Supplemental Online Material

MATERIALS & METHODS

Gold spheres
We used commercially available gold spheres (BBI international, UK).

Synthesis of Au-Rods:
We synthesized gold nanorods in batch using a wet-chemical synthesis method following Nikoobakht and El-Sayed[1] by adding small spherical gold seeds to a growth solution.

Synthesis of inhomogeneous silver sample
Silver nanoparticles are prepared using a seed-mediated synthesis according to Jana *et al.*[2] by adding 180µl preformed silver seeds to a CTAB-containing growth solution. Particle growth is induced by the addition of sodium hydroxide solution.

Synthesis of Ag-Triangles:
Silver triangles were synthesized by a photo-induced process (radiation time: 5 hours) using poly(vinyl pyrrolidone) (PVP) and citrate anions. During illumination silver spherical colloids transform into triangular nanoplates according to literature procedure.[3]

Synthesis of Ag-Cubes:
Samples of silver nanocubes were obtained by reducing silver nitrate with ethylene glycol in the presence of PVP and a mmolar amount of sodium sulfide (Na_2S) as described in Xia *et al.*[4] The molar ratio between the PVP monomer and $AgNO_3$ is set to 1.9:1. The reaction time was 5 min.

Synthesis of Ag-rods:
For the silver nanorod synthesis, we used the same approach as for cubes, but at higher temperature (180°C) and longer reaction time (9 min). We used size-selective precipitation with acetone to separate rods from the other particles and remove excess of reactants.

Setup
The microscope setup itself is based on a standard transmission dark-field microscope with white light excitation from a 100 W halogen lamp, a 40x water-immersion objective (NA 0.8), a high numerical aperture condenser (NA 1.2–1.4), and coupled to either peltier-cooled CCD (CoolSnapHQ2, Photometrics) or a consumer digital DSL camera (EOS 400D, Canon).[5] For spectral imaging, we place a linear variable interference filter (VERIL S 200, Schott AG) moved by a stepper motor (T-LLS260, Zaber Technologies Inc.) in front of the CCD. Each filter position has a unique transmission wavelength (from 400-700nm with 10 nm width), so that a full spectrum is obtained by moving the filter step by step in front of the camera. The transmission wavelength offset over the width of the CCD chip is accounted for during data analysis.

Real color images
For images taken with the consumer digital camera an exposure time between 10 and 30 seconds and an ISO setting between 100 and 400 was chosen. In Fig.5a the contrast was slightly increased, to make the two loops more clearly visible for the reader (details: see supplementary material Fig. S7). All other images shown in the paper and the supplementary online material, including the video of the growth process, show the raw images and were not edited in any way.

Polarization analysis
The unique component for the rotPOL polarization resolved single particle spectroscopy is a rotating polarizer. We use a standard polarization filter (analyzer for polarization contrast imaging) rotated by an external motor at a frequency of more than 4 Hz. The (non-rotating) polarizer slightly displaces the image by a few pixels, which means that images taken with exposure times longer than the full rotation time will show a ring for a normally point-like single particle. Each point on the ring corresponds to the light intensity $I(\theta)$ in the corresponding polarization direction. A dipole, for example, will show two loops at opposite sides. If the interference filter is in the light path, the measured intensity $I(\theta)$ is the polarization dependent scattering intensity $I(\theta,\lambda_0)$ at the corresponding transmission wavelength λ_0 of the filter. Polarization dependent scattering spectra $I(\theta,\lambda)$ are obtained by moving the interference filter with a stepper motor and recording one image for each position with the exposure time adjusted to correct for the spectral characteristic of the setup.

We extract the polarization dependent scattering intensity $I(\theta)$ for each frame with an image analysis algorithm which finds the center of each ring by minimizing the differences between the intensity of opposite sides of the ring. A starting point for the algorithm is provided by summing all frames up and selecting the particles by hand. The intensity at the center of the ring is used to correct for background signal (e.g. CCD-noise and scattering from out-of-focus dust particles).

Performance of this setup:
To check the polarization inhomogeneity of the setup itself, we measured polarization-dependent spectra of perfectly spherical SiO2-spheres (∅ 314 nm, Corpuscular Inc.) and obtained a median PA of 0.1 (see supplementary information Fig. S10). The error in the polarization values reported is therefore in this range.

A polarization dependent spectral image (450-700nm, spectral resolution: 5 nm, angle resolution 1-2°) with a field of view of 133 µm x 100 µm (with a 40x objective) takes about 10-20 minutes, depending on the exposure time and the sample studied. We tested the stability of the setup by measuring one sample repeatedly (see supplementary information Fig. S9).

