Invited Paper

New Numerical Methods for the Design of Efficient Nonlinear Plasmonic Sources of Light and Nanosensors

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ABSTRACT

During the last decade, important attention has been devoted to the observation of nonlinear optical processes in plasmonic nanosystems, giving rise to a new field of research called nonlinear plasmonics. The cornerstone of nonlinear plasmonics is the use of the large field enhancement associated with the excitation of localized surface plasmon resonances to reach high nonlinear conversion yields. Among all the nonlinear optical processes, second harmonic generation (SHG), the process whereby two photons at the fundamental frequency are converted into one photon at the second harmonic frequency, is undoubtedly the most studied one due to the relative simplicity of its experimental observation. However, the physical origin of SHG from plasmonic nanostructures hides a lot of subtleties, which are mainly related to its particular behavior upon inversion symmetry. In order to catch all the peculiarities of SHG, it is mandatory to develop dedicated numerical methods able to accurately describe all the underlying physical processes and the influence of the initial assumptions needs to be well-characterized. In this presentation, we discuss and compare different methods (namely full-wave computations based on the surface integral equations method, mode analysis, the Miller's rule, and the effective nonlinear susceptibility method) proposed for the evaluation of the SHG from plasmonic nanoparticles emphasizing their limitations and advantages. In particular, the design of double resonant antennas for efficient nonlinear conversion at the nanoscale is addressed in detail.

Keywords: Second harmonic generation, Nonlinear optics, Nonlinear plasmonics, Numerical simulations, Metal, Sensing

1. INTRODUCTION

Nonlinear plasmonics is the research field devoted to the study of nonlinear optical processes in metallic nanostructures.[1] The basic idea associated with nonlinear plasmonics is to use the enhancement of the electromagnetic field induced by the surface plasmon resonances to boost the efficiency of nonlinear optical processes.[1] Various nonlinear optical processes have been observed in plasmonic nanostructures including SHG,[2] third harmonic generation,[3, 4] multi-photon photoluminescence,[5] and Kerr effect.[6] Beyond the simple enhancement of the nonlinear responses due to localized surface plasmon resonances (LSPR), a lot of fundamental questions arise in nonlinear plasmonic.[1] For example, SHG is forbidden in centrosymmetric nanostructures in the electric dipole approximation, meaning that centrosymmetry needs to be broken either by the nanoparticle shape or by the retardation effect.[2] The latter mechanism results in the observation of high order multipolar modes, as such quadrupolar[7] and octupolar emissions.[8] As a consequence, most of the methods used in linear plasmonic and developed in the electric dipole approximation cannot be exploited for SHG and new methods must be developed for a fast, efficient, and accurate determination of the second harmonic responses of plasmonic nanostructures. In this work, we focus on split-ring resonators (SRR) since they are the basic elements for the fabrication of nonlinear plasmonic metasurfaces and we compare different methods for the evaluation of their second harmonic responses. Following the experimental work published by O'Brien *et al.*,[9] we compare the predictions of the Miller's rule and of the effective nonlinear susceptibility method with the results given by an accurate full-wave solution of Maxwell's equations.[10] All the numerical simulations are performed with a surface integral equation (SIE) method.[11] A plane wave propagating along the normal to the SRR is considered in all the computations. The incident wavelength is λ = 1305 nm. All the nanostructures are considered in a homogeneous refractive index n = 1.3, mimicking the presence of a substrate and a 2 nm ITO layer.[9] Here, we first provide the reader with a short description of all these methods, before comparing them to assess their validity and their limitation. Finally, an eigenmode analysis, well-suited for the identification of the relation between the fundamental and the second harmonic modes and the design of double resonant nanostructures is presented.[12]

