Supporting Information

Enhancement of the second harmonic signal of nonlinear crystals by a single metal nanoantenna

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1. SAMPLE FABRICATION

The Y-cut $LiNbO_3$ crystal (Precision Micro-Optics) and ITO-coated glass were cut into 5 x 5 mm^2 pieces and cleaned with acetone and isopropanol in an ultrasonic bath. Poly-methyl-metacrylate (PMMA) was spin-coated onto the substrate in a first step with 6s @ 2600 rpm and a second step with 60s @ 5000 rpm. The next step was soft baking in a convection oven at 150 °C for 45 min. After an evaporation of 15 nm aluminum (only for the Y-cut $LiNbO_3$ crystal, to provide a conductive surface) the substrate was exposed with a focused electron beam (Philips XL 30). The development process started with maD 331 (only for the Y-cut $LiNbO_3$ crystal), by which the aluminum layer on the resist was removed. After this step a solution of methyl-iso-butyl-ketone (MIBK) diluted with isopropanol (1:3) was prepared to develop the exposed pattern. Then 2 nm titanium (as an adhesion layer, only for the Y-cut $LiNbO_3$ crystal) and 50 nm gold were evaporated. Finally the gold nanodiscs were obtained after a lift-off in acetone.

2. DARK-FIELD SETUP

For the linear optical characterization we used a customized dark-field spectroscopy setup [1]. The samples were illuminated by a laser driven transverse electric (TE) polarized light source (Energetiq EQ-99-FC) at an incident angle of about 50°. A 50x objective with a numerical aperture NA= 0.42 (Mitutoyo BD Plan APO SL 50X) was positioned to collect part of the light that was scattered from the substrate. The signal was detected by a spectrometer (Andor Shamrock SR-303i) with a slit size of 100 μm with 10 s integration time. The spectra were background corrected and normalized by the lamp spectrum.

3. NONLINEAR OPTICAL SETUP

The nonlinear optical measurements were carried out using a homebuilt, confocal parabolic mirror setup with a femtosecond laser source at 774 nm (Toptica Femto Fiber, repetition rate: 89 MHz, pulse length: 110 fs). This pulsed laser source is expanded and spatially filtered by a pinhole to yield a linear polarized laser beam that matches the dimension of the parabolic mirror. Via a beam splitter (Semrock HC 720 SP) the beam is directed to the parabolic mirror, where the light is focused from large angles (NA: 0.988, 28-82°) onto the sample. The emitted signal (SHG and TPL) is directly collimated by the parabolic mirror and directed by the beam splitter to the detectors, either an avalanche photo diode (MPD-Single Photon Counting Detector) or a spectrometer with a CCD-Camera (Acton SP2500 with 150 BLZ grating, Pixis 100 camera). An optical short pass filter (Semrock FF01 680SP) blocks all light above 680 nm before the detectors.

4. SIMULATIONS

The linear optical far-field scattering spectra were simulated using the MNPBEM toolbox [2]. We simulated single gold nanodiscs with diameters ranging from 95 nm to 130 nm and with 50 nm thickness. The refractive indices for gold and $LiNbO_3$ (ordinary and extraordinary) were taken from literature [3, 4]. For ITO n=1.9 was chosen as in [5]. The gold nanodiscs in Fig. 4(b, d) are excited with white light in a spectral range from 500 nm to 900 nm in 5 nm steps. The incident

angle of light corresponds to the incident angle of the laser driven light source (50°). Since TE polarized light was used in the measurements, the same polarization was used in the simulations. In analogy to the collection angle of the 50x objective, the far-field scattering spectra in the model system were calculated by integrating the Poynting vector on the air side from 0° to 25°. The electric field strengths in the vicinity of the nanodiscs under excitation at 774 nm in Fig. 1, the light absorption efficiencies at 387 nm in Fig. 2, and the vector field under 774 nm excitation in Fig. 3(c) were calculated for excitation from the air side (0°, TE).

5. DETERMINATION OF NANODISC HEIGHT

Taking into account the proportionality between the scattering cross section and the electric field strength on the particle surface, the light scattering efficiency can be determined to:

$$\eta(\omega) = \frac{C_{sca}}{C_{ext}} \qquad (1)$$

where C_{sca},C_{ext} are the simulated scattering and extinction cross sections [6]. Figure S1 shows an example of the scattering, absorption, and extinction cross section of a gold nanodisc of 120 nm in diameter (D) and 50 nm in height (H) to determine the light scattering efficiency.