DDA calculations
Simulations were performed with the freely available program DDScat[6] and maximum dipole distances of 1 nm. As shapes, we used spherical capped cylinders, ellipsoids, cubic shapes with slightly rounded corners and truncated triangles with rounded corners (see supplementary information, Fig. S8).
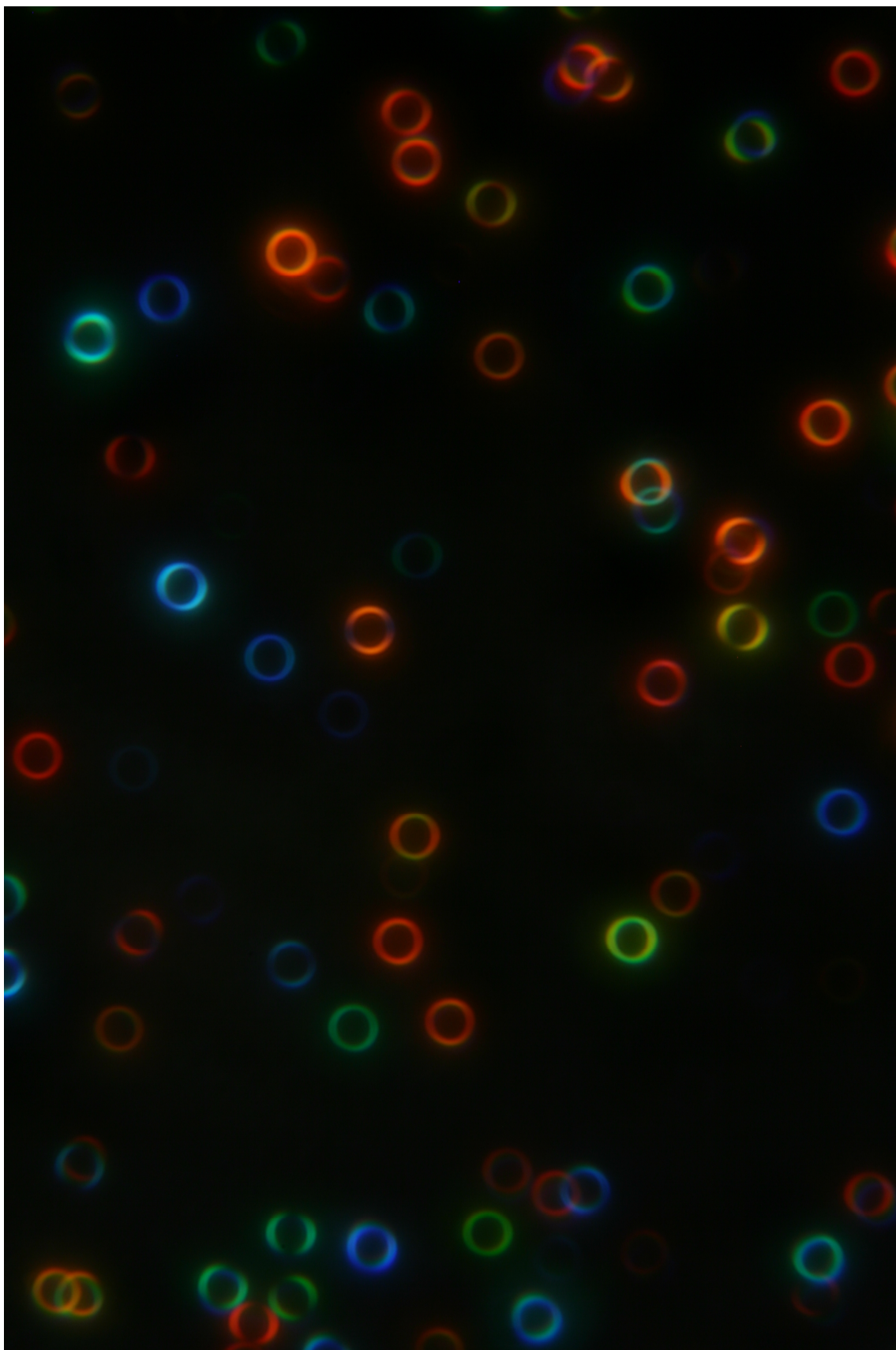
