

Phase matched second harmonic generation from nanostructured metallic surfaces

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Abstract

Planar structures containing oriented and ordered metallic nanoparticles with shapes lacking an inversion centre can act as a nonlinear medium for generation of second harmonic optical radiation by a process whose directional features resemble those of phase matched second harmonic generation (SHG) in bulk media. The nonlinearity of the metallic patterns stems from the asymmetric modulation of the local field inside nanoparticle by electron oscillations and is deeply rooted in the nanostructured nature of the system. The SHG efficiency is inversely proportional to the second power of the nanoparticle size.

Keywords: nanoparticles, second harmonic generation, metamaterials

Microstructured and nanostructured metallic surfaces offer a range of unusual and useful optical properties that give them a well-deserved place in meta-material research. For instance, chiral structuring brings about strong polarization effects in light transmitted, reflected and scattered from a planar structure [1], while plasmon excitations provide unexpectedly high levels of light transmission through microperforated metallic screens [2] and are behind the complex polarization properties and efficiency of metallic gratings [3, 4]. Nanostructured planar structures containing non-centrosymmetric metallic inclusion show second order nonlinear properties and may be used to generate second harmonic optical radiation [5–7]. The main advantage of these nonlinear media is their simplicity and the fact that they can be fabricated using well-established microfabrication/nanofabrication techniques developed for the semiconductor industry. However, there has so far been no discussion of the significance of the inclusion size or the phase matching conditions specific to ordered arrays of nanoparticles. This paper will demonstrate that the nonlinearity of metallic non-centrosymmetric structures is deeply rooted in the nanostructured nature of the system. A simple scaling formula is introduced which shows that the second harmonic efficiency decreases as the second power of the nanoparticle size.

The optical second harmonic generation (SHG) process—the conversion of radiation at a fundamental *pump* frequency

into radiation at a *harmonic* with twice the frequency—is a symmetry breaking effect. In the dipole approximation it can only be seen in systems lacking an inversion centre. SHG was first seen in bulk non-centrosymmetric crystal and powders, and later in geometries of reflections from solid surfaces, where symmetry is broken by the presence of the interface [8]. Here we show that a regular planar structure containing metallic nanoparticles lacking inversion symmetry provides a nonlinear medium capable of converting the pump energy into the second harmonic in a single-layer structure. The relative efficiency of this process increases rapidly with decreasing nanoparticle size, and the arrangement of nanoparticles in regular 2D arrays provides coherent addition of second harmonic fields in a manner analogous to the non-collinear phase matching process in 3D bulk crystals.

Let us consider a planar structure containing metallic nanoparticle inclusions lacking an inversion centre. The electron's classical Drude-type equation of motion can be written as

$$\ddot{x} + \Gamma \dot{x} + \omega_0^2 x = \frac{e}{m} L E$$

where L is the local field correction factor and E is the electric field strength of the incident light wave at frequency ω (wavelength $\lambda = 2\pi c/\omega$). It is assumed that the wave is polarized along the x -axis (figure 1). In a nanoparticle lacking an inversion centre a displacement x of the electron gas affects the local field in asymmetric fashion, thus

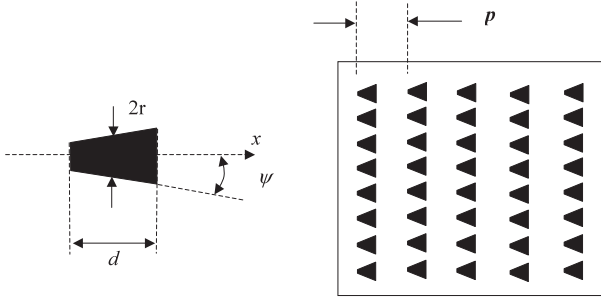


Figure 1. On the left is a plan view of a wedge shaped metallic nanoparticle (i.e. one lacking an inversion centre). The diagram on the right shows a fragment of regular planar structure capable of generating second harmonic radiation that propagates in a direction different from that of reflected, transmitted or diffracted pump radiation. It contains an array of oriented non-centrosymmetric metallic inclusions, for instance, fabricated by microlithography.

allowing a non-zero term, proportional to the displacement: $L = L_0 + (\partial L/\partial x)x + \dots$. The Drude equation of motion can be readily solved by means of consecutive approximations to give the following amplitudes for electron oscillations at frequency ω :

$$x_\omega = \frac{1}{\omega_0^2 - \omega^2 + i\omega\Gamma} \frac{eLE}{m},$$

and at frequency 2ω :

$$x_{2\omega} = \frac{e}{m} \frac{x_\omega}{\omega_0^2 - 4\omega^2 + 2i\omega\Gamma} \frac{\partial L}{\partial x} E.$$

By making the reasonable assumption that in noble metals such as silver and gold at optical wavelengths $\omega \gg \Gamma$ and using the free-electron approximation for optical electrons ($\omega_0 = 0$), one arrives at the following estimate for the ratio between the amplitudes of electron oscillations at frequencies ω and 2ω in the nanoparticle:

$$\mu = \left| \frac{x_{2\omega}}{x_\omega} \right| = \left| \frac{\partial L}{\partial x} \right| \frac{|e|E}{4m\omega^2}.$$