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2. MILLER'S RULE

In 1964, R. C. Miller published a study in which he observed that, in various piezoelectric crystals, the ratio between the nonlinear susceptibility and the product of the linear susceptibility of the same material at the fundamental and second harmonic wavelengths is almost a constant.[13] This empirical rule is very important, since it attempts to make a direct link between the nonlinear response of a nonlinear material and its linear responses both at the fundamental and nonlinear wavelengths. In other words, only linear calculations or experiments need to be performed in order to determine the nonlinear response. With the Miller's rule, the second harmonic intensity from SRR is given by:

$$I_{SHG} \propto I_{x,Scat}^2(\omega) I_{y,Scat}(2\omega), \tag{1}$$

where the subscripts x and y denote an incident wave polarized along the SRR basis and the SRR arms, respectively. A planewave polarized along the SRR arms is chosen at the second harmonic frequency since SHG polarized along the SRR basis is forbidden in the forward direction, as easily derived from the selection rules of SHG. In the present implementation of the Miller's rule, the scattered electric field is evaluated 50 μm away from the gold SRR in the forward direction for an incident planewave oscillating at the fundamental frequency and polarized along the SRR basis (Fig. 1, step 1) and an incident planewave oscillating at the second harmonic frequency and polarized along the SRR arms (Fig. 1, step 2). This permits to determine the linear susceptibility at the fundamental and second harmonic frequencies, and then the nonlinear susceptibility according to the Miller's rule.

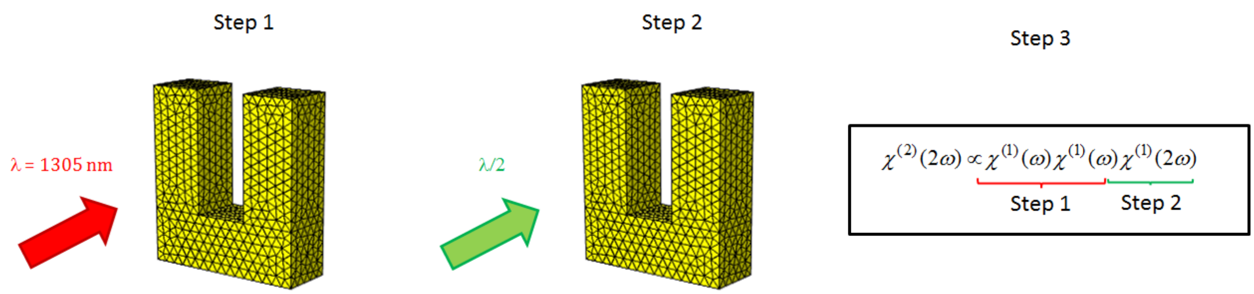

Figure 1: The different steps involved in the evaluation of the SHG from plasmonic metasurfaces using the Miller's rule. Step 1: The forward scattering in evaluated for an incoming planewave with a wavelength corresponding to the fundamental wavelength. Step 2: The forward scattering in evaluated for an incoming planewave with a wavelength corresponding to the second harmonic wavelength. Step 3: the second order nonlinear susceptibility is expressed as the linear susceptibility at the fundamental frequency squared multiplied by the linear susceptibility at the second harmonic frequency.

3. EFFECTIVE NONLINEAR SUSCEPTIBILITY

The effective nonlinear susceptibility method is a linear-nonlinear hybrid method, which also attempts to bridge the gap between the linear and the second order nonlinear responses of plasmonic metasurfaces exploiting Lorentz's reciprocity.[9, 14] Indeed, the effective nonlinear susceptibility method exploits the equality between the overlap integral of the field emitted by the nonlinear polarization and a current source located at the detector position and the overlap integral of the field emitted by the current source at the detector position with the nonlinear polarization.[14] The first step is to compute the surface nonlinear polarization induced by a planewave coming from the source. The surface nonlinear polarization is derived from the fundamental near-field distribution, as $P_n = \chi_{surf,nnn}^{(2)} E_n^2(\omega)$ (Fig. 2, steps 1 and 2). The second step is to evaluated the near-field distribution induced at the SRR surface induced by an incident planewave propagating from the detector towards the SRR and oscillating at the second harmonic frequency (Fig. 2, step 3). Finally, according to the effective nonlinear susceptibility method, the second harmonic electric field is provided by the following surface integral:[9]

$$\mathbf{E}_{SHG} \propto \iint \chi_{surf,nnn}^{(2)} E_n^2(\omega) E_n(2\omega) dS, \tag{2}$$

where the surface integration is performed over the SRR surface (Fig. 2, step 4). For the sake of simplicity, only the component $\chi^{(2)}_{surf,nnn}$ of the surface tensor is considered, where *n* denotes the component normal to the surface. Indeed, recent experimental results indicate that this term dominates the surface response of metallic nanoparticles.[15,16] The electric near-field is evaluated 1 nm away from the metal surface. The second harmonic intensity is obtained by multiplying $\mathbf{E}_{SHG}$ by its complex conjugate.