Fig S01a: Real color image of a typical sample containing silver rods, triangles, and spheres as seen through the rotPol-microscope (recorded with a Canon EOS400D, ISO 100, exposure time 30s).
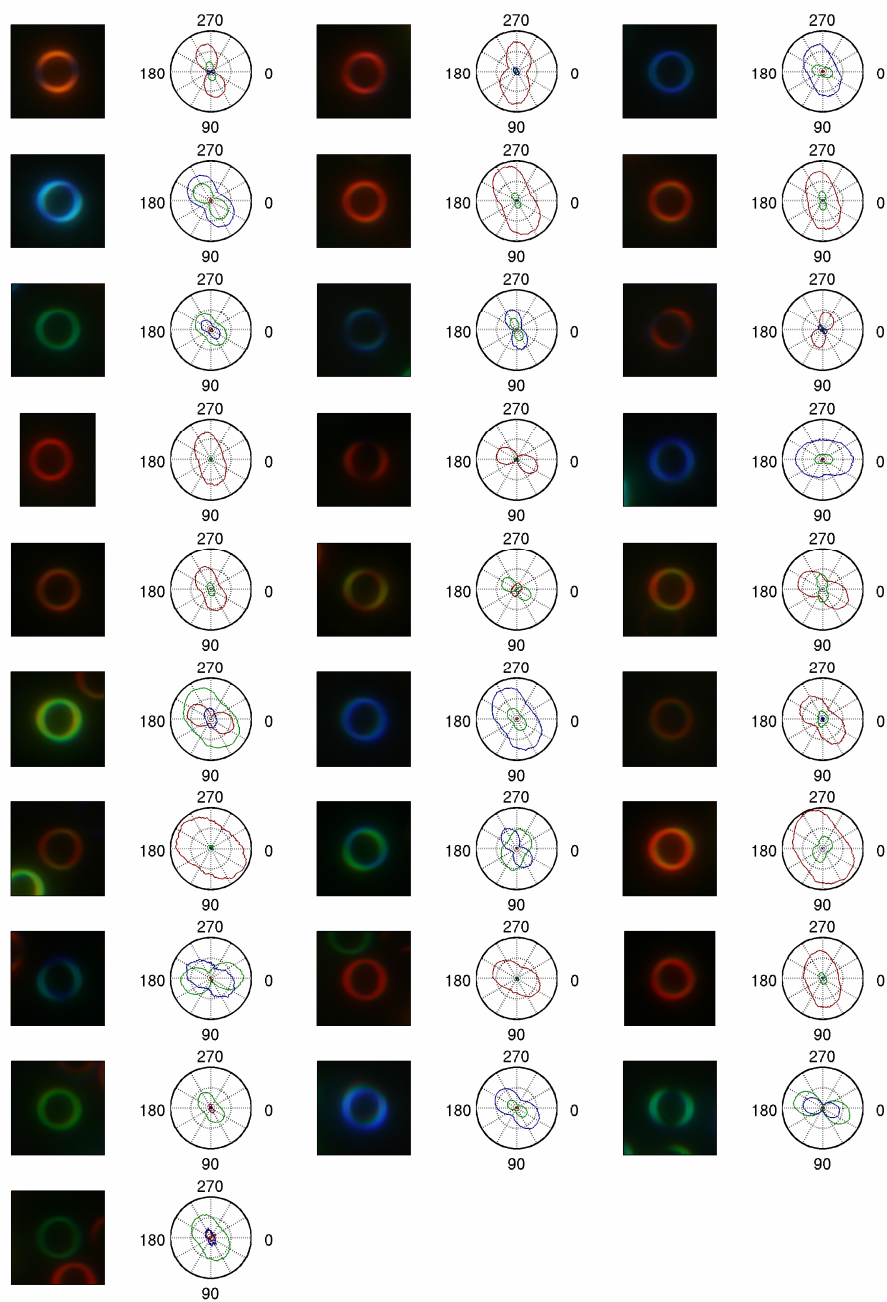
Fig S01b: Analysis of the real-color image shown in Fig.S01a for selected particles. For each particle, the scattering intensity as a function of angle is shown for the three color-components (red, green, blue) of the image.
