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Nonlinear plasmonic metasurfaces

Mikko J. Huttunen*, Robert Czaplicki† and Martti Kauranen*

* *Photonics Laboratory, Physics Unit, Tampere University,
P. O. Box 692, FI-33014 Tampere, Finland*

† *Institute of Physics, Faculty of Physics, Astronomy, and Informatics,
Nicolaus Copernicus University, Grudziądzka 5/7, 87-100 Toruń, Poland*

Nonlinear plasmonic metasurfaces have recently attracted considerable interest, due to their potential for enabling nanoscale nonlinear optics. Here, we review the current progress in this topic while paying special attention to existing challenges. In order to limit our scope, we concentrate on nonlinear metasurfaces utilizing inter-particle and lattice effects and focus on metasurfaces operating close to visible and near-infrared frequencies. We will also critically discuss the short and longer term prospects of nonlinear metasurfaces to start rivalling traditional nonlinear materials in applications.

Keywords: metamaterials; metasurfaces; surface lattice resonances; metal nanoparticles, nonlinear optics, plasmonics.

1. Introduction

Metamaterials and metasurfaces are artificial, man-made structures consisting of sub-wavelength building blocks, often termed as *meta-atoms*.⁸⁰ There is a growing interest towards photonic metamaterials as they can provide optical properties that natural materials lack, including magnetism at optical frequencies, strong optical activity, negative refractive index and epsilon-near-zero materials.^{2, 58, 90}

In addition to linear optical properties, nonlinear optical responses of photonic metamaterials are of increasing interest. This is due to the fact that many technologically relevant photonic applications rely on nonlinear responses of the material, and include frequency conversion, photon-pair generation, all-optical switching, ultra-short pulse generation, frequency combs and supercontinuum generation.^{44, 53, 78, 81} However, current nonlinear metamaterials have not dissolved, at least yet, the everyday challenge in nonlinear optics, which is the problem that optical nonlinearities of materials are intrinsically very weak.¹⁰

Recently, nonlinear plasmonics has been introduced as a promising route towards more efficient nonlinear metamaterials.⁴¹ This is because metal nanoparticles support collective resonant oscillations of conduction electrons, known as localized surface plasmon resonances (LSPRs), which can considerably enhance the local field near the particles. Since nonlinear processes scale with higher powers of the local field, plasmon-assisted field enhancement can result in a dramatic enhancement of the otherwise very weak nonlinear process. Consequently, numerous investigations

have been carried out during the past decade in order to understand and utilize nonlinear responses of plasmonic nanoparticles.^{12,54,56,74} Despite steady progress, many challenges still remain raising a question of whether nonlinear plasmonic metamaterials could ever rival traditional nonlinear materials.

Here, we review the current status of nonlinear plasmonic metamaterials and seek to address the above question. In particular, we focus our treatment to plasmonic metasurfaces operating close to optical and near-infrared frequencies. Single particles and propagating surface plasmons are also excluded from the scope, as they are already well covered in Ref. 41. In addition, several reviews exist already on this topic with their emphasis on material aspects, fabrication, quantum effects and exotic nonlinear phenomena.^{12,42,49,54,56,71,74} Therefore, here we exclude those considerations and instead focus on discussing principles of nonlinear optics, modelling aspects and SHG-emitting metasurfaces. We highlight problems associated with previous approaches and discuss how those could be alleviated by utilizing lattice and inter-particle effects, such as surface lattice resonances (SLRs).⁵¹

The structure of this review is following. First, in section 2 we introduce the basic concepts in nonlinear optics. In section 3 we cover main approaches and methods to understand and model nonlinear responses of metasurfaces. Special attention is paid to local fields occurring near plasmonic nanoparticles and their enhancement through lattice effects. In section 4, we review the current status of plasmonic metasurfaces concentrating on their second-order nonlinear responses. Finally, in section 5 we provide a critical outlook and conclusions.

2. Principles of nonlinear optics

The optical response of a material can be described by its polarization. The applied optical field is often weak resulting in a linear dependence between the induced polarization and the applied field. However, when the applied field is sufficiently strong (or the material is highly nonlinear), the dependence becomes nonlinear giving rise to nonlinear optics.¹⁰ When the resulting nonlinearities remain relatively weak they can be treated perturbatively, and the material polarization $\tilde{\mathbf{P}}$ can be expanded as a power series in the optical field $\tilde{\mathbf{E}}$ as¹⁰

$$\tilde{\mathbf{P}} = \epsilon_0 \left[\chi^{(1)} \tilde{\mathbf{E}} + \chi^{(2)} : \tilde{\mathbf{E}} \tilde{\mathbf{E}} + \chi^{(3)} : \tilde{\mathbf{E}} \tilde{\mathbf{E}} \tilde{\mathbf{E}} + \dots \right], \quad (2.1)$$