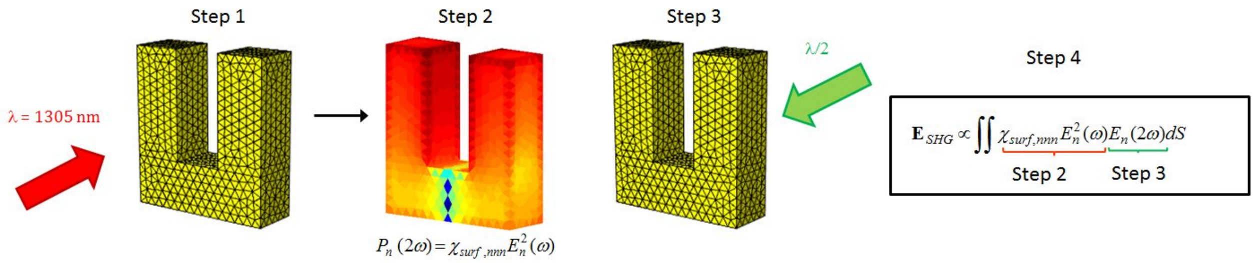

Figure 2: The different steps involved in the evaluation of the SHG from plasmonic metasurfaces with the effective nonlinear susceptibility method. Step1: The fundamental electric near-field is evaluated at the nanostructure surface. Step 2: The surface nonlinear polarization oscillating at the second harmonic frequency is evaluated. Step 3: The electric near-field induced by a wave propagating from the detector position towards the metasurface and oscillating at the second harmonic frequency is evaluated. Step 4: The overlap integral between the quantity evaluated at the steps 2 and 3 is computed, giving the second harmonic electric field at the detector position.

4. FULL-WAVE COMPUTATIONS

For the full-wave computations of SHG, we use a SIE method first developed by Mäkitalo *et al.*,[17] and then extended to study *2D* arrays of plasmonic structures.[18] In this framework, the magnetic and electric linear surface currents are used to evaluate the fundamental electric fields just below the gold surfaces and then utilized for the calculation of the surface second harmonic polarization (Fig. 2, steps 1 and 2).[17,18] These two first steps are similar to the ones of the effective nonlinear susceptibility method. The second harmonic surface currents are obtained by solving the SIE, enforcing the boundary conditions at the nanostructure surface considering the presence of the surface nonlinear polarization.[19] This results in a new set of magnetic and electric surface currents oscillating at the second harmonic, from which the second harmonic field can be evaluated everywhere (inside and outside the SRR).

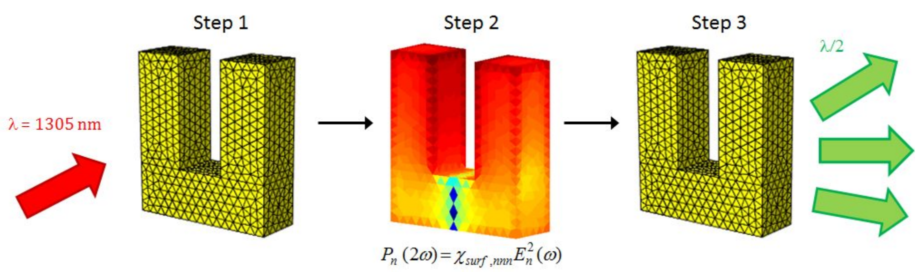

Figure 3: The different steps involved in the evaluation of the SHG from plasmonic metasurfaces with Full-wave computation. Step1: The fundamental electric near-field is evaluated at the nanostructure surface. Step 2: The surface nonlinear polarization oscillating at the second harmonic frequency is evaluated. Step 3: The second harmonic wave, scattered in various and arbitrary directions, is evaluated.