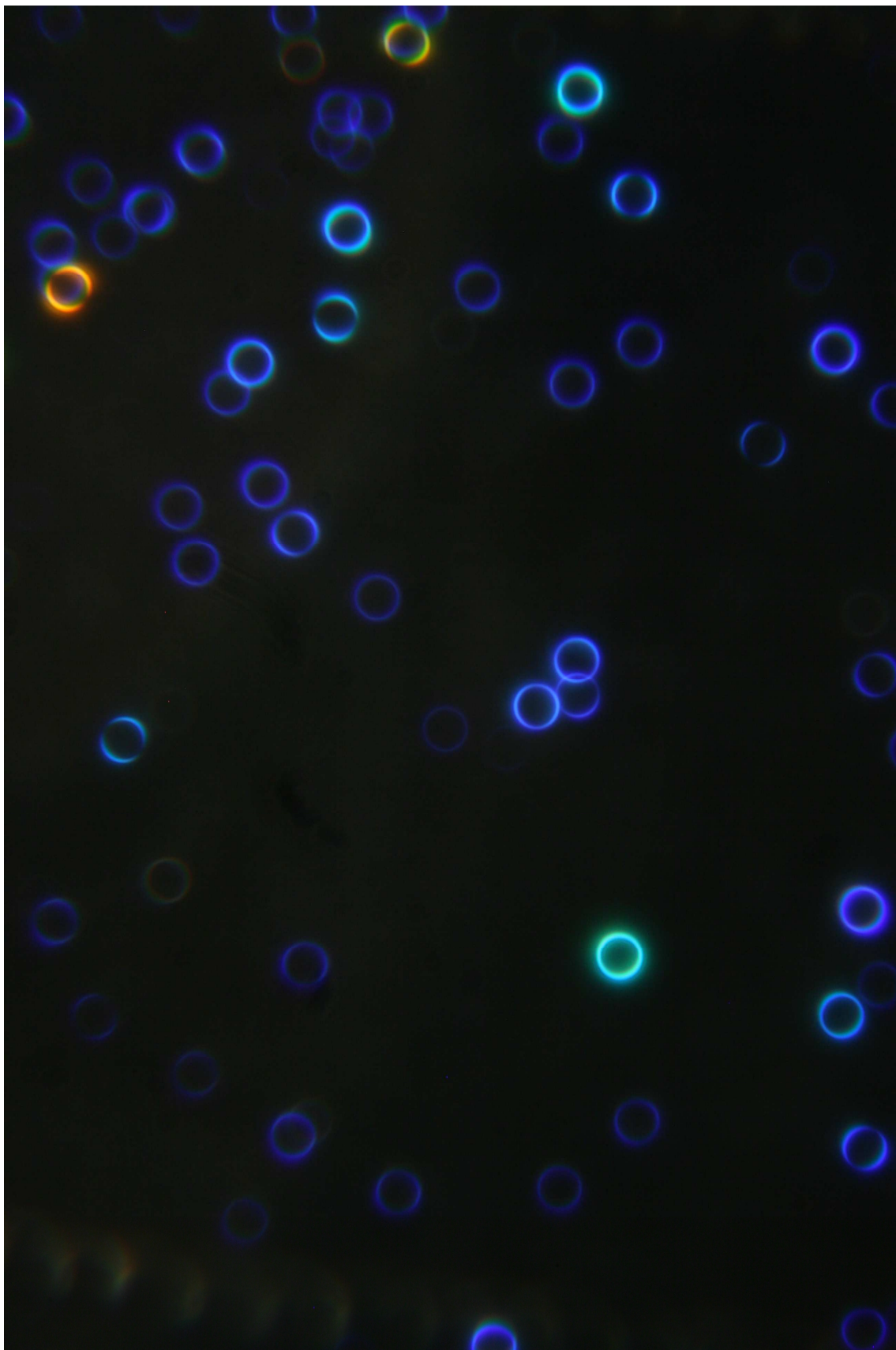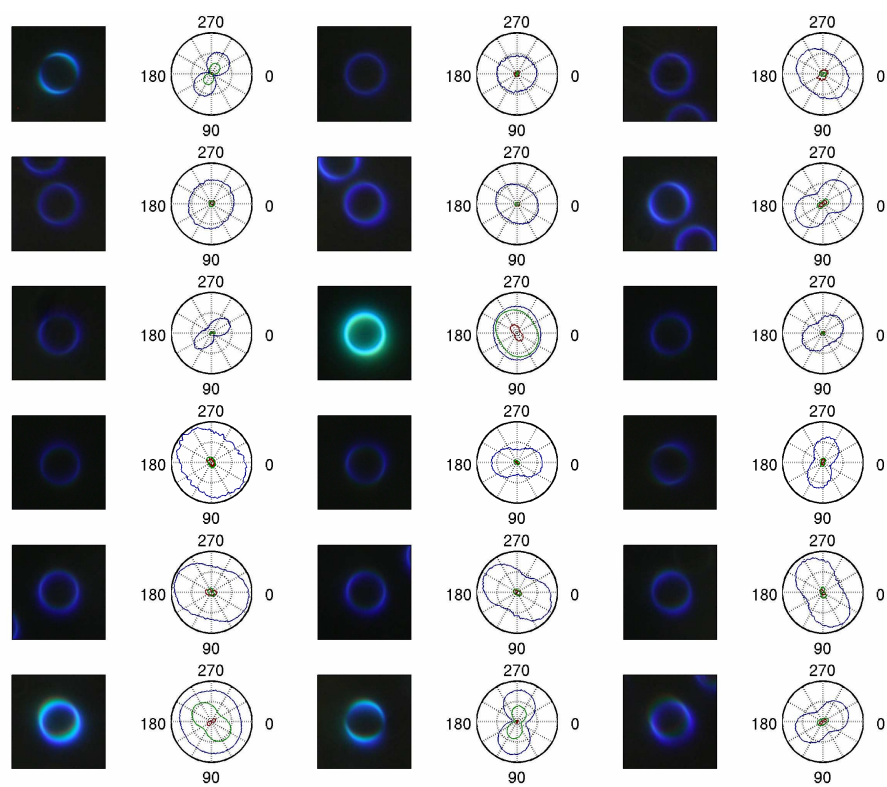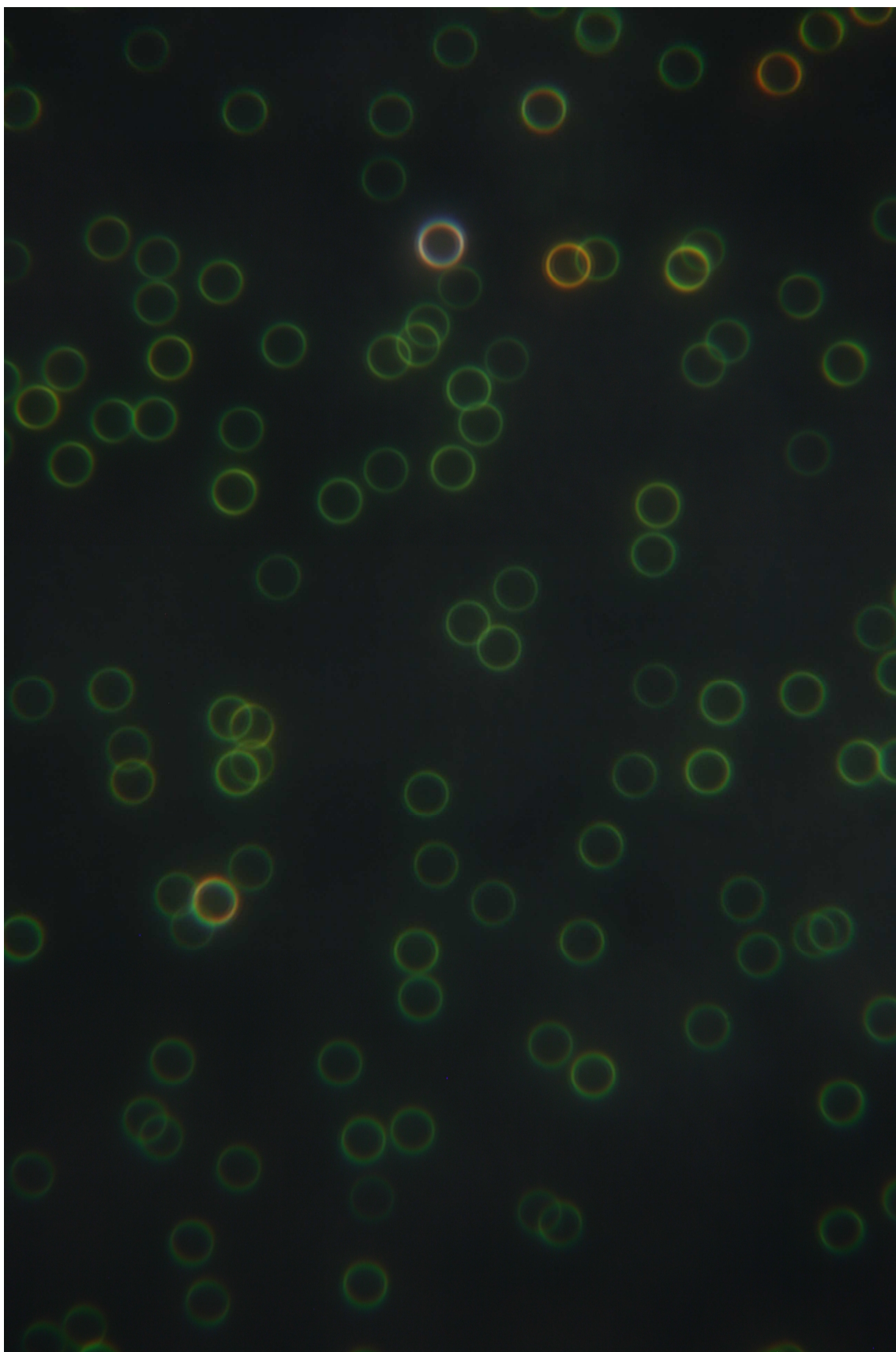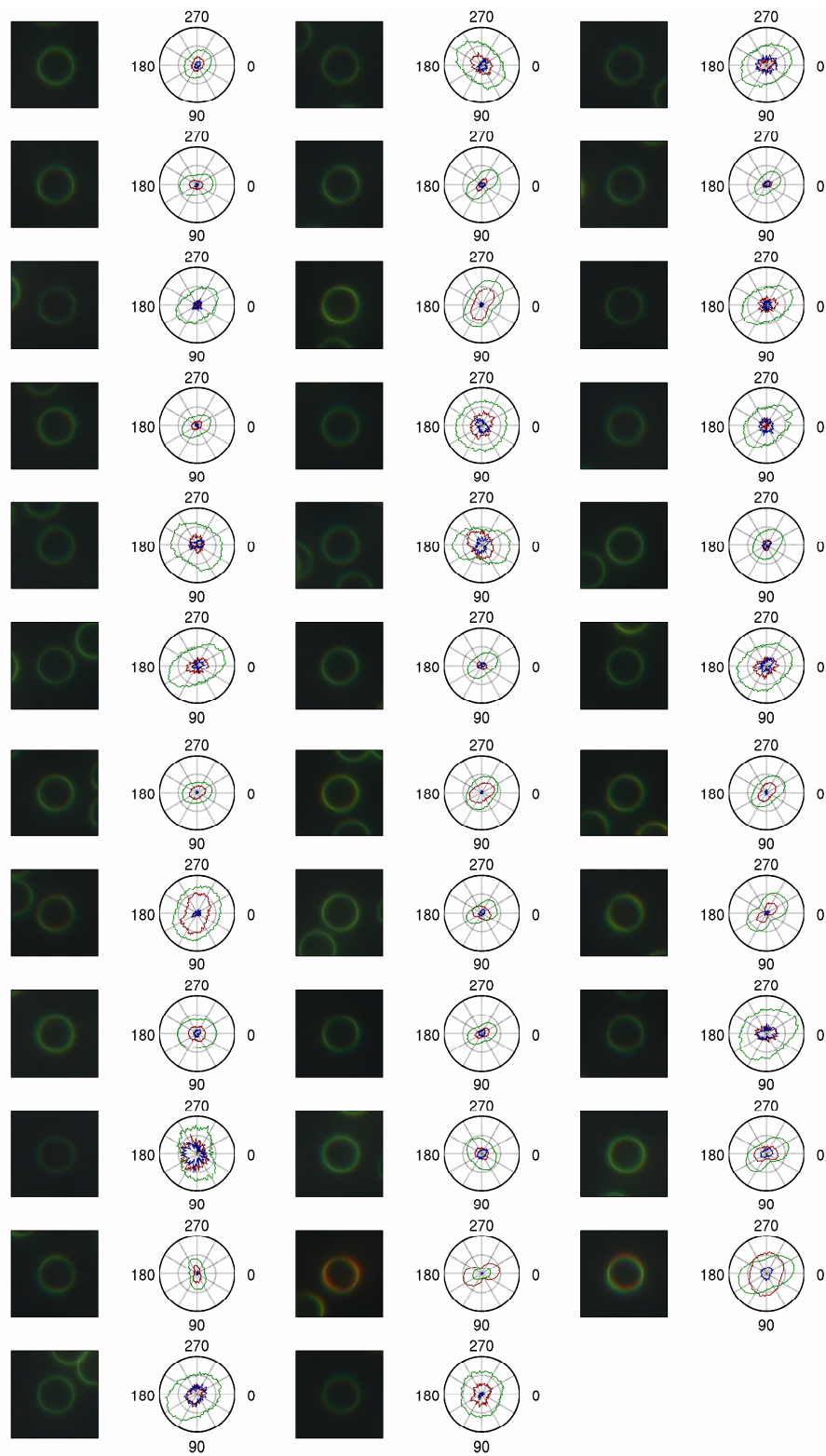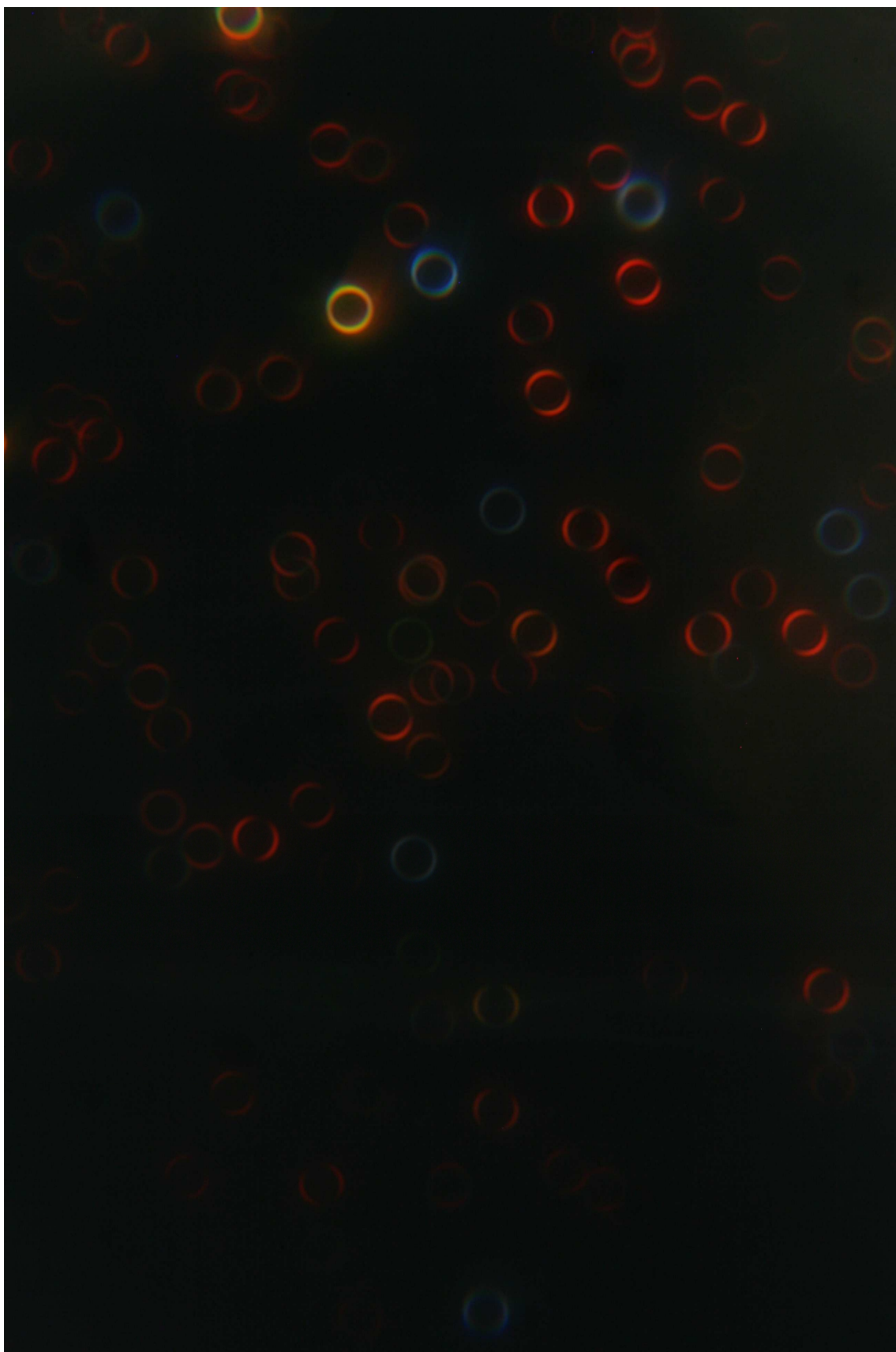
Fig S02a: Real color image of a typical sample containing mainly silver rods and spheres as seen through the rotPol-microscope (recorded with a Canon EOS400, ISO 400, exposure time 30s).