where ϵ_0 is the vacuum permittivity, $\chi^{(1)}$ is the linear susceptibility and $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order nonlinear susceptibilities, respectively. The applied optical field is conveniently described as a sum of n frequency components

$$\tilde{\mathbf{E}} = \sum_n \mathbf{E}(\omega_n) = \sum_n \mathbf{E}_n e^{-i\omega_n t}, \quad (2.2)$$

where the summation is over positive and negative frequencies ω_n . By assuming time-harmonic incident field $\tilde{\mathbf{E}} = \mathbf{E}(\omega_1)$, it becomes evident through use of Eq. (2.1) that polarization components oscillating also at harmonic frequencies of $2\omega_1$ and

$3\omega_1$ exist. Because $\tilde{\mathbf{P}}$ acts as a source of radiation, new field components oscillating at these harmonic frequencies are created in the material.

The second-order term of Eq. (2.1) is the most important in frequency conversion applications. The simplest and most intensely studied second-order process is called second-harmonic generation (SHG) where a field component oscillating at the doubled frequency $2\omega_1$ is created.¹⁰ In the presence of two (or more) time-harmonic incident field components $\tilde{\mathbf{E}} = \mathbf{E}(\omega_1) + \mathbf{E}(\omega_2)$, sum frequency- and difference frequency generation processes can also occur and give rise to a richer output spectra. Importantly, these and all even-order nonlinear effects are heavily affected by symmetry considerations. As an example, by assuming electric-dipole approximation of the light-matter interaction, these effects can only occur in a noncentrosymmetric media.¹⁰ Therefore, this simple symmetry rule and symmetry considerations in general are particularly important in the development of new nonlinear materials.

The third term in Eq. (2.1) results in third-order nonlinear responses, which provide more possibilities for applications. In general, up to four different fields interact with the material giving rise to four-wave mixing (FWM) processes. Besides third-harmonic generation (THG), processes such as self-phase modulation (SPM) and cross-phase modulation (XPM) can also occur giving rise to nonlinear phase shifts in the applied fields. Several important applications of nonlinear optics are based on these second- and third-order effects and include all-optical switching, photon-pair generation, pulse compression, THz generation, frequency combs and supercontinuum generation.^{53, 61, 72, 78}

As noted in Eq. (2.1), the incident field $\tilde{\mathbf{E}}$ and material polarization $\tilde{\mathbf{P}}$ are vectors. Consequently, the N th-order susceptibilities are tensors of rank $N + 1$. In addition, the material responses are dispersive, which is especially true for metals and plasmonic materials due to their non-instantaneously responding conduction electrons. In this case, we can express the second- and third-order responses as

$$P_i(\omega') = \epsilon_0 \sum_{j,k} \chi_{ijk}^{(2)}(\omega'; \omega_o, \omega_p) E_j(\omega_o) E_k(\omega_p), \quad (2.3a)$$

$$P_i(\omega') = \epsilon_0 \sum_{j,k,l} \chi_{ijkl}^{(3)}(\omega'; \omega_o, \omega_p, \omega_q) E_j(\omega_o) E_k(\omega_p) E_l(\omega_q), \quad (2.3b)$$

where ω' is the signal frequency and indices (i, j, k, l) refer to the vector components of $\tilde{\mathbf{P}}$ and $\tilde{\mathbf{E}}$. In general, susceptibilities $\chi_{ijk}^{(2)}$ and $\chi_{ijkl}^{(3)}$ consist of 27 and 81 components. However, use of symmetry arguments can considerably simplify the structure and number of non-zero components of the susceptibilities.

For conventional nonlinear crystals, an order-of-magnitude estimate for the second-order (third-order) susceptibility value is 10^{-11} m/V (10^{-20} m²/V²). Therefore, either excitation with high peak intensities (around 10^6 – 10^9 W/cm²), or use of crystals with long interaction lengths are necessary in order to realize strong nonlinear responses. Alternatively, nonlinear fibers can be utilized, where the often intrinsically weaker material nonlinearities are compensated by the possibility to use very long interaction lengths.

