Recent Progress on Optical Frequency Conversion in Nonlinear Metasurfaces and Nanophotonics

Chen Wang, Yongzheng Wen* Jingbo Sun and Ji Zhou*

Abstract

Frequency conversions, such as second harmonic generation (SHG), third harmonic generation (THG), high harmonic generation (HHG), and wave mixing, are typical processes in nonlinear optics, which have a wide range of applications in new light sources, bioimaging and sensing, quantum optics, and holography. To engineer and manipulate these nonlinear optical processes, metasurfaces and nanophotonic structures have been introduced, which have been successfully demonstrated as powerful tools to tailor the key features of light and excite the extraordinary phenomena in linear optics. In this review, we highlight the recent progress on frequency conversion in plasmonic metasurfaces, all-dielectric metasurfaces as well as other nanophotonic structures, ranging from SHG, THG to HHG and wave mixing. The origin of optical nonlinearity and its coupling with subwavelength resonators are discussed, which fundamentally determine the conversion efficiency and functionality. Finally, we summarize the challenges that nonlinear metasurfaces and nanophotonics now face and offer an outlook on further development and application potential.

Keywords: Nonlinear metasurfaces; Nanophotonic; Nonlinear optics.

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1. Introduction

As the limitations of material design are increasingly exposed, it has become an important task to develop new strategies for material design beyond the limits of conventional material properties. Metamaterial is a kind of artificial material with subwavelength structures as basic functional units, which derive their properties not from the intrinsic properties of the base materials, but from the specific structures. In the past two decades, metamaterials have opened up a new way to further improve the ability to design material properties at will. Metamaterials can achieve many extraordinary physical properties that natural materials do not have. This extraordinary ability to control electromagnetic waves has been proven in the applications of linear optical regimes, such as left-handed metamaterials,[1-5] invisibility cloaks,[6-8] absorbers,[9,12] and metalenses.[13-17] Recently, efforts have focused on the nonlinear responses of metamaterials,[18-27] which play an important role in the implementation of myriad applications, such as new light sources, compact optical information systems, and quantum computing and communications. The differences and applications of linear and nonlinear metamaterials are given in Table 1. The exploitation of nonlinear metamaterials will improve the already remarkable performance of photonic metamaterials as well.

Compared with metamaterials, their two-dimensional counterparts, metasurfaces are easier to achieve by engineering the shape and arrangement of these subwavelength meta-atoms. Micro-and nanofabrication techniques such as photolithography, electron beam lithography and reactive ion etching are commonly used to fabricate conventional metasurfaces. Percolative composites can function as the building block of plasmonic metasurface as well, which will make breakthrough in integrating metasurface with conventional materials and thus decrease the difficulty in designing the geometrical configuration and arrangement mode of metasurfaces,[5] The phase matching requirements, which are crucial for conventional harmonic generation, are greatly relaxed in metasurfaces as the nonlinear processes occur at a thickness much thinner than the coherence length. Various methods have been reported to achieve nonlinear metasurfaces. In the microwave and lower terahertz frequencies, nonlinear elements, such as varactor diodes,[37,38] can be added to the meta-atom. The nonlinear
response of the elements can affect current in the meta-atom, which may be induced by an electric or magnetic field, resulting in a corresponding nonlinear response. In infrared and visible wavelengths, plasmonics with nonlinearity from the metal surface and meta-atoms embedded in nonlinear host media are usually used to form nonlinear metasurfaces.\cite{18,39-43} All-dielectric resonators with high efficiency, low loss, and high optical damage thresholds would also be a promising route to obtaining strong nonlinear responses.\cite{27,44} Among the various nonlinear phenomena, frequency conversion has attracted increasing attention due to its potential in a wide variety of applications, including broadening frequency range,\cite{32,33} generating entangled photon pairs,\cite{34} and nonlinear holography.\cite{35,36}

