Tailorable nonlinear metamaterials

Martti Kauranen[1], Robert Czaplicki[1], Hannu Husu[1], Jouni Mäkitalo[1], Goëry Genty[1], Henna Pietarinen[1], Mariusz Zdanowicz[1], Kalle O. Koskinen[1], Roope Siikanen[1], Joonas Lehtolahti[2], Janne Laukkanen[2], and Markku Kuittinen[2]

[1]Department of Physics, Tampere University of Technology
P. O. Box 692, FI-33101 Tampere, Finland
Fax: + 358–3–31152600; email: martti.kauranen@tut.fi
[2]Department of Physics and Mathematics, University of Eastern Finland
P. O. Box 111, FI-80101 Joensuu, Finland
Fax: + 358–9–4512152; email: markku.kuittinen@uef.fi

Abstract

Defects give rise to effective quadrupole effects in second-harmonic generation from metal nanostructures. Samples with improved quality, however, allow the desired dipole limit to be reached. This opens the path for tailorable nonlinear metamaterials, as demonstrated by varying the ordering of anisotropic metal nanoparticles in an array.

1. Introduction

The optical response of metal nanoparticles is based on plasmon resonances, which are collective oscillations of the conduction electrons in the particles. The resonances are sensitive to particle size and shape, the dielectric environment, and the mutual arrangement of the particles. The plasmons give rise to strong local electromagnetic fields, which enhance the optical responses of the nanostructures. Nanoscale variations in the local fields can enable higher multipoles, like magnetic dipoles and electric quadrupoles, to contribute to the responses [1]. Tiny nanoscale features, such as defects, can attract very strong hot spots and thereby modify the optical responses [2]. The role of defects is particularly important in second-harmonic generation (SHG), which is extremely sensitive to the symmetry of the structures and the local fields. We have earlier observed interference between electric dipoles and higher multipoles in SHG from arrays of L-shaped gold nanoparticles [3] and interpreted the results in terms of local defect modes [4]. In this Paper, we show that the higher multipoles in SHG are almost completely suppressed when samples with significantly improved quality are used. We also show that the dipole limit allows nonlinear metamaterials with tailorable properties to be designed.

2. Samples and experiments

L-shaped gold nanoparticles were prepared by electron-beam lithography and lift-off. The samples are strongly dichroic with eigenpolarizations shown in Fig. 1a [5]. The nanoparticles are arranged in a square array with 500 nm period on top of a fused silica substrate. The particles are 20 nm thick, there is a thin adhesion layer of chromium, and the particles are covered by a 20 nm thick protective layer of silica. In each sample, the L's have 100 nm arm width and the arm length is either 200 nm (results in Fig. 3) or 250 nm (results in Fig. 4).

ISBN 978-952-67611-0-7

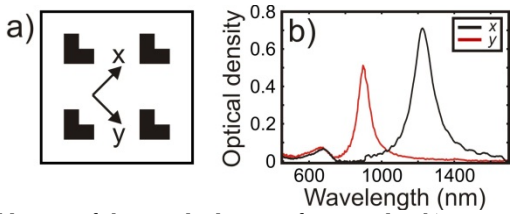

Fig. 1: a) The geometry and layout of the standard array of L particles. b) Extinction spectra of an array of L-shaped nanoparticles (arm width 100 nm, arm length 200 nm).

SHG measurements were performed with an Nd:glass laser (1060 nm, 200 fs, 80 mW, 82 MHz). The polarization of the fundamental beam applied onto the sample was controlled with a half-wave plate (to set initial polarization) and quarter-wave plate (to modulate polarization continuously during the experiment). Our measurements are based on the fundamental differences in the radiative properties of electric dipoles and higher multipoles. To investigate the effect of the multipoles, we measured SHG both in transmission and in reflection, and for both sample and substrate side incidence. In essence, all four signals should show the same dependence on the polarization if only electric dipoles play a role, whereas the presence of higher multipoles would lead to differences in the signals [4, 6].

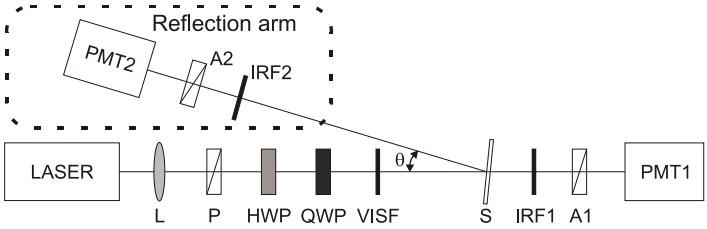

Fig. 2: Experimental setup for SHG. L – lens, P – polarizer, A1, A2 – analyzers, HWP – half-wave plate, QWP – quarter wave plate, VISF – visible blocking filter, IRF1, IRF2 – infrared blocking filters, PMT1, PMT2 – photomultiplier tubes, S – sample (tilted slightly off-normal, by less than 2°).

3. Evidence of dipole limit

The experimental results clearly show that all four measured lineshapes overlap almost perfectly (Fig. 3a), whereas the differences in the lineshapes are clearly visible for nanoparticles with similar parameters but lower quality (Fig. 3b). The lack of differences for the high quality particles indicates that the SHG responses are strongly dominated by dipole interactions. The calculated values of the tensor components related to higher multipoles are found to be close to zero, which provides direct evidence of the dipole limit. Furthermore, comparing the absolute signals between the new and old samples, we found that the higher quality samples give rise to over one order of magnitude stronger SHG signals under similar conditions for specific measurement geometry.