Fig S02b: Analysis of the real-color image shown in Fig.S02a for selected particles. For each particle the scattering intensity as a function of angle is shown for the three color-components (red, green, blue) of the image.

Fig S03a: Real color image of a typical sample containing gold spheres as seen through the rotPol-microscope (recorded with a Canon EOS400, ISO 200, exposure time 15s).

Fig S03b: Analysis of the real-color image shown in Fig.S03a for selected particles. For each particle the scattering intensity as a function of angle is shown for the three color-components (red, green, blue) of the image.

Fig S04a: Real color image of a sample of gold rods exposed to a growth solution as seen through the rotPol-microscope. This image was taken at the beginning of the growth process. The full sequence of the growth is shown in Fig. S05 (recorded with a Canon EOS400, ISO 400, exposure time 30s)
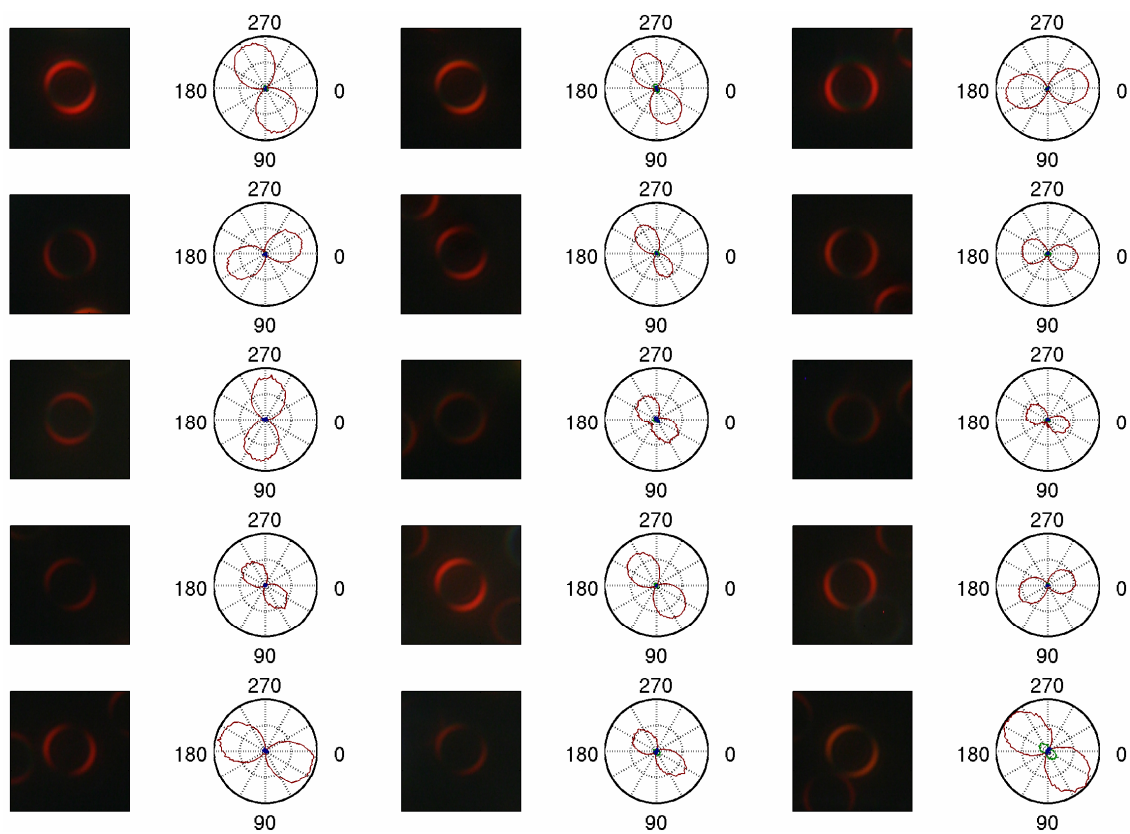
Fig S04b: Analysis of the real-color image shown in Fig.S04a for selected particles. For each particle, the scattering intensity as a function of angle is shown for the three color-components (red, green, blue) of the image. The extremely high polarization anisotropy is evident in both the image and the polar plot.