Table 1. The differences and applications of linear and nonlinear metamaterials.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Linear metamaterials</th>
<th>Nonlinear metamaterials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlation between physical parameters and field intensity</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Frequency conversion</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Energy exchange and phase</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Information transfer between multiple beams</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pump light intensity</td>
<td>weak</td>
<td>strong</td>
</tr>
<tr>
<td></td>
<td></td>
<td>laser mode locking</td>
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<tr>
<td>Applications</td>
<td></td>
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<tr>
<td>Left-handed metamaterials</td>
<td></td>
<td></td>
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<tr>
<td>Invisibility cloaks, absorbers</td>
<td></td>
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<td>Metalenses, and holography</td>
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In this review, we focus on the recent progress on frequency conversion in nonlinear metasurfaces and nanophotonics. We describe the principles and properties of nonlinear metasurfaces in realizing frequency conversion and manipulation, with a particular concentration on second-, third- and high-order harmonic generations and wave mixing. Finally, the progress of nonlinear metasurfaces is summarized and prospected.

2. Theoretical background of nonlinear optical processes

The propagation of light in materials is the process of interaction between light and material systems. If the polarization $P$ responds nonlinearly to the electric field $E$ of the light, the phenomena are in the nonlinear optics regime. The relationship between the nonlinear polarization $P^{NL}$ and electric field $E$ can be expressed in the following power series as:

$$
P^{NL} = \varepsilon_0 \left( \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots + \chi^{(n)} E^n \right)$$

where $\varepsilon_0$ is the vacuum permittivity and $\chi^{(n)}$ is the $n$th-order nonlinear susceptibilities.\cite{45} With increasing field intensity, these nonlinear terms become sufficiently large, and the nonlinear polarization acts as a source for new frequencies owing to the mixing of the pumping waves. The first term in Eq. (1) is related to second-order nonlinear phenomena such as second harmonic generation (SHG), sum frequency generation (SFG), difference frequency generation (DFG) and optical rectification (OR); the second term is related to third-order nonlinear phenomena such as third harmonic generation (THG), four-wave mixing (FWM) and self-focusing. In addition, high harmonic generation (HHG) - phenomena that are related to higher-order terms in Eq. (1) - are also observed with very strong field excitation. As shown in Fig. 1a, the $n$th harmonic generation contains a process in which $n$ photons are combined to generate a single photon with a frequency $n$ times higher than the original value. As shown in Fig. 1b, the FWM is a third-order nonlinear optical phenomenon caused by the interaction of four light waves. The FWM has many interactional forms in materials. When light waves at three different frequencies $f_1$, $f_2$, and $f_3$ are illuminated simultaneously into a material, the FWM can theoretically produce new light waves at frequencies $f_4 = \pm f_1 \pm f_2 \pm f_3$. The frequency of the new light can be selected by tuning the FWM process at proper phase matching conditions, which could be achieved by various methods including using appropriate nonlinear materials, adjusting the wavevectors and polarization states of the pump light. The discovery of SHG is generally regarded as the beginning of the field of nonlinear optics, and one of the most important practical applications of nonlinear optics is to explore new coherent optical frequencies through harmonic generation and wave mixing. Therefore, in the following chapters, we mainly discuss SHG, THG, HHG and wave mixing based on metasurfaces and nanophotonics, including the generation principle, device structure and various performances.