To evaluate the SHG efficiency in a particle lacking an inversion centre we approximate it by a wedge of thickness h with an opening angle 2ψ , length d , and mid-diameter $2r$, as presented on figure 1. The light-induced displacement of electrons x creates a negative surface charge with density $\sigma_- = enx(1 + \psi(x - 2d)/2r)$ on one side of the particle, and a positive surface density $\sigma_+ = -necx$ on the other. The depolarization field could therefore be represented as $E_{\text{dep}} = (\sigma_+ - \sigma_-)/2\epsilon_0 \equiv -\beta(x)enx/\epsilon_0$, where $\beta(x)$ is the depolarization factor in the x -direction. Neglecting the dipole-dipole interaction between particles and the influence of the substrate, the local field factor [9] may be written as $L = (1 + (\epsilon - 1)\beta(x))^{-1}$. Here ϵ is the complex bulk dielectric permeability of the metal at frequency ω . From here we obtain the first term in the series describing the local field factor dependence on the particle asymmetry $\partial L/\partial x = \psi L_0^2(1 - \epsilon)/4r$, and arrive at the following estimate:

$$\mu = \frac{|x_{2\omega}|}{|x_\omega|} = \frac{\psi}{16r} \frac{|e|E}{m\omega^2} \frac{|\epsilon - 1|}{|1 + \beta(0)(\epsilon - 1)|^2}.$$

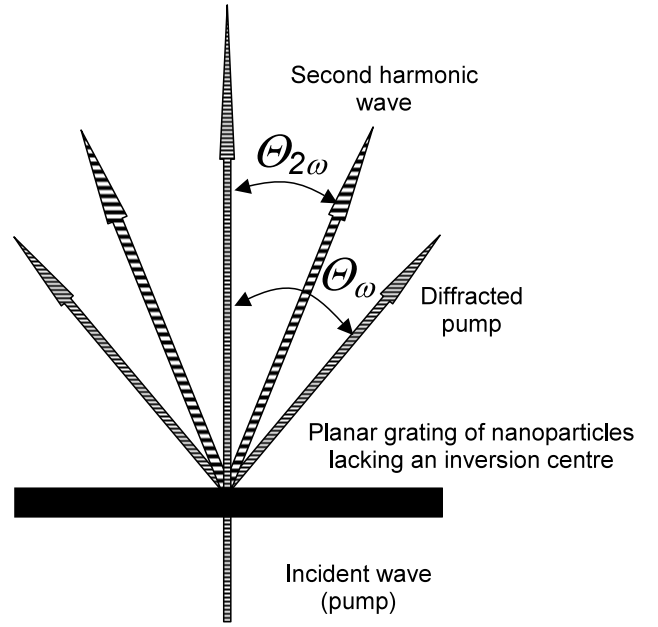


Figure 2. Diffraction of a pump beam and generation of a coherent second harmonic wave by a grating pattern of non-centrosymmetric metallic nanoparticles.

In accordance with the Huygens principle, the oscillations at 2ω will give rise to a secondary scattered wave at this frequency. If all of the metallic nanoparticles are oriented in the same direction, the scattered waves may interfere constructively if the nanoparticles are arranged in the form of a regular grating with pitch p (see figure 1). If the incident wave falls normal to the grating, it will be diffracted at an angle $\Theta_\omega = \sin^{-1}(\lambda/p)$ and the amplitudes of the secondary waves emitted by the metallic inclusions will *add coherently* to give a second harmonic wave at a substantially different angle $\Theta_{2\omega} = \sin^{-1}(\lambda/2p)$; see figure 2. The ratio between the intensities of the diffracted waves at the two frequencies will be $|\mu|^2$. Arranging the nanoparticles in a grating helps to separate the second harmonic signal generated at the substrate interface from that generated by the nanoparticles. The coherent harmonic generation is stable against small shape imperfections of individual particles as long as the particles are much smaller than the wavelength acting as ‘point sources’ of the secondary waves. Additionally, the nanoparticles’ SHG efficiency should be sensitive to the angle ξ between the polarization direction of the incident light and the main axis of the nanoparticles and should vary as approximately $\cos^2 \xi$. This fact may also be used for characterization. This situation, in which the second harmonic is generated in a direction distinctively different from that of the pump, resembles the non-collinear SHG process in bulk crystals. In both cases, the photon momentum conservation law dictates the direction in which harmonics are generated efficiently. The peculiarity of the planar case is the involvement of the grating vector.

For the purposes of estimating the SHG efficiency in the nanoparticle array we assume that the intensity of the incident wave $I = 1 \text{ GW cm}^{-2}$ and that the nanoparticles are made of gold, with $2r \approx 10 \text{ nm}$ and $2\psi \sim 0.5 \text{ rad}$. By changing the ratio r/d the shape-dependent depolarization factor may be adjusted over a wide range of values. In

addition to that the factor is also significantly influenced by the dipole–dipole interactions between the particles and between a particle and the substrate. We will consider two extreme cases corresponding to a nearly spherical nanoparticle with $\beta(0) \approx 0.25$ and an elongated nanoparticle with $\beta(0) \approx 0.021$. For such particles resonance in the second harmonic efficiency is achieved at wavelengths $\lambda = 0.517$ and $1.00 \mu\text{m}$ respectively. Under the resonance, the intensity of the second harmonic wave will be approximately 0.34% of that of the diffracted fundamental wave for $\beta(0) \approx 0.021$, dropping to $5 \times 10^{-8}\%$ for $\beta(0) \approx 0.25$. In the case of silver nanoparticles, if $\beta(0) \approx 0.0125$ could be achieved, which corresponds to a resonance at $\lambda = 1.24 \mu\text{m}$, the second harmonic efficiency would rise to 6%.

One should note that the SHG process described here is deeply rooted in the nanostructured nature of the system. Indeed its efficiency is strongly dependent on the shape and size of the particle: $|\mu|^2 \propto (\psi/r)^2$. The arrays of metallic nanoparticles lacking an inversion centre may be readily manufactured on semiconductor and dielectric substrates using standard lithographic techniques, or electron and ion beam milling.

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