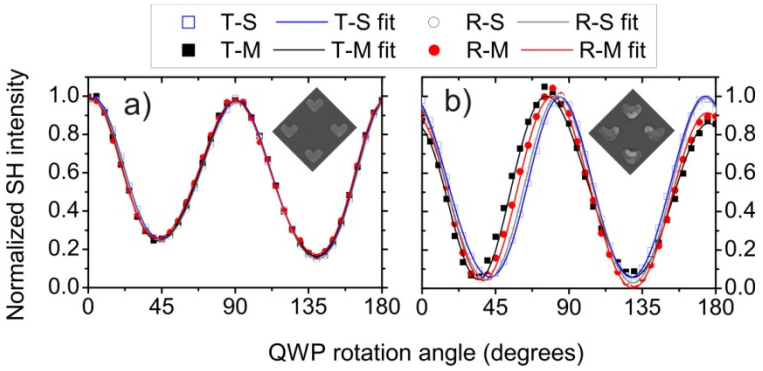

Fig. 3: Normalized transmitted (T-) and reflected (R-) SHG signals from an array of L-shaped gold nanoparticles for metal incidence (-M) and substrate incidence (-S), and from a) the new and b) the old samples. Symbols represent the data from the measurements and solid lines are theoretical fits. Scanning electron microscope images show the quality of the samples. All signals have been normalized separately to overcome variations in their collection efficiency.

ISBN 978-952-67611-0-7

4. Tailorable nonlinear metamaterials

Reaching the dipole limit allows designing nonlinear metamaterials. We demonstrate this by considering several samples where the mutual orientation of the particles in 2×2 particle cells is varied (Fig. 4a). The building block for the different samples is an L-shaped gold nanoparticle with 100 nm arm width and 250 nm arm length. SHG is measured using a setup similar to the one shown is Fig. 2, but only in transmission and from the sample side.

The normalized SHG signal levels are illustrated in Fig. 4a. The second-order response is very sensitive to the structural details of the sample. Sample A and B belong to the same symmetry group, but differ in the details of particle ordering in that two particles in each 2×2 cell are pairwise interchanged. However, their SHG signals differ by more than an order of magnitude. Sample C, on the other hand, is centrosymmetric and gives rise only to very weak SHG, as expected.

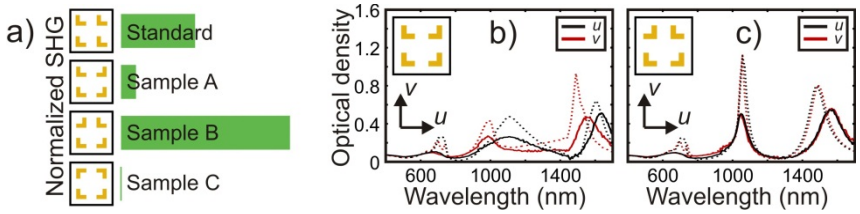

Fig. 4: a) Normalized SHG from different samples (length of green bars). The extinction spectra of b) Sample A, and c) Sample B for their eigenpolarizations *u* and *v*. Solid lines are calculated and dashed lines measured spectra.

To explain the large differences in the SHG responses of Samples A and B, we measured their extinction spectra (Fig. 4b and c). The spectra are completely different even qualitatively from the spectra of individual particles (Fig. 2b). In particular, Sample A has a very broad resonance for *u* polarization and the resonance of Sample B at 1050 nm is surprisingly narrow. These features arise from a long-range diffractive coupling between the unit cells of the structures. Also, the strong SHG from Sample B can be understood by the narrow resonance close to the laser wavelength of 1060 nm.

5. Conclusions

We have shown that the SHG response of high-quality metal nanostructures is strongly dominated by dipole effects. We have thus reached the desired dipole limit, which is a prerequisite for designing nonlinear metamaterials with engineered properties. We have demonstrated this possibility in a set of samples, where the optical properties are modified by the ordering of anisotropic particles in an array. Even minute changes in ordering can lead to huge differences in the nonlinear response.

References

[1] G. Bachelier, I. Russier-Antoine, E. Benichou, Ch. Jonin, and P.-F. Brevet, Multipolar second-harmonic generation in noble metal nanoparticles, *Journal Optical Society of America B*, vol. 25, p. 955–960, 2008.

[2] M. I. Stockman, D. J. Bergman, C. Anceau, S. Brasselet, and J. Zyss, Enhanced second-harmonic generation by metal surfaces with nanoscale roughness: Nanoscale dephasing, depolarization, and correlations, *Physical Review Letters*, vol. 92, p. 057402, 2004.

[3] S. Kujala, B. K. Canfield, M. Kauranen, Y. Svirko, and J. Turunen, Multipole interference in the second-harmonic optical radiation from gold nanoparticles, *Physical Review Letters*, vol. 98, p. 167403, 2007.

[4] S. Kujala, B. K. Canfield, M. Kauranen, Y. Svirko, and J. Turunen, Multipolar analysis of second-harmonic radiation from gold nanoparticles, *Optics Express*, vol. 16, p. 17196–17208, 2008.

[5] H. Husu, J. Mäkitalo, J. Laukkanen, M. Kuittinen, and M. Kauranen, Particle plasmon resonances in l-shaped gold nanoparticles, *Optics Express*, vol. 18, p. 16601–16606, 2010.

[6] M. Zdanowicz, S. Kujala, H. Husu, and M. Kauranen, Effective medium multipolar tensor analysis of second-harmonic generation from metal nanoparticles, *New Journal of Physics*, vol. 13, p. 023025, 2011.

ISBN 978-952-67611-0-7