3. Second-order nonlinear processes

Second-order processes are the most fundamental ones in nonlinear optics. Optical nonlinearities in the context of metasurfaces and nanophotonics were also first studied in plasmonic nanostructures for SHG because the interaction between light and matter can be significantly enhanced in the presence of plasmons.\cite{18,46} The split-ring geometry shown in Fig. 2a typically embodies the initial design philosophy of nonlinear metasurfaces, in which the localized surface plasmons resonance (LSPR) at the excitation frequency dramatically enhances the local field and thus improves the second harmonic conversion efficiency.\cite{18} Taking one step further, a higher conversion efficiency of SHG can be
achieved by designing nanostructures resonating at both the excitation and second harmonic frequencies (Fig. 2b). In addition to the LSPR, metasurfaces with surface lattice resonance are also employed to improve the efficiency of SHG. As depicted in Fig. 2c, the split-ring metasurface efficiently generates second harmonic at oblique incidence due to the excitation of surface lattice resonance, which is more than 30 times stronger than those at normal incidence. The second-order nonlinear responses in plasmonic metasurfaces come from the surface nonlinearity of the metal as the bulk metal is centrosymmetric. Although the effective second-order susceptibility may be high, the conversion efficiency is very low due to the nanoscale interaction vicinity, which greatly hinders the practical applications of plasmonic metasurfaces. Metasurfaces combining metal resonators with natural nonlinear host media, such as quantum semiconductors and two-dimensional materials, have been explored to improve nonlinear efficiency. A metasurface coupling doubly resonant structures with multiple quantum wells (MQWs) semiconductor heterostructures is depicted in Figs. 3a and b. Large $\chi^{(2)}$ can be achieved by tuning the energy levels in GaAs/AlGaAs heterostructures and combining MQWs. Combining with the metasurface makes the effective $\chi^{(2)}$ even higher and obtains a SHG power conversion efficiency of almost $2 \times 10^{-6}$ at a pump intensity of 15 kW/cm$^2$, which is 8 orders of magnitude larger than that in any previous devices at that time.

In almost all nonlinear metasurfaces, the optical nonlinear responses are from nonlinear composite materials, while the metasurface structure only enhances the natural nonlinearity, which makes it difficult to directly design and manipulate optical nonlinearity. In recent years, people have paid increasing attention to the intrinsic structural nonlinearity of metasurfaces. Wen et al. proposed a purely artificial optical nonlinear mechanism based on classical electromagnetic interactions in metasurfaces. In the absence of any natural nonlinear materials, the signature second-order nonlinear behavior is generated by the intensive Lorentz force in the metasurface. As shown in Figs. 3c and d, the free electrons in the cut wire interact with the magnetic field generated by the split ring, resulting in anharmonic oscillation under the action of the magnetic force, thus generating a nonlinear response. This purely artificial nonlinear mechanism, which does not involve any photoinduced electronic, thermal, mechanical or quantum processes in natural materials, provides a metamaterial-based approach to the design of nonlinear optical materials.

Plasmonic metasurfaces have been widely used to enhance and control nonlinear optical processes, but their high dissipative losses and Ohmic heating result in lower optical damage thresholds and conversion efficiency. All-dielectric metasurfaces have attracted much attention because of their advantages including low loss, high damage threshold and relatively large nonlinear susceptibility. From the perspective of the compositions, semiconductors and dielectrics, such as AlGaAs, GaAs, GaP, GaSe, (In, Ga)N/GaN MQW, ZnO, and LiNbO$_3$ have all been demonstrated to provide highly efficient SHG in all-dielectric metasurfaces. For the resonant mode, the quasi bound states in the continuum (quasi-BIC) with an ultrahigh quality (Q) factor have been

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Fig. 1 Schematic diagram of nonlinear processes. (a) $n^{th}$ harmonic generation; (b) four-wave mixing.

Fig. 2 Plasmonic metasurfaces for SHG. Schematic diagram of (a) gold split-ring metasurface (Reproduced with the permission from [18]. Copyright 2006 The American Association for the Advancement of Science), (b) V-shaped and rod-shaped nanoantennas and electric field intensity distribution of double resonance (Reproduced with the permission from [47]. Copyright 2015 Springer Nature) and (c) split-ring metasurface with surface lattice resonance (Reproduced with the permission from [49]. Copyright 2017 American Physical Society).
Fig. 3 SHG in metasurface combined metal resonators with semiconductors. (a) Schematic of metasurface coupling doubly resonant structures with MQW semiconductor heterostructures; (b) conduction band diagram of quantum well structure designed for SHG. (Reproduced with the permission from [33], Copyright 2014 Springer Nature). (c) Schematic of the unit cell of a purely artificial optical nonlinear metasurface and (d) its frequency-domain transmission spectra (Reproduced with the permission from [53], Copyright 2017 American Physical Society).