Metals are highly nonlinear materials and have stronger intrinsic nonlinearities than conventional materials (for example $\chi_{\text{gold}}^{(3)} \sim 10^{-15}\text{--}10^{-19} \text{ m}^2/\text{V}^2$).^{9, 11, 84, 87} Therefore, it seems highly plausible, albeit challenging, to utilize plasmonic materials and metasurfaces for nonlinear optics.⁴¹ Consequently, considerable efforts have been taken to demonstrate the usefulness of nonlinear metasurfaces.^{12, 41, 43, 56, 74} Despite impressive amount of progress, nonlinear metasurfaces have not yet truly rivalled conventional materials. This is because several challenges still exist, such as relatively low material damage threshold levels, difficulties in fabricating 3D metamaterials and naturally the intrinsic losses of metals. In addition, it is important to further advance the understanding of nonlinear responses of metasurfaces in order to realize the full potential of nonlinear plasmonic metasurfaces. In the next section, we will focus on the latter challenge and introduce some of the existing approaches to understand and predict nonlinear responses of metasurfaces. Discussion of the other challenges is left to the subsequent sections.

3. Nonlinear responses of metasurfaces

It is imperative to understand the nonlinear responses of metasurfaces well in order to use models and simulation tools with good predictive power. In this section, we provide a tutorial on how to describe nonlinear responses of metasurfaces. We start by describing how nonlinear responses of individual meta-atoms can be understood. After this we generalize the discussion to metasurfaces.

3.1. *Nonlinear responses of individual meta-atoms*

Since the beginning of nonlinear plasmonics, many approaches to calculate nonlinear responses of individual meta-atoms have been developed. Due to extensive amount of previous work,^{12, 41} we cover this topic only briefly and focus on understanding nonlinear responses of metasurfaces.

A starting point is to estimate the microscopic material susceptibility, which is often done by using so-called hydrodynamic model.⁷⁹ Alternatively, experimentally estimated values can be used.^{50, 87} Once the intrinsic material nonlinearity is known, analytical methods such as equivalent circuit theory,^{66, 73} nonlinear Rayleigh scattering or multipole expansion can be used to predict the nonlinear response of the whole meta-atom.^{24, 25} In addition to analytical methods, several numerical approaches exist and are based either on finite-difference time domain (FDTD) method,³⁹ boundary- or finite-element methods^{8, 13, 62, 63} or nonlinear discrete-dipole approximation (NDDA) approach.⁶ These methods commonly assume that undepleted-pump approximation holds making it possible to solve the otherwise quite complicated nonlinear scattering problem using a few straightforward steps. First the local fields near the meta-atom due to the applied field are numerically solved for [see Fig. 1(a)]. These local fields are then used to estimate the nonlinear source polarization distribution (see Eqs. 2.3). Finally, the linear scat-

tering problem at the nonlinear signal frequency is solved.

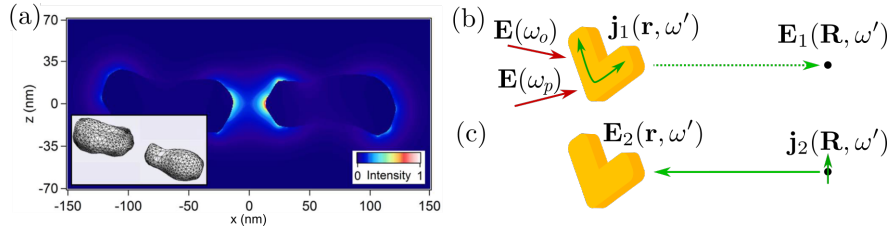


Fig. 1. (a) Near-field distribution of the fundamental intensity close to a gold nanoantenna. The mesh was adapted from a scanning electron microscope image (see inset). Adapted with permission from Ref. 14. Copyright 2013, American Chemical Society. (b) and (c) Illustration of an indirect way to solve the nonlinear scattering problem (here for SFG) by taking use of the Lorentz reciprocity theorem.²⁵ (b) Fields $\mathbf{E}(\omega_0)$ and $\mathbf{E}(\omega_p)$ incident on a meta-atom give rise to a nonlinear source polarization and thus a current distribution $\mathbf{j}_1(\mathbf{r}, \omega')$. Solving the associated nonlinear scattering problem allows determination of the scattered signal field $\mathbf{E}_1(\mathbf{R}, \omega')$ at far-field point \mathbf{R} . (c) The scattered signal field $\mathbf{E}_1(\mathbf{R}, \omega')$ can also be estimated indirectly by taking use of Lorentz reciprocity theorem. In this approach, calculation of an overlap integral between the current distribution $\mathbf{j}_1(\mathbf{r}, \omega')$ and the emitted field $\mathbf{E}_2(\mathbf{r}, \omega')$ near the meta-atom due to a point source $\mathbf{j}_2(\mathbf{R}, \omega')$ provides an estimate for $\mathbf{E}_1(\mathbf{R}, \omega')$.