Time: 1 min   Time: 2 min   Time: 3 min   Time: 4 min
Time: 5 min   Time: 6 min   Time: 7 min   Time: 8 min
Time: 9 min   Time: 10 min   Time: 11 min   Time: 12 min
Time: 13 min   Time: 14 min   Time: 15 min   Time: 16 min
Time: 17 min   Time: 18 min   Time: 19 min   Time: 20 min
Time: 21 min   Time: 22 min   Time: 23 min   Time: 24 min
Time: 25 min   Time: 26 min   Time: 27 min   Time: 28 min
Time: 29 min   Time: 30 min   Time: 31 min   Time: 32 min
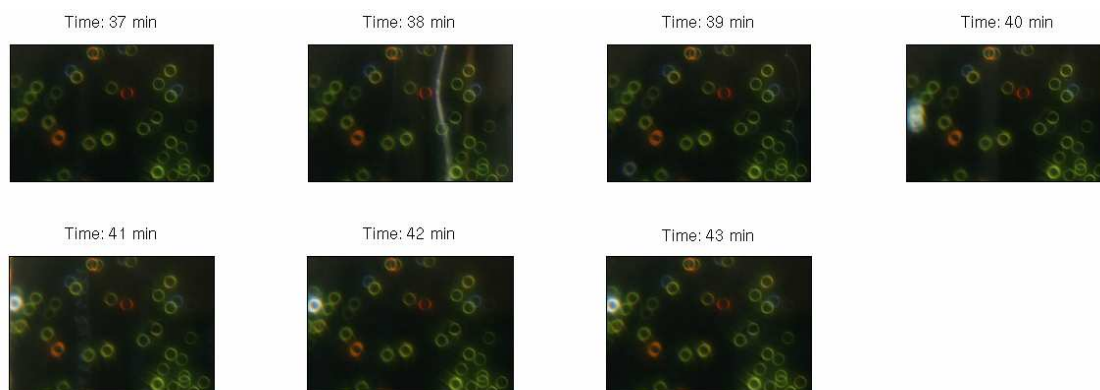Time: 33 min   Time: 34 min   Time: 35 min   Time: 36 min

Fig S05a: All images of the growth process (raw-data, part of the full field of view selected, full field of view is available as video). The growth process is monitored while the particles are rinsed with growth solution. Sometimes dust particles swim in the solution, which, due to the high exposure time of 30 seconds, lead to the white lines observed in some frames.
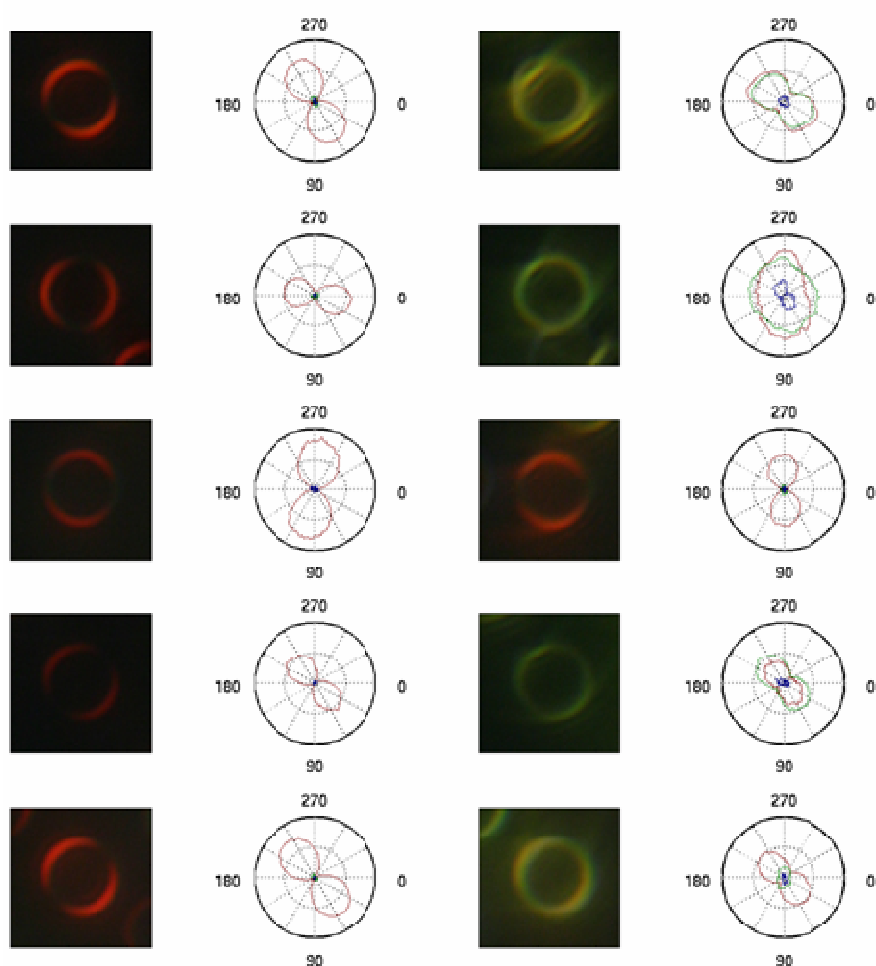