widely used in nonlinear all-dielectric metasurfaces,[55,58,64] and have achieved successful developments in the miniaturization and integration of nonlinear metamaterial devices. Koshelev et al.[27] used the optical constraint mechanism of quasi-BIC to obtain enhanced SHG in a nanoscale subwavelength AlGaAs independent cylindrical resonator (Figs. 4a and b). A cylindrical vector beam with azimuthal polarization matches the spatial profile of the pump with the distribution of the excitation mode. The all-dielectric resonator simultaneously resonates at the pump (quasi-BIC with a Q-factor close to 200) and SHG wavelengths (high-order Mie mode), thus the SHG conversion efficiency $\eta_{\text{SHG}} = 4.8 \times 10^{-5}$ W$^{-1}$ is observed. This

Fig. 4 SHG in all-dielectric resonators. (a) Diagram and (b) experimentally measured SHG for a AlGaAs nanoresonator (Reproduced with the permission from [27], Copyright 2020 The American Association for the Advancement of Science). (c) The symmetry breaking of the resonator surface and the electrical multipole response in the bulk induced SHG; (d) measured second harmonic spectrum (red) and the corresponding pump (black) (Reproduced with the permission from [65] Copyright 2018 Springer Nature). Schematic of the resonator (e) and photogalvanic SHG with perfect phase matching in a microring (f) (Reproduced with the permission from [66], Copyright 2021 Springer Nature).
method of using subwavelength dielectric resonators to significantly enhance the light-matter interaction has a wide range of applications in the fields of nanometer lasers, quantum photons and sensors, and provides a platform for the development of integrated nonlinear nanophotonic devices.

Technologically important silicon-based materials (e.g., SiO\(_2\), Si, Si\(_3\)N\(_4\)) essentially lack bulk second-order nonlinear responses due to their centrosymmetric crystalline structure, and only present weak \(\chi^{(2)}\) at the surface. Therefore, the chip-scale integration of nonlinear applications has become a very challenging topic. Xiao et al.\(^{[65]}\) prepared silica whispering-gallery optical microcavities with an ultrahigh Q factor (Figs. 4e and f). A strong second-harmonic signal was observed experimentally with a conversion efficiency as high as 0.049% W\(^{-1}\). Lu et al.\(^{[66]}\) achieved SHG in silicon nitride by combining photoinduced effective \(\chi^{(2)}\) with resonant enhancement and perfect phase matching (Figs. 4e and f). The conversion efficiency reaches \((2500 \pm 100)\%\) W\(^{-1}\), which is two to four orders of magnitude larger than previous works in typical silicon-based materials. All these researches realize efficient \(\chi^{(2)}\) in silicon photonics and promote the further integration of self-reference frequency combs and ultrasensitive surface analysis.

In addition to SHG, metasurfaces are also widely used in other second-order effects, such as SFG, DFG and OR\(^{[67-72]}\). As noted above, semiconductor heterojunctions with MQWs are integrated with resonators as metasurfaces, yielding giant nonlinear responses in ultrathin devices. However, the strongly enhanced light-matter interaction on the metasurface promotes electron transition into the excitation subbands, leading to nonlinear saturation, which fundamentally limits the efficiency of various nonlinear processes. Nefedkin et al.\(^{[73]}\) optimized designs for excitations with a strong pump coupled with unpopulated upper electron subbands and a weak signal coupled with ground and excited states (Fig. 5a). The saturation limits of MQW-based metasurfaces are markedly extended, which provides an upconversion efficiency more than 10 times higher than the conventional techniques based on strong resonant pumping of the optical transition between the ground and excited states. However, this method is not applicable for SHG, THG or HHG. In this case, the signal and the pump are at the same photonic energy, which cannot achieve strong pump light only to excite the transition between unpopulated upper electron subbands, and the low saturation limit of the MQW remains. Figs. 5b and c show a rapidly time-variant metasurface as a platform for frequency up and down conversions.\(^{[68]}\) Ultrafast light excitation merges two distinct metallic meta-atoms into one, creating a spectrally designed temporal boundary that thus achieves frequency up and down conversion. For metasurfaces supporting OR effects, femtosecond laser pumped high performance terahertz sources are a hotpot due to their important application prospects in material inspection, imaging, and biomedical science. McDonnell et al.\(^{[71]}\) proposed a functional terahertz emitter based on the Pancharatnam-Berry phase (Fig. 5d). By precisely designing the principal axis and array of the metasurfaces, they demonstrated few-cycle terahertz pulses generation with controllable polarization states and wave vectors, providing an alternative method for building functional terahertz sources.