It is also possible to estimate the nonlinear response of a meta-atom by using the Lorentz reciprocity theorem.^{25,70} However, in this approach the nonlinear signal emission is estimated only into one direction or point location [see Figs. 1(b) and 1(c)]. If it is of interest to simulate the full nonlinear signal emission pattern, it is notably more efficient to solve the full scattering problem using, for example the above-mentioned approaches, as has been discussed in Ref. 62.

We also note that approaches entirely based on the hydrodynamic model have been recently demonstrated for understanding the nonlinear responses of individual meta-atoms.^{18,32,77} These fully hydrodynamic approaches are in general computationally most expensive. However, their strength lies in the fact that a minimal amount of assumptions and material parameters are needed to perform simulations.

As is clear from the above, many approaches have been already developed to predict and understand nonlinear responses of individual meta-atoms. Every approach has their advantages and disadvantages, and therefore it is in practise almost a matter of taste which approach to follow. However, despite a fair amount of work,^{5,18,50,82,87} origins of microscopic responses are still not entirely understood or well characterized remaining an open question.⁸⁹

3.2. Nonlinear responses of metasurfaces

Once the nonlinear responses of an individual meta-atom are understood, it is possible to move forward to understand the responses of periodic structures, such as metasurfaces. Before proceeding, we note that a recent review focusing on the design considerations of metasurfaces exists.⁷⁴

In general, two different approaches to understand nonlinear metasurfaces can be taken. First, most of the numerical approaches mentioned above can be extended to periodic structures by using the Floquet-Bloch theory, periodic Green's functions and/or appropriate boundary conditions.^{13,28,30,76} Although the extension principle is conceptually straightforward, efficient and robust implementation can be nontrivial.^{13,59,85}

An alternative strategy is to rely on computationally simpler approaches, such as the NDDA approach,³⁸ which can be readily extended to arrays containing a large number of meta-atoms. Advantages of this approach include the possibility to simulate finite or even *aperiodic* arrays, allowing, for example, to investigate how small variations in the fabrication parameters, such as in meta-atom dimensions, can affect the overall performance of the metasurface. Finally, and most importantly for this review, the NDDA approach provides a simple means to elucidate the underlying physics of how the nonlinear response of a metasurface is affected and can be engineered by arranging meta-atoms into periodic arrays. Due to this reason, we chose to emphasize here the NDDA method for estimating the local fields and their enhancements occurring in a metasurface.^{27,37,38}

Local-field enhancement in periodic structures

We consider a situation schematically shown in Fig. 2, where an applied field \mathbf{E}_{inc} oscillating at frequency ω_p is incident on the metasurface. In addition to \mathbf{E}_{inc} , the response of the i th meta-atom is also affected by the scattered field due to all other meta-atoms present in the array. Therefore, the local field at the location of i th meta-atom $\mathbf{E}_{loc,i}$ can be written as

$$\mathbf{E}_{loc,i} = \mathbf{E}_{inc,i} - \sum_{k \neq i} \mathbf{A}_{ik} \mathbf{p}_k, \quad (3.1)$$

where \mathbf{A}_{ik} is a 3×3 matrix describing the interaction between j th and k th particles. The detailed form of \mathbf{A}_{ik} has been given elsewhere.^{27,38} The dipole moment of the i th meta-atom \mathbf{p}_i is defined through relation

$$\mathbf{p}_i = \epsilon_0 \alpha \mathbf{E}_{loc,i}, \quad (3.2)$$

where α is the polarizability of the meta-atom. By using notation $\mathbf{A}_{ii} = \epsilon_0^{-1} \alpha_i^{-1}$, we see that for an array consisting of N meta-atoms, Eq. (3.1) can be re-written to form a system of $3N$ linear equations given by

$$\mathbf{E}_{inc,i} = \sum_{k=1}^N \mathbf{A}_{ik} \mathbf{p}_k, \quad (3.3)$$

which can be combined with Eq. (3.2) to solve for \mathbf{E}_{loc} in a straightforward manner.^{27,37} Interestingly, the contribution due to other meta-atoms can have a quite dramatic effect on \mathbf{E}_{loc} and thus on the optical response of the metasurface, as it for example gives rise to collective array resonances known as SLRs.^{4,40,65,92}

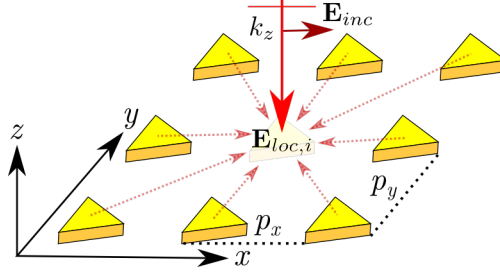


Fig. 2. An incident field \mathbf{E}_{inc} excites periodically arranged meta-atoms. The local field near the i th meta-atom $\mathbf{E}_{loc,i}$ is affected, in addition to \mathbf{E}_{inc} , also by the fields scattered by all other meta-atoms (dotted arrows).