5. COMPARISON BETWEEN THESE THREE METHODS

In this part, we compare these three methods for the evaluation of the SHG from SRR with various shapes. The evolution of the shape is quantified by a factor R, called asymmetry ratio. The factor R is defined as the ratio between the length of the SRR arm and total length of the SRR (two times the SRR arm length plus the basis length). The total length of the SRR is fixed to 300 nm here. Figure 4(a) shows the second harmonic intensity in the forward direction as a function of the asymmetry ratio R evaluated with the Miller's rule (dashed blue line), the effective nonlinear susceptibility method (black line), and the full-wave method (red line). The full-wave computation and the effective nonlinear susceptibility method predict that the asymmetry ratio giving the highest SHG is close to 0.20, in agreement with the experimental results reported by O'Brien *et al.*.[9] However, the Miller's rule results in a SHG optimized for a lower asymmetry ratio, for R= 0.10, emphasizing that this method fails to determine the best SRR geometry. This inadequacy of the Miller's rule is explained by its inability to reproduce the evolution of the near-field enhancement as the SRR geometry changes. It is worth to note that the anharmonic oscillator model, which is deeply related to the Miller's rule,[20] has been successfully applied for the determination of the third harmonic generation from plasmonic nanoantennas[3] and metamolecules supporting Fano resonances.[4] In these two studies, some of the important geometrical parameters are kept constant. This could explain why the Miller's rule provides adequate results in these two cases. However, it seems that the Miller's rule cannot be blindly applied in the field of nonlinear plasmonics, but requires a careful use. Having discussed the Miller's rule, we now compare the effective nonlinear susceptibility with full-wave computations. Figure 4(b) shows the far-field second harmonic intensity as a function of the scattering angle for a 40 nm x 40 nm x 300 nm gold nanobar (an asymmetry ratio R = 0). The full-wave computations emphasizes that the SHG is higher close to the forward direction than close to the backward direction, while the effective nonlinear susceptibility method predicts that the second harmonic intensities close to the backward and forward directions are the same. The inability of the effective nonlinear susceptibility methods arises from its intrinsic nature. Due to the surface integration performed in Eq. (2), the information on the exact position of the nonlinear sources is lost and the retardation effects are not accurately reproduced, explaining that the second harmonic emission pattern is identical in the forward and backward directions. This result shows that the effective nonlinear susceptibility method is not able to reproduce the SHG from centrosymmetric nanoparticles. In plasmonic nanostructures, the border between the SHG induced by shape and retardations effects is not well-defined and the nonlinear susceptibility method must be applied with great care.[21]

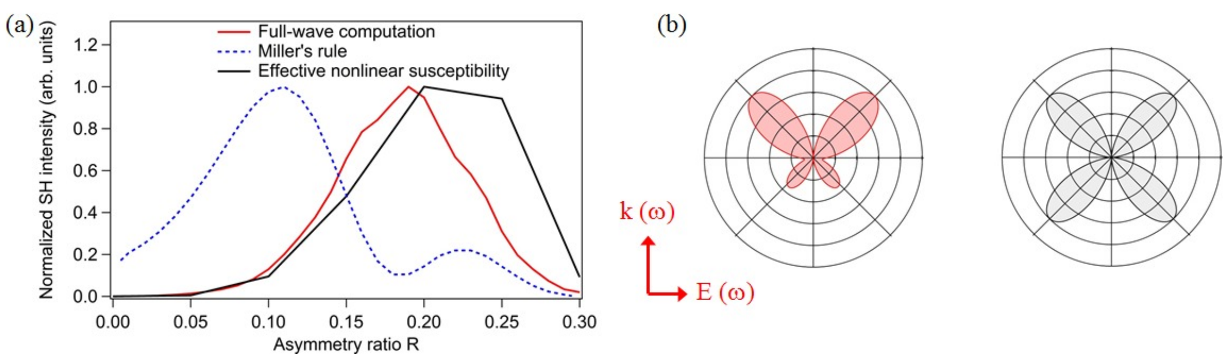

Figure 4: (a) Second harmonic intensity from SRR with asymmetry ratio R ranging from 0 to 0.30 emitted in the forward direction. The predictions of different methods (the Miller's rule, the nonlinear effective susceptibility, and full-wave computation) are compared. (b) The far-field second harmonic intensity as a function of the scattering angle for an asymmetry ratio R = 0 (corresponding to a 40 nm x 40 nm x 300 nm gold nanobar). The red curve shows the prediction of full-wave computation and the black curve the one of the effective nonlinear susceptibility method.