4. Third-order nonlinear processes

Similar to SHG, metasurfaces achieve efficient THG and harmonic manipulation by combining the nonlinearity of the material with various types of resonances, such as multipole interference between magnetic dipoles and electric quadrupoles,\(^{[74]}\) magnetic dipole,\(^{[75]}\) toroidal dipole,\(^{[76]}\) anapole mode,\(^{[77-79]}\) and Fano resonance.\(^{[80]}\) As shown in Fig. 6a, Li et al.\(^{[81]}\) achieved ultrafast highorder nonlinear processes in silicon metasurfaces. By designing the principal axis and array of the metasurfaces, they demonstrated few-cycle terahertz pulses generation with controllable polarization states and wave vectors, providing an alternative method for building functional terahertz sources.

**Fig. 5** (a) Schematic of SFG with a strong pump coupled with the upper two electron subbands. (b) Schematic of the time-variant metasurface structure; (c) measured amplitude transmission of the time-variant metasurface for various pump fluence levels (Reproduced with the permission from \[68\]. Copyright 2018 Springer Nature). (d) Schematic illustration of a metasurface for generation of spatially separated left circularly polarized and right circularly polarized THz waves (Reproduced with the permission from \[71\], Copyright 2021 Springer Nature).
al[81] constructed nonlinear metasurfaces composed of an organic coating and nanoantennas with rotational symmetry, which realized continuous control of the nonlinear phase for harmonic generations by introducing the geometric phase into the nanoantennas (Fig. 6b). Because both organic coating and nanoantennas produce nonlinear responses and the localized field enhancement of nanantennas enhances the overall nonlinear response efficiency, the THG efficiency in the organic/gold hybrid metasurface is much higher than that from organic- or gold-only devices. These metasurfaces seamlessly combine the generation and manipulation of harmonic waves, providing a platform for highly compact nonlinear devices.

Third harmonics from plasmonic metasurfaces are limited by low conversion efficiency and damage threshold as well. Following the strategy of improving the SHG efficiency, metasurfaces composed of metal resonators and semiconductors, dielectrics or two-dimensional materials open up a new way to improve the conversion efficiency of THG[76,82,84-86]. As the third-order effects are not restricted by symmetry and possessed in all materials, people actively introduce silicon into the metasurface. Shibanuma et al.[82] built a nanostructure with Au and silicon, as illustrated in Figs. 6c and d. The Au nanoring with plasmonic resonance can enhance the anapole mode of a Si nanodisk, strongly boosting the electric field inside the dielectric. Hence, the third harmonic conversion efficiency of 0.007% is obtained, which is three orders of magnitude larger than that of the isolated Si nanodisk, and that of the bare Au nanoring, respectively. Xu et al.[83] constructed a silicon anapole resonator on a metal mirror (Figs. 6e and f). The Cartesian electric and toroidal dipole moments overlap near field enhancement and the nonlinear source of the mirror image under the interface achieve an efficient conversion efficiency of 0.011%.