Next, we extend the approach to second-order nonlinear responses by assuming that undepleted-pump approximation holds.¹⁰ In this case, the local field components $\mathbf{E}_{loc,i}(\omega_j)$ with $j = (o \text{ or } p)$, solved as above, drive the nonlinear dipole moment term written as

$$\mathbf{p}_{exc,i}(\omega') = \epsilon_0 \beta_i(\omega'; \omega_o, \omega_p) : \mathbf{E}_{loc,i}(\omega_o) \mathbf{E}_{loc,i}(\omega_p), \quad (3.4)$$

where β_i is the first-order hyperpolarizability. The relation between the signal frequency ω' and the input frequencies ω_j depends on the nonlinear process in question. For example, for SFG $\omega' = \omega_o + \omega_p$. Now we are left to find self-consistent dipole moment components $\mathbf{p}(\omega')$. In other words, we need to take into account how the other dipoles and their scattered fields at the frequency ω' modify the i th dipole moment component $\mathbf{p}_i(\omega')$. This is done by solving another system of $3N$ linear equations given by

$$\epsilon_0^{-1} \alpha_i^{-1}(\omega') \mathbf{p}_{exc,i}(\omega') = \sum_{k=1}^N \mathbf{A}_{ik}(\omega') \mathbf{p}_k(\omega'). \quad (3.5)$$

The nonlinear response of a metasurface can now be predicted by using the above equations. As an example, a calculated SFG response of a metasurface consisting of triangular meta-atoms with periods $p_x = 759$ nm and $p_y = 792$ nm is shown in Fig. 3, where depending on the input polarization a notable 400–800-fold enhancement of the SFG dipole moment amplitude is predicted to occur for a meta-atom at the center of the array.³⁸ Finally we note, that due to Eq. (3.5), the nonlinear response of a metasurface can be enhanced also by a resonant contribution in the scattered field at the signal frequency ω' . This point is elucidated further by introducing next a simple but powerful approximation of the above NDDA approach.^{4, 37, 65, 68, 92}

Lattice sum approach

The lattice sum approach (LSA) is a simple method to understand and provide order-of-magnitude estimates for nonlinear responses of periodic metasurfaces.^{37, 68} The approach is based on the above-discussed NDDA method, which is further

8 *M. J. Huttunen, R. Czaplicki and M. Kauranen*

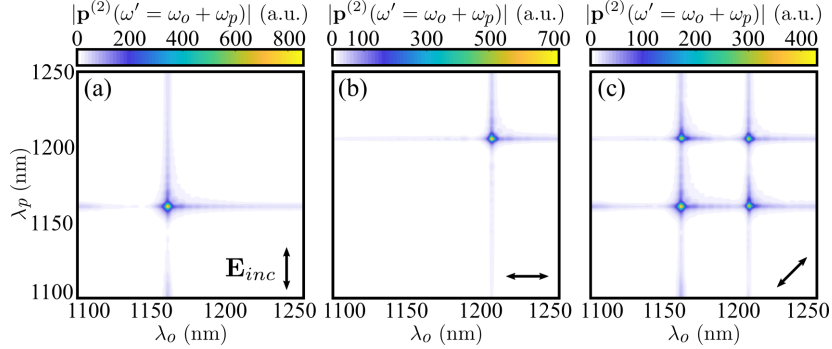


Fig. 3. Nanoparticle array with periods $p_x = 759$ nm and $p_y = 792$ nm, respectively, exhibits enhanced SFG and SHG responses when the wavelengths of the incident fields coincide with the SLRs. We plot the SFG dipole moment amplitude for the particle at the center of the array for incident fields, linearly polarized either along the (a) y , (b) x , and (c) $(x+y)$ direction. The dipole moment is scaled with respect to that of a single isolated particle. Adapted from 38.

simplified by making two additional assumptions. First we assume that the metasurface of interest extends to infinity. Second, we assume that all the constituent meta-atoms and their associated dipole moments are identical ($p_i = p_k = p$), implying also that the applied fields are normally incident on the metasurface.^{37,92} Under these assumptions, Eq. (3.3) is considerably simplified and can be solved for p :

$$p = \frac{\epsilon_0 \alpha E_{inc}}{1 + \alpha S} = \epsilon_0 \alpha^* E_{inc}, \quad (3.6)$$

where the effect of the inter-particle coupling is due to the lattice sum $S = \sum_{k \neq i} A_{ik}$, and

$$\alpha^* = \frac{\alpha}{1 + \alpha S}, \quad (3.7)$$

is the effective polarizability. The explicit form of the lattice sum S depends on the type of the array and the SLR.³⁷ However, even without going into such details, it is clear from Eq. (3.7) that when the real part of the term $1 + \alpha S$ vanishes, the effective polarizability α^* peaks and a resonance occurs due to the lattice effect.⁴ More interestingly, by recalling Eq. (3.2) we see that the local field present in the array is heavily affected by this resonance.

