQUID's due to their high sensitivity and resolution. Optical techniques in the visible regime, like Kerr microscopy or conventional magnetic circular dichroism spectrometers based on a transmission geometry are restricted to bulk or ensemble measurements. In a proof-of-principle experiment, we show that PT CD is sensitive to the polar Kerr effect in single magnetite nanoparticles. By applying a tunable external magnetic field and simultaneously following the CD signal, we recorded a magnetization curve and confirm the superparamagnetic behaviour of these particles, due to absence of a remanent magnetization. If combined with a suitable heating and probing laser and if the measurements are performed in super-critical conditions, we envisage to perform studies of the random flipping of the magnetization of single-domain superparamagnetic particles.