All-dielectric resonators can effectively confine the electromagnetic field below the diffraction limit and enhance the localized field within the resonator, thus maximizing the volume of nonlinear interaction.[44,75,87,88] Thus, the THG of all-dielectric metasurfaces, especially the silicon-based ones, have received extensive attention and in-depth research. Shecherbakov et al.[87] observed a blue-shifted THG by excitation of high-Q collective resonances in the metasurface, demonstrating for the first time the photon acceleration on the ultrathin silicon metasurface (Figs. 7a and b). In this study, tunable broadband THG is realized, and the nanostructures of photon acceleration also represent a new time-varying nonlinear photon platform, which can be found in a variety of applications in new pulsed light sources. As amorphous silicon can be conveniently deposited on various substrates, advanced functions can be achieved in the metasurface, which is more than simple generation of third harmonics. One typical example is nonlinear optical topological nanophotonics. Nonlinear optical topological structures can adjust the light intensity to tune topological properties and break optical reciprocity to achieve full topological protection.[89-95] As shown in Fig. 7c, the third harmonic enhanced by multipole Mie resonance of hydrogenated amorphous silicon cylinders has been observed in two-dimensional photonic crystal metasurfaces,[89] where the topological states are protected on the boundary of the shrinking and expanding hexamers region. By changing the wavelength of the incident fundamental wave, the third-order nonlinearity of the body and boundary states can be characterized, and the propagation direction of the boundary state depends on the polarization state of the third
Fig. 7 (a) Schematic of the sample and the MIR beam setup; (b) experimentally measured THG in the metasurface (blue curve) and in an unstructured Si film (black curve) (Reproduced with the permission from [87], Copyright 2019 Springer Nature). (c) The variation in the fundamental wavelength realizes the third harmonic nonlinear characterization of body state and boundary state (Reproduced with the permission from [90], Copyright 2019 American Physical Society). (d) Illustration of the third-harmonic signal from topological zigzag arrays (Reproduced with the permission from [91], Copyright 2019 Springer Nature).

A strong enhancement of THG at the edge states was also observed in a topologically non-trivial zigzag array of amorphous silicon disks (Fig. 7d) [91]. The signal enhancement is attributed to the interaction between the topological localization of the electric field at the edge and the Mie resonance of the silicon disks. In addition, the system with high robustness can resist a variety of interference and structural defects. This research facilitates the development of nanoscale integrated and robust photonic circuits.

In addition to the THG, wave mixing phenomena, such as FWM and degenerate FWM, in metasurfaces have also drawn great interest as they generate light with more new frequencies [96-98]. Suchowski et al. [22] reported a zero-index optical metasurface, which is a stack of metal-dielectric multilayers with perforated holes (Figs. 8a and b), and degenerate FWM can be efficiently generated in this fishnet metasurface. Particularly, the zero refractive index feature of the metasurface removes the requirement for phase matching and allows the FWM to occur efficiently in both forward and backward directions. Almeida et al. [99] demonstrated full phase control of FWM in plasmonic metasurfaces, as illustrated in Fig. 8c. By changing the aspect ratio of the nanoholes, the direction of forward FWM can be tailored while maintaining the FWM intensity. Liu et al. [97] took advantage of the large nonlinear coefficient in gallium arsenide (GaAs) and the enhanced localized field and the relaxed phase matching requirements in metasurface to simultaneously induce SHG, THG and fourth harmonic generation, SFG, two-photon absorption-induced photoluminescence, FWM and six-wave mixing. They demonstrated that all-dielectric frequency mixers generate eleven new frequencies ranging from ultraviolet to near-infrared, as illustrated in Figs. 8d and e.