It is straightforward to extend LSA to nonlinear interactions by following the approach of Ref. 68. For simplicity, here we only show the results for the SFG process. Under the above-mentioned assumptions, Eq. (3.5) can be simplified and

solved for $p_i(\omega') = p_k(\omega') = p(\omega')$ as follows

$$\begin{aligned} p(\omega') &= \frac{\epsilon_0 \beta(\omega') E_{loc}(\omega_o) E_{loc}(\omega_p)}{1 + \alpha(\omega') S(\omega')} \\ &= \frac{\epsilon_0 \beta(\omega') E_{inc}(\omega_o) E_{inc}(\omega_p)}{[1 + \alpha(\omega') S(\omega')] [1 + \alpha(\omega_o) S(\omega_o)] [1 + \alpha(\omega_p) S(\omega_p)]} \\ &= \epsilon_0 \beta^*(\omega'; \omega_o, \omega_p) E_{inc}(\omega_o) E_{inc}(\omega_p), \end{aligned} \quad (3.8)$$

where the last equality follows by defining an effective hyperpolarizability for a meta-atom as

$$\beta^*(\omega'; \omega_o, \omega_p) = \frac{\beta(\omega'; \omega_o, \omega_p)}{[1 + \alpha(\omega') S(\omega')] [1 + \alpha(\omega_o) S(\omega_o)] [1 + \alpha(\omega_p) S(\omega_p)]}. \quad (3.9)$$

Interestingly, the effective hyperpolarizability of an individual meta-atom β^* is now seen to depend on the meta-atom and array parameters not only at the input frequencies ω_o and ω_p , but also at the signal frequency ω' . Therefore, it seems clear that the nonlinear response of a metasurface could be dramatically enhanced by proper array designs, taking advantage of the resonant lattice terms and SLRs. But so far, only a few works exist where these considerations have been utilized. These approaches are discussed in the next section.^{20, 21, 33, 38, 68}

4. Nonlinear plasmonic metasurfaces

In this section, we review the current status of nonlinear plasmonic metasurfaces. In order to limit the scope of this vastly expanding topic, we focus our discussion on plasmonic second-order nonlinear responses. In order to provide a better overall view on the topic, we first discuss briefly metasurfaces where lattice effects have not played a marked role and shift progressively the discussion to metasurfaces utilizing lattice effects.

Most of prior research in nonlinear metasurfaces has been focused on SHG, because it is the simplest nonlinear optical process to investigate both theoretically and experimentally. Since the early works on nonlinear optical metamaterials, various shapes of metal nanostructures have been proposed (Fig. 4) including U-shaped split-ring resonators (SRRs),^{45, 46} L-shaped nanoparticles,^{15, 52, 83} G-shaped particles,⁶⁴ noncentrosymmetric dimers,^{16, 34} nanocups,⁹¹ triangles,⁴⁷ and multiresonant structures.^{3, 17, 31, 60, 67} Other nanostructures including nanoapertures in metal films have been also investigated.^{7, 36, 48, 55, 88} Similar to conventional materials, symmetry considerations dictate also the nonlinear responses of metasurfaces, meaning that the local symmetry of individual meta-atoms and the overall symmetry of the array configuration both affect responses. Consequently, noncentrosymmetric structures permitting dipole-allowed SHG responses to occur even at normal incidence have been often investigated. However, in the early works the symmetry was also heavily influenced by fabrication-related defects and deviations in particle dimensions. This, in turn led to low quality of nanostructures [Fig. 4 (b)]. In these

