

## Mapping the Polarization Pattern of Plasmon Modes Reveals Nanoparticle Symmetry

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Single molecule labeling, cancer treatment, enhancement of non-linear optical effects, or light guiding have demanded much attention from the scientific community, and as a possible solution, plasmon resonances of noble metal nanoparticles are explored. A major advancement in single molecule optics has been the polarization analysis of light from single fluorescent emitters. This analytical method has been utilized to study the conformational dynamics of biomolecules and their spatial arrangement. At different wavelengths of the excitation light, different oscillation modes are excited making it important to know the polarization pattern as a function of wavelength.

“Knowing the polarization pattern of plasmonic nanostructures is therefore not only important to understand the fundamental physics of light interaction with these structures, but also allows to discriminate different oscillation modes within one particle and to distinguish differently shaped particles within one sample. Several techniques have been used to extract optical spectra of single plasmonic nanoparticles, most efficiently using dark-field microscopy, but little is known about the polarization state. So far, the very few reported plasmon polarization studies were obtained by rotating a polarizer by hand or on ensembles and not combined with spectroscopic information,” Prof. Carsten Sonnichsen explains to Nano Spotlight.

“We have developed a new microscope setup (RotPOL), which allows obtaining polarization-dependent scattering spectra in a fast and easy way,” Olaf Schubert continues explaining to Nano Spotlight. “RotPOL uses a wedge shaped quickly rotating polarizer which splits the light of a point source into a ring in the image plane, encoding the polarization information in a spatial image.” (Scheme 1)

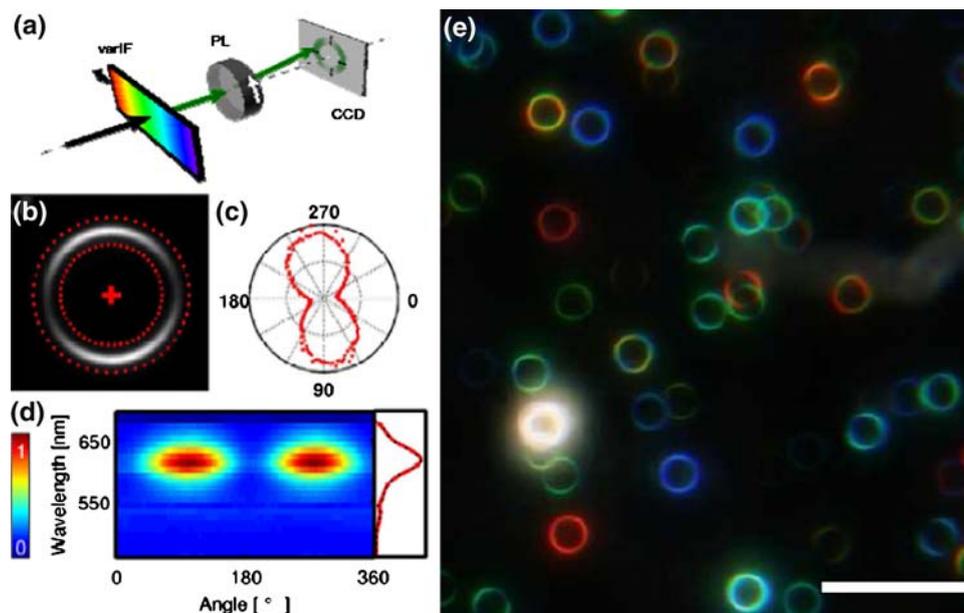
Prof. Sonnichsen’s team reveals that the polarization intensity in a given direction is simply taken from the

corresponding position on the ring recorded with an exposure time larger than the rotation time. A dipole, for example, will show two loops at opposite sides, and with this in mind, the team can combine this rotating polarizer with a variable wavelength interference filter, which transmits light only in a narrow wavelength window. If mounted in front of the digital camera, the filter allows them to record simultaneously the spectral and polarization information for up to 50 particles in parallel.

“With the RotPOL setup, we study plasmon modes of a large variety of plasmonic structures—from rod-shaped particles to triangles, cubes, and pairs of spheres,” said Olaf Schubert. “Each plasmonic particle has a characteristic ‘footprint’, which allows deducing the approximate particle shape from the polarization-dependent single-particle scattering spectra. This is important for the optimization of particle synthesis, because it makes a quick and efficient estimation of the quality and mono-dispersal of a sample possible, without complex and expensive tools like electron microscopy.”

“For rod-shaped and even just slightly elongated particles, we found that the scattered light is highly polarized. Our simulations show that this high polarization anisotropy is not only due to the particle symmetry, but a plasmonic effect. This could be exploited for the design of miniature rotation sensors,” Prof. Sonnichsen explained enthusiastically.

In addition to yielding orientation information, plasmonic particles can be used to measure absolute distances on a nanometer scale. “Such a ‘plasmonic ruler’ makes use of the coupling of two spherical particles: If they are close to each other, the inter-particle plasmon resonance shifts from green to red. We measured the full polarization-dependent spectrum of such pairs of two spheres and found



**Scheme 1** (a) Schematics of the RotPOL setup. One wavelength is selected by a linear variable interference filter (varIF), and then the light is dispersed into different polarization directions by a wedge-shaped rotating polarizer (PL), resulting in ring-shaped intensity profiles of a point-like light source on the digital camera (b). In order to get the polarization profile shown in (c) (intensity  $I(q)$  as a function of polarization angle  $q$ ), we integrate the image between an inner and an outer ring diameter (dashed lines in (b)). The center of the rings is chosen to minimize asymmetry between opposite sides. Repeating

this procedure for each wavelength produces intensity values as a function of wavelength and polarization angle  $I(l,q)$ , which we show color-coded in (d). The same analysis is possible for all particles within the field of view in parallel. (e) Real-color image of an inhomogeneous silver sample containing spheres, rods, and triangles as seen through the RotPol-microscope. Two colors in one ring correspond to two different plasmon modes at the respective wavelengths. Scalebar is 25  $\mu\text{m}$

nice agreement with simulations.” This investigation has demonstrated that the polarization-dependent spectrum contains information about both the distances of the two spheres and the orientation and environment of the particles. In addition, such “multi-sensors” could possibly find a place in biological applications that require high time resolution.

“As an example of a time-resolved measurement, we have monitored the changes of plasmon modes in single gold nanoparticles during a growth process, in situ,” explains Olaf Schubert to Nano Spotlight. The researchers highlight that their RotPOL method is a versatile tool that can be used to study polarization anisotropy of the light emission pattern from nanoparticles, particularly for plasmonic structures, but can possibly be extended to fluorescent quantum structures. This method provides a wide range for optimization for applications such as light

guiding and allows detailed theoretical modeling of plasmon modes due to the wide variety of plasmon emission patterns observed for the simple particle morphologies that have been investigated (spheres, rods, triangles, cubes, and particle pairs).

The researchers have recently published their results in Nano Lett, 2008. Their work reveals that the high polarization anisotropy found for even moderately elongated spheres “highlights” the strong influence of polarization even for nominally round particles. The possibility to record dynamic changes of the polarization emission pattern of single particles allows studying particle growth modes in situ and improving schemes for single nanoparticle binding and distancing assays.

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