5. High-order nonlinear processes
By keeping increasing the driving field of light, nonlinear optical systems reach high-order regime, and HHG is the most typical phenomenon. The understanding of HHG processes in noble gases has played a key role in the development of attosecond science. In recent years, high-order harmonics have also been found in mixtures of gases and solids [19] and pure solids [99,100], which provide a new way to study novel strong field optical effects that are difficult to achieve in gases. Considering the success in second- and third-order regimes, metasurfaces are expected to achieve efficient generation of high harmonics [101-104] with localized enhanced fields of various resonances. Due to its high damage threshold and significant local field enhancement capability, all-dielectric metasurfaces were first studied as promising candidates for HHG and other high-order nonlinear interactions in solids. Sivis et al. [25] explored efficient and controllable HHG in
solid-state by constructing zinc oxide nanostructures and selective ion implantation of silicon (Figs. 9a-c). The total internal reflection on the zinc oxide cone wall leads to local field enhancement, which results in enhanced HHG at the hotspot. The implanted zones of silicon can produce stronger HHG than the unmodified zones, so a rational design forms a Fresnel zone plate, which focuses the high harmonics. These two different methods (adjusting the geometry or composition) provide a reference for new HHG devices in solid state. A series of monopole Au nanoantennas in silicon were designed to demonstrate plasma-assisted HHG, and up to 9th harmonics were observed. [103] Enhanced non-perturbative HHG of silicon metasurfaces based on Fano resonance has also been reported (Fig. 9d). [32] The three-level Fano-resonant system is a classic analog of electromagnetically induced transparency (Fig. 9e), which enhances the localized electric field and the HHG (Fig. 9f).

It should be noted that all these higher-order processes are essentially from nonlinear media instead of metasurfaces or nanophotonics, and studies of HHG metasurfaces mainly focus on the near infrared and visible regimes, and most of them only present odd-order harmonics. In 2018, graphene showed unusually large high-order nonlinearity at terahertz frequencies, which is the first demonstration of terahertz HHG. [105] Soon after, Deinert et al. [86] combined graphene with photonic grating structures that provide localized field enhancement to realize terahertz HHG. The fifth and seventh harmonics can be easily obtained in graphene by using the localized field enhancement effect of the metasurface (Figs. 9g and h). By introducing gallium phosphide (GaP) with a lack of inversion symmetry, Scherbakov et al. reported the generation of even and odd high harmonics in an ultra-thin resonant metasurface (Figs. 9i and j). [106] Before that, a theoretical method of generating even and odd high harmonics based on the artificial nonlinearity in metasurfaces was proposed. [104] Despite these pioneering works, many challenges still remain in HHG metasurfaces, such as tailoring the harmonics at will, exceeding the record of harmonics orders with the help of nanostructures, and HHG metasurfaces for advanced applications such as attosecond lasing and extreme ultraviolet (EUV) sources.