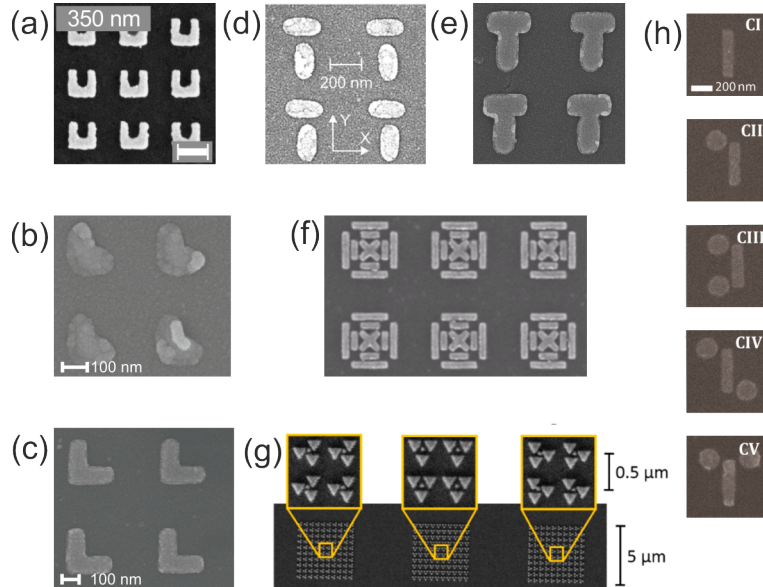


Fig. 4. Examples of arrays of metal nanostructures of different shapes. (a) split-ring resonators, (b) low- and (c) high-quality L-shaped nanostructures. (d) T-shaped dimers and (e) T-shaped particles. (f) multiresonant nonamers, (g) nanotriangles and (h) multiresonant nanoantennas. (a) Reprinted from Ref. 57. Copyright 2012, American Physical Society. (b) and (c) Adapted with permission from Ref. 23. Copyright 2011, Optical Society of America. (d)–(h) Adapted with permission from Refs. 16, 22, 60, 47, 31. Copyright 2007, 2015, 2016, American Chemical Society.

metasurfaces, higher-order multipole effects were also present in the overall effective nonlinear signal.⁵² However, advances in fabrication techniques dissolved such effects allowing to reach the dipole limit.²³

The nanoparticles of shapes such as SRRs or L's, exhibit resonances that are of electric or magnetic property. The latter resonances were suspected to play a significant role in the SHG response of metamaterials.⁴⁶ However, careful investigations of complementary arrays of U-shaped holes in metal films, have led to a conclusion that the role of such resonances is more complicated than initially concluded.²⁹ The role of magnetic contribution to the SHG response has been re-investigated very recently and it has been shown that it is possible to design nanostructures with dominant magnetic Lorentz contribution to SHG.⁷⁵

Already from the beginning, it was obvious that stronger nonlinear responses can be achieved by tuning the fundamental beam to the resonance frequency of the LSPR. Because the quality factors of LSPRs are related also to the fabrication quality of nanoparticles, stronger nonlinear responses were reported along with advances in nanofabrication techniques.²³ In the case of metasurfaces, however, where nanoparticles are periodically arranged into arrays, mutual orientations of particles as well as lattice parameters can play important roles as well. In regular arrays, individual meta-atoms determine the size of the unit cell and the lattice

parameters. Therefore, by changing the nanoparticle arrangement in the array, it is possible to tune these parameters and thus modify related optical properties. This was demonstrated recently by investigating arrays of L-shaped nanoparticles with similar orientational distribution, where changes in detailed ordering of nanoparticles in the array led either to enhancement or suppression of the emitted SHG light (see Fig. 5).³⁵ This effect was enabled by lattice interactions between particles in the array, because varying particle arrangements in the unit cell resulted in changes in the resonance wavelength and thereby in detuning from the wavelength of the incident fundamental beam.

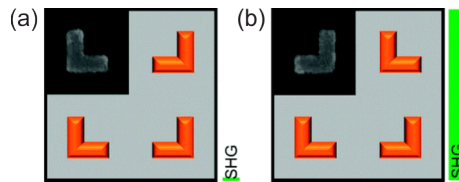


Fig. 5. Metasurfaces of L-shaped nanoparticles with different orientation in the array. Adapted with permission from Ref. 35. Copyright 2012, American Chemical Society.

Lattice interactions were also used to optically couple different types of nanoantennas.¹⁹ In that work, SHG signal from L-shaped nanoparticles was enhanced by combining noncentrosymmetric L-particles with centrosymmetric passive elements not themselves exhibiting noticeable second-order responses (see Fig. 6). Such ideas rely on the fact that metasurfaces effectively act as gratings and are associated with grating-related effects such as Rayleigh and Wood anomalies and diffraction orders (see also section 3.2). Consequently, remarkably narrow resonances can be realized by utilizing SLRs resulting in stronger resonance-enhancement factors. In fact, changing the lattice constant is the simplest way to tune the spectral positions of diffraction orders and modify resonances. However, such an approach has some limitations due to dilution effects and/or broadening of resonance when the lattice constant becomes too large or too small.^{26,57} As a result, SHG emission experiences non-monotonic conversion efficiency with respect to the lattice constant.^{57,86}

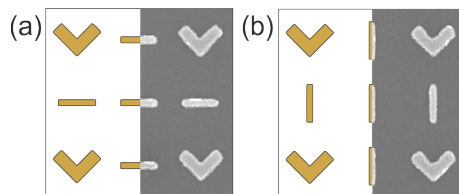


Fig. 6. (a) and (b) Metasurfaces of SHG-active L-shaped nanoparticles combined with SHG-passive elements (nanobars). Adapted with permission from Ref. 19. Copyright 2013, American Physical Society.