6. EIGENMODE ANALYSIS

Finally, we present the eigenmode analysis that we developed for the study of the SHG from plasmonic nanostructures. In the methods discussed previously, the gold SRR is driven by an incident wave oscillating at the fundamental frequency, generating a nonlinear polarization oscillating at the second harmonic frequency. However, the incoming planewave is able to excite various eigenmodes of the SRRs and distinct excitation channels for the SHG are available, resulting from the combination of these different eigenmodes.[19] As a consequence, it is not possible to unambiguously discriminate between all the symmetry-allowed excitation channels. To overcome this limitation, we propose to evaluate the SHG directly from the eigenmodes themselves. Figure 5 shows the different steps involved in this process. The fundamental mode is first determined using a SIE method developed for searching nanostructure eigenmodes.[12, 22]

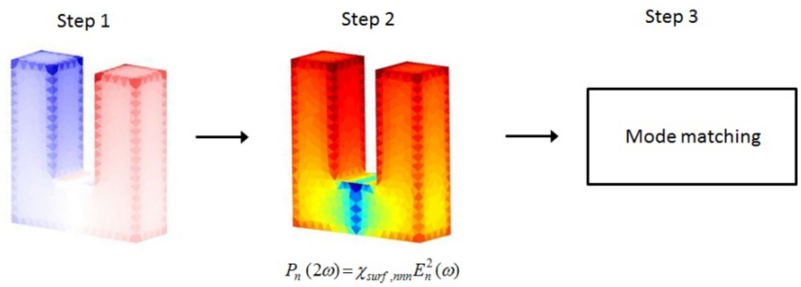

Figure 5: The different steps involved in the optimization of the SHG from plasmonic metasurfaces with the eigenmode analysis. Step 1: The fundamental mode is determined. Step 2: The surface nonlinear polarization oscillating at the second harmonic frequency is evaluated. Step 3: The different parameters are optimized to improve the mode matching between the fundamental and the second harmonic modes.

The nonlinear surface polarization is then directly evaluated from the charge distribution associated with the fundamental eigenmode. With further analysis of both the second harmonic near-field distributions and second harmonic emission patterns, it is possible to determine which second harmonic mode is indeed related to the fundamental one. For example, this approach confirms that, in the case of SRR, the fundamental magnetic mode is coupled to an electric dipole mode.[23] This final step consists to optimize the SRR geometry to satisfy the mode matching condition and to improve the SHG.[22] The main advantage of this approach is to avoid cross coupling between different modes at the fundamental excitation. This is important for the design of double resonant nanoantennas, for which the mode matching is fully satisfied.

7. CONCLUSIONS

In summary, we have presented and compared different methods for the evaluation of the SHG from plasmonic nanostructures.[10] Considering SRR as an example, the building blocks of most of nonlinear plasmonic metasurfaces studied so far as,[24, 25] and using full-wave computations as a benchmark, we have determined the validity range of Miller's rule and the effective nonlinear susceptibility method. As previously observed by O'Brien *et al.*,[9] Miller's rule is not able to determine the SRR geometry resulting in the highest SHG and must be used with a great care. On the other hand, the effective nonlinear susceptibility method permits to predict this geometry but fails to reproduce the properties of the second harmonic wave generated in plasmonic nanoparticles with centrosymmetric shapes. This observation emphasizes the necessity to accurately include the retardation effects and the exact positions of the nonlinear sources in this case. Finally, we have presented an eigenmode analysis of the SHG from plasmonic nanostructures, tailored for the identification of the excitation channels and for the design of double resonant nanoantennas. These results pave the way for an efficient and accurate design of the nonlinear optical conversion in plasmonic nanostructures and metasurfaces.

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