Fig S05b: Zoomed images and polar-plots for selected particles before (left, t = 3min) and after (right, t = 43min) the growth process.
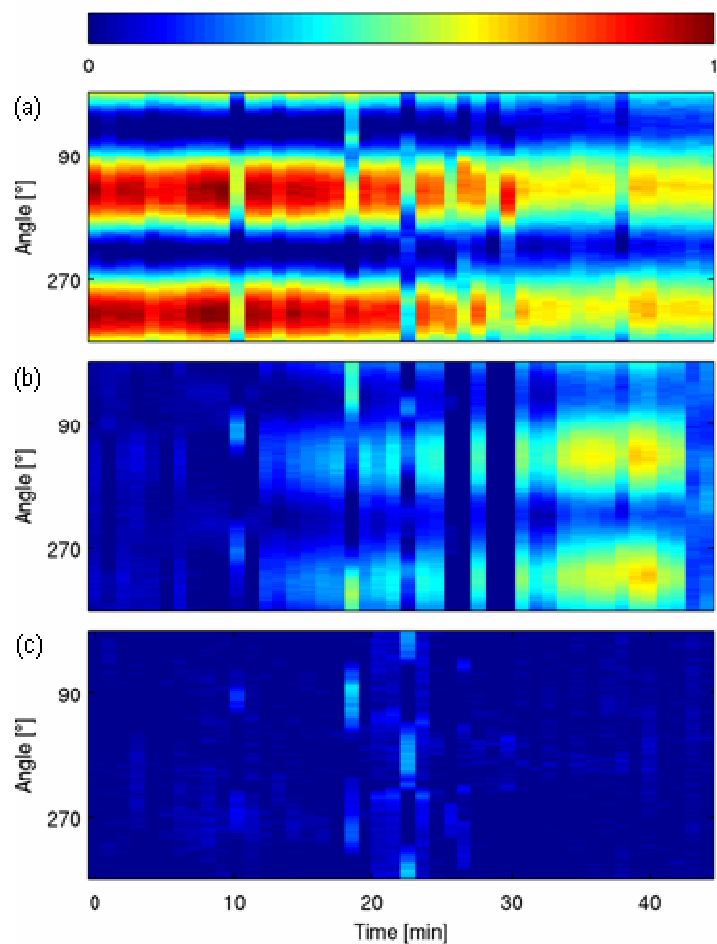
Fig S06: Development of the polarization dependent scattering intensity during the growth process of a rod-shaped gold particle. a), b) and c) correspond to the red, green and blue channel of the digital camera, respectively. The decrease of the total polarization anisotropy and the shift of the plasmon resonance into the green can be clearly seen.
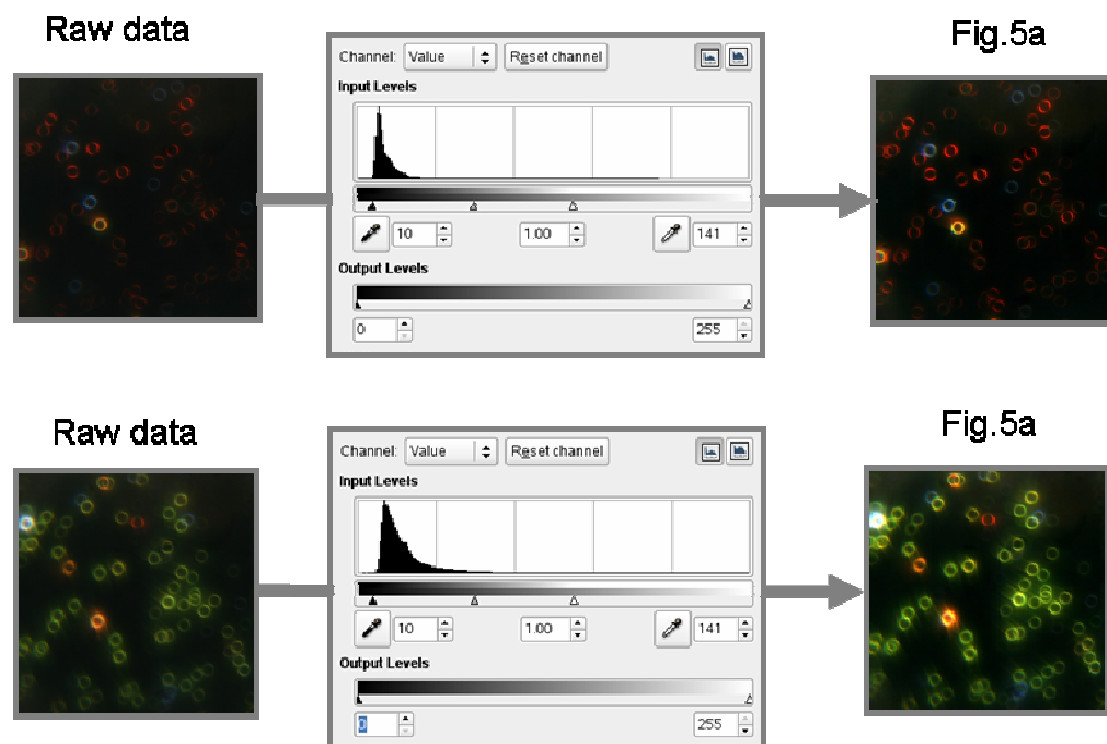
Fig S07: To make the two loops in Fig.5a (left) more clearly visible, the colorspace of the image was stretched using the program "The GIMP". The details of this process, and the exact values used are shown above. As can be seen from the histograms, nearly all the data in the images (raw data) are concentrated into a narrow band, so that no information is lost during this manipulation. The parameters used for both images are the same. All other real color images presented here and in the paper show the raw data and were *not* edited.
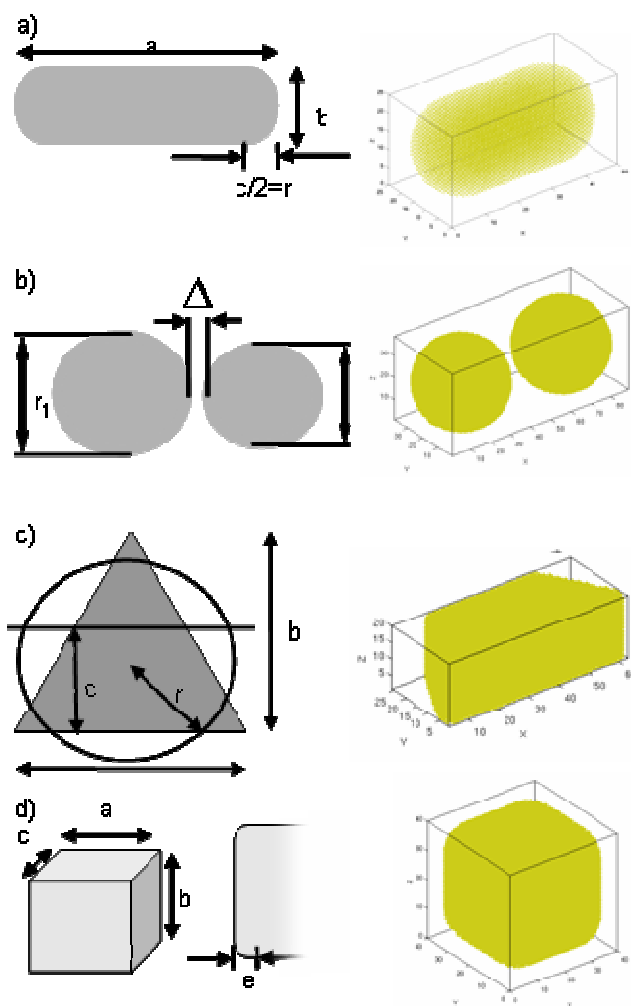
Fig S08: Definition of the shapes used for DDA-simulations (left) and typical examples of the dipole grids (right). Rods are modelled as a cylinder with spherical endcaps (a), triangles and truncated triangles are created by cutting the corners of a two-dimensional isosceles triangle with a circle of radius r, (optionally) cutting the top of the triangle at a height c, and subsequently extruding it in the third dimension (c). For simulations of cubes, a cubic shape with slightly rounded corners is used.