Spectral positions of diffraction orders and Rayleigh anomalies can also be tuned by changing the angle of incidence of the fundamental beam. This fact allows to investigate more deeply the effect of SLRs on the nonlinear response already from a single metasurface sample. A modest around 10-fold enhancement of SHG emission was reported early on from a non-optimized surface.²¹ Later, around 30-fold SHG enhancement was demonstrated by using a metasurface consisting of SRRs [see Figs. 7(a) and (b)].⁶⁸ Interestingly, the reported enhancement was achieved by designing the metasurface to exhibit a Rayleigh anomaly and a subsequent SLR at the SHG frequency, demonstrating the usefulness of the LSA (see section 3.2). Promisingly, around 450-fold SHG enhancement has been very recently reported using a metasurface consisting of silver nanoparticles [see Fig. 7(c)].³³ In overall, these few examples and the rapid improvement in the achieved SHG enhancement factors imply that lattice effects could be utilized to realize considerably more efficient nonlinear metasurfaces, as has been recently proposed.³⁸

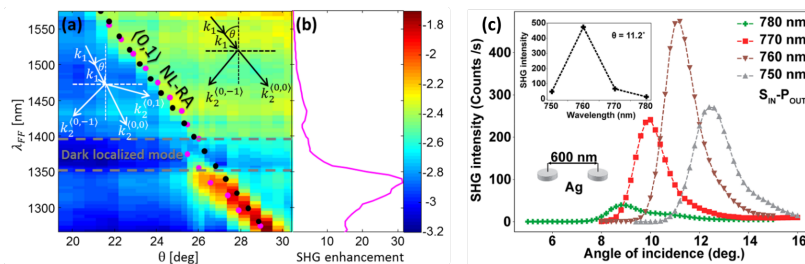


Fig. 7. SHG emission and nonlinear Rayleigh anomaly (NL-RA). (a) Measured zero-order SHG emission as functions of the fundamental wavelength and the incident angle θ . The black dots indicate the NL-RA of $\langle 0, 1 \rangle$ order, and the magenta dots indicate the strongest measured response at each wavelength. The arrow diagrams demonstrate the existing diffraction modes in both sides of the NL-RA. (b) SHG enhancement along the position of strongest measured emission relative to normal incidence. Adapted from Ref. 68. Copyright 2017, American Physical Society. (c) Enhanced SHG at different fundamental wavelengths for silver nanoparticle array with period of 600 nm. Strong enhancements follow the angles of incidence that correspond to a Rayleigh anomaly induced SLR at the fundamental wavelength. Adapted with permission from Ref. 33. Copyright 2018, American Chemical Society.

5. Outlook and conclusions

Looking at the extensive amount of work discussed in this review, it is evident that nonlinear plasmonic metasurfaces have attracted considerable scientific interest over the last few years. Despite rapid progress, several challenges should be solved before metasurfaces can start rivalling traditional nonlinear materials and their use in applications. Even the highest conversion efficiencies reported so far ($\sim 4.5 \times 10^{-3}$, see Ref. 69) are still too low for practical frequency conversion applications. However, we are optimistic to see further progress in the future, especially by metasurfaces utilizing lattice effects, since so far only a few works exist.^{20, 33, 38, 68}

It should also be possible to further improve the performance of nonlinear metasurfaces by realizing nanostructures that could sustain orders-of-magnitude stronger pumping conditions (up to 10 GW/cm²) compared to the currently often used peak intensities of the order of 10–100 MW/cm².¹

The main true advantage of nonlinear metasurfaces over traditional materials is currently their small size. This is because there is a growing interest to add nonlinear functionalities into smaller and smaller photonic components, such as into integrated photonic circuits, which is very difficult by using traditional approaches and materials. Therefore, it can be envisaged that nonlinear plasmonic metasurfaces will find interesting applications once the field progresses even further to help in overcoming this challenge.

To summarize, we do not expect the interest in nonlinear metasurfaces to be in decline. Although major challenges still persist, we are confident that this emerging field is bound to see many new experiments, steady progress and novel applications in the future.

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18 *M. J. Huttunen, R. Czaplicki and M. Kauranen*

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