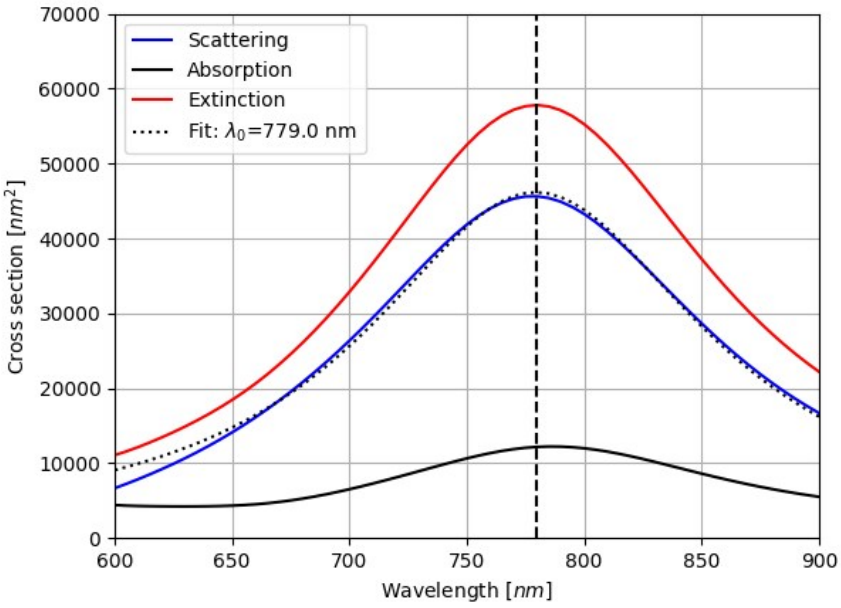

Figure S1: Cross sections of a gold nanodisc (D = 120 nm, H = 50 nm) on $LiNbO_3$

To determine a suitable height for the nanodiscs, the light scattering efficiency is calculated this way for gold nanodiscs with diameters from 50 nm to 120 nm and heights from 20 nm to 80 nm in 10 nm steps. The result of the light scattering efficiency is shown in Figure S2. Each line corresponds to a fixed height, in which the diameter is increased from left to right.

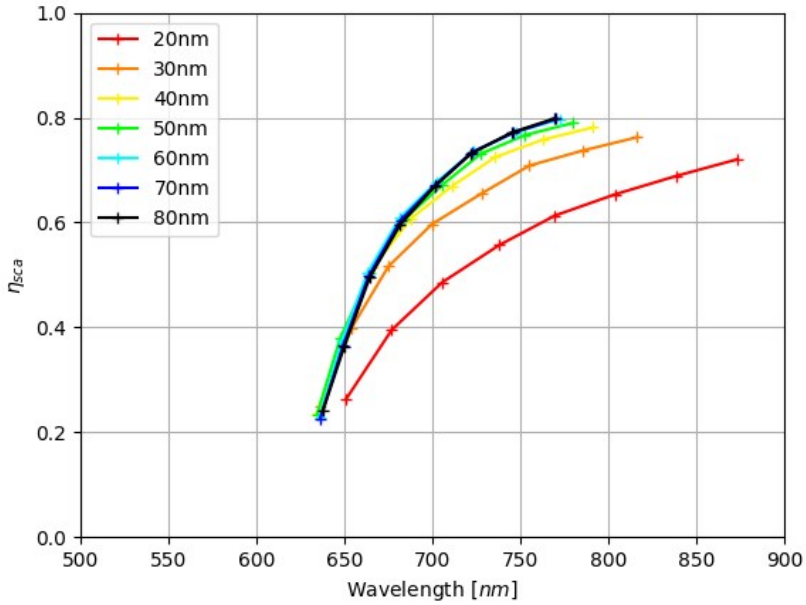

Figure S2: Light scattering efficiency of gold nanodiscs (D = 50 nm to 120 nm in 10 nm steps, H = 20 nm to 80 nm in 10 nm steps) on $LiNbO_3$

The particles with low heights show a strong red-shift in the spectral region, which is not desirable for matching the excitation wavelength of the laser. For the lowest particles the gold thickness is smaller than the penetration depth of the electric field (skin depth), which results in a thickness dependence. After a height of 40-50 nm the discs show a saturation in the light scattering efficiency, for this reason 50 nm are chosen.

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