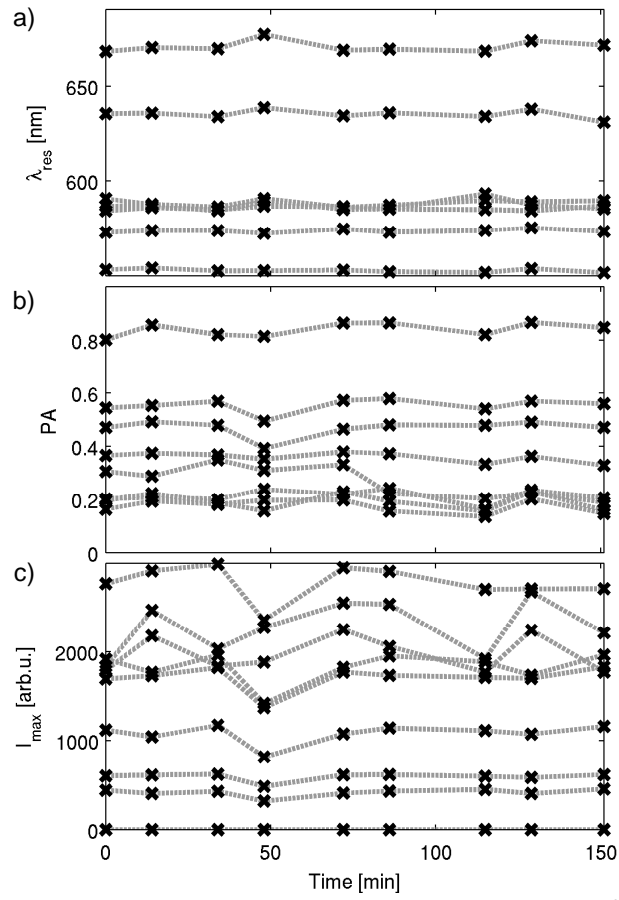
Fig S09: Stability of the setup. The same particles were measured repeatedly for more than two hours. The standard deviation is below 1%, about 6% and about 10% for the resonance energy, PA and maximum intensity, respectively.
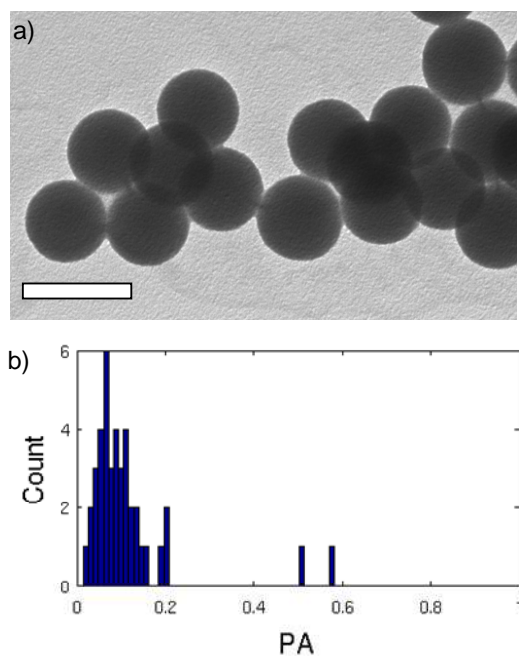
Fig S10: (a) TEM-image (scalebar: 500nm) of SiO_2-spheres and (b) results of a measurement of these perfectly spherical spheres, using the rotPol-setup. The imperfections of the optical components induce an error of about 0.1 in the polarization anisotropy (PA).
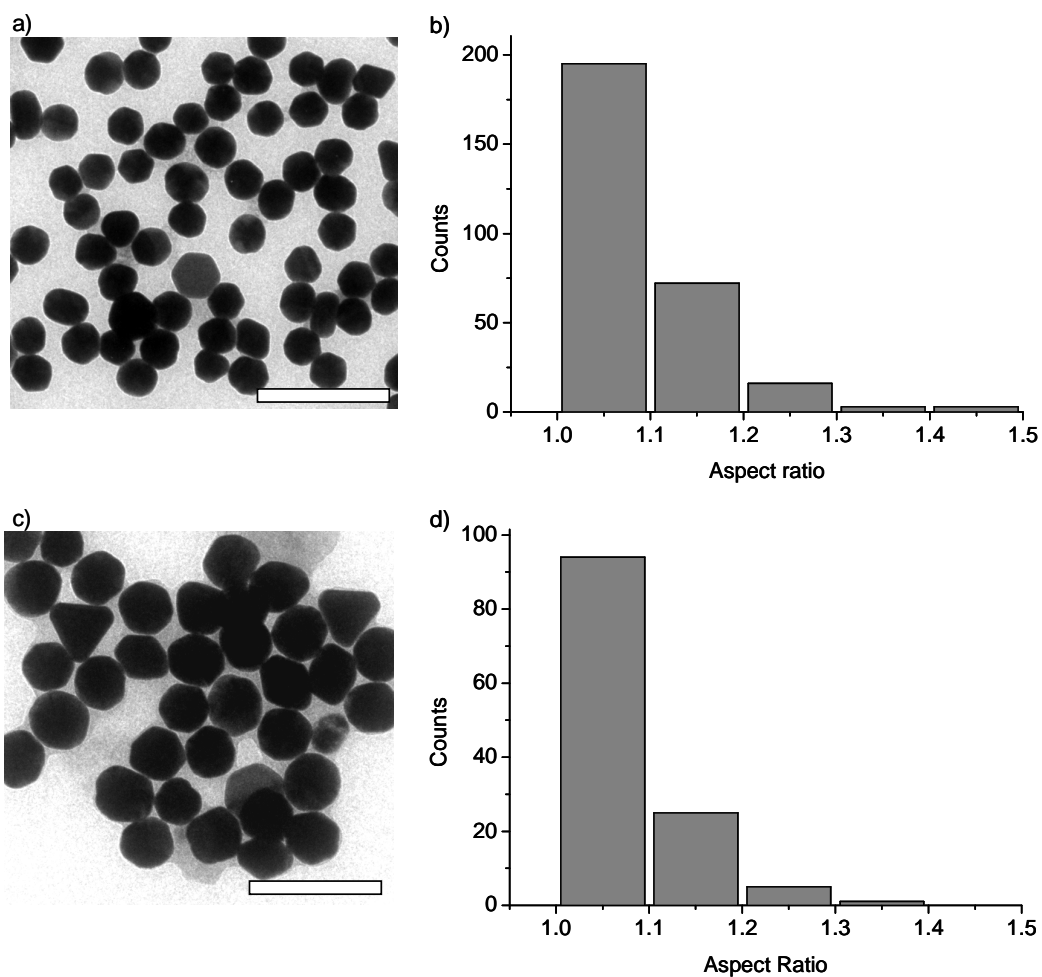
Fig S11: Shape of gold nanospheres (BBI Inc. UK.) determined from TEM images for 60 nm particles (a) and 80 nm particles (c) (scalebars 200nm). Histograms of the aspect ratio determined from such TEM images for more than 100 particles per sample are shown in b) and d) for the 60nm and 80nm particles, respectively. The nominally round particles have a mean aspect ratio (shape anisotropy) of about 1.1 for both samples, which is enough to induce strongly polarized light scattering.

References

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(4)   Siekkinen, A. R.; McLellan, J. M.; Chen, J. Y.; Xia, Y. N. *Chem. Phys. Lett.* **2006**, *432*, 491-496.
(5)   Sönnichsen, C.; Franzl, T.; Wilk, T.; von Plessen, G.; Feldmann, J.; Wilson, O.; Mulvaney, P. *Phys. Rev. Lett.* **2002**, *88*.
(6)   Draine, B. T.; Flatau, P. J. *arXiv:astro-ph/0409262v2* **2004**.