6. Summary and perspectives
Metasurfaces have been developed rapidly because of their exciting nonlinear phenomena and emerging applications in many important fields. In this review, we investigate major advances in the field of nonlinear metasurfaces and nanophotonics, with emphasis on SHG, THG, HHG, and wave mixing. Some representative results of nonlinear metasurfaces and nanophotonics are summarized in Table 2. In the early stage, plasmonic metasurfaces were a powerful platform for nonlinear processes due to the localized field enhancement and the interaction between surface electrons and light. However, the low damage threshold and small interaction volume of metal lead to a low conversion efficiency, greatly limiting its practical application in nonlinear optics. The conversion efficiency of the metasurface that integrates two-dimensional materials or MQW semiconductor heterojunctions with metal resonators is enhanced compared with those of plasmonic metasurfaces, and the saturation limitation of frequency upconversion in the MQW-based metasurfaces is also alleviated to a certain extent, but the metal
damage threshold is still low. At present, all-dielectric resonators with high damage thresholds, large interaction volumes and local field improvement have become a research hotspot.
Nonlinear metasurfaces and nanophotonics are emerging research fields whose potential in basic science and technical applications has not been fully developed. Their developments mainly face the following challenges: (i) Bandwidth. Metasurfaces usually amplify nonlinear processes by the localized field enhancement of resonance. The nature of resonance inevitably leads to the narrow bandwidth, which limits the broadband applications of nonlinear metasurfaces. (ii) Conversion efficiency. Although the ultra-thin thickness of the metasurface relaxes the requirement of phase matching, it also reduces the interaction length of light and materials, which limits the nonlinear conversion efficiency to some extent. Compared with natural nonlinear crystals, the low efficiency seriously hinders the practical application of nonlinear metasurfaces. (iii) Response. Higher conversion efficiency can be obtained by using resonant modes with a higher quality factor, but it is often accompanied by the slow response time, which limits the application of metasurfaces in high-speed optical information processing. The key points of research on nonlinear metasurfaces and nanophotonics are to solve the above three contradictions and realize tailored bandwidth, high efficiency and high-speed nonlinear responses. In addition, fabrication techniques and system compatibility will affect the development of nonlinear metasurfaces applications. The majority of nonlinear metasurfaces work at short wavelength regimes, such as near-infrared and visible light. They usually require micro-and nanofabrication techniques, making materials with good fabrication compatibility, for instance Si\textsubscript{3}O\textsubscript{2}Si\textsubscript{7}, GaAs\textsubscript{1}, LiNbO\textsubscript{3}\textsuperscript{62,63} more feasible to fabricate metasurfaces. However, those materials cannot fulfill all the performance requirements. The nanofabrication technologies of materials with large nonlinear susceptibilities, such as potassium dihydrogen phosphate (KDP) and barium borate (BBO), still need to be further explored. High compatibility of nonlinear metasurfaces with existing optical system ensures that the nonlinear metasurfaces could be implemented in a variety of equipment without too much modification. It requires that metasurfaces comply with certain standardized designs to ensure that the pumping mode, detection mode, and operating environment of metasurfaces are compatible with existing optical systems. Metasurfaces made of advanced materials, such as topological insulators or twisted two-dimensional materials\textsuperscript{107-110} may be used to overcome those challenges owing to their rich potentials. Artificial nonlinearity generated by the metasurface instead of the nonlinear composite may also open up a new path due to its high design freedom. Nonlinear metasurfaces and nanophotonics will grow rapidly in the coming years, driven by a deepening understanding of nonlinear physical processes and advances in materials science and manufacturing technology. Current and future technologies will allow the creation of even finer metasurfaces that have broad applications in on-chip integrated devices such as subwavelength optical laser sources, deep subwavelength optical imaging, ultrafast optical switching, and ultra-small frequency combs.

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Conflict of Interest
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Supporting Information
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References
Author Information

**Chen Wang** received her B.S. degree from Tsinghua University at 2018. She is currently studying for a PhD degree of Materials Science and Engineering at Tsinghua University. Her research focuses on nonlinear metasurface.

**Yongzheng Wen** is an associate professor of Materials Science and Engineering at Tsinghua University. He received his B.S. degree from Sichuan University at 2010 and Ph.D. from Peking University at 2015. His research interests include metamaterials, nonlinear optics, infrared and terahertz technologies, and micro/nano electromechanical systems. In recent years, he has published over 40 papers and presided over 5 national projects.

**Jingbo Sun** is an associate professor of Materials Science and Engineering at Tsinghua University. He received his B.S. degree from Jilin University at 2007 and Ph.D. from Tsinghua University at 2012. His research focuses on optical metamaterials. He has published more than 60 papers and 1 academic monographs, and won the second prize of National Award of Natural Science as the fourth accomplisher.

**Ji Zhou** is Professor of Materials Science and Engineering at Tsinghua University, and Academician of Chinese Academy of Engineering. He received his B.S. degree from Jilin University at 1983, and Ph.D. from Peking University at 1991. He has engaged in the research of metamaterials, photonic materials, as well as functional ceramic materials and devices. He has published over 400 papers and hold over 50 patents. He is the chairman of the Academic Committee of the State Key Laboratory for New Ceramics and Fine Processing, the chairman of the Metamaterial Branch of the Chinese Materials Research Society (C-MRS), the chairman of the Science and Technology Committee of the China Electronic Components Industry Association.

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