Tailoring of the polarization-resolved second harmonic generation in two-dimensional semiconductors

Abstract: Second harmonic generation is a non-linear optical phenomenon in which coherent radiation with frequency \( \omega \) interacts with a non-centrosymmetric material and produces coherent radiation at frequency \( 2\omega \). Owing to the exciting physical phenomena that take place during the non-linear optical excitation at the nanoscale, there is currently extensive research in the non-linear optical responses of nanomaterials, particularly in low-dimensional materials. Here, we review recent advancements in the polarization-resolved second harmonic generation properties from atomically thin two-dimensional (2D) crystals and present a unified theoretical framework to account for their nonlinear optical response. Two major classes of 2D materials are particularly investigated, namely metal chalcogenides and perovskites. The first attempts to tune and control the second harmonic generation properties of such materials via the application of specific nanophotonic schemes are additionally demonstrated and discussed. Besides presenting recent advances in the field, this work also delineates existing limitations and highlights emerging possibilities and future prospects in this field.

Keywords: second harmonic generation; 2D materials; 2D chalcogenides; 2D perovskites; nanophotonics

1 Introduction

Second harmonic generation (SHG) was first demonstrated in 1961 by Franken et al. in crystalline quartz [1]. SHG is a non-linear optical (NLO) phenomenon in which coherent radiation with frequency \( \omega \) interacts with a non-centrosymmetric material and produces coherent radiation at frequency \( 2\omega \). Nowadays, there is extensive research for microscale and nanoscale materials that show NLO optical responses, namely low-dimensional NLO materials. Numerous studies are performed in the SHG optical properties of low-dimensional materials [2]. Such materials are key to developing future photonic and optoelectronic devices that offer high SHG efficiency, low energy usage, and very small size. Recently, two-dimensional (2D), atomically thin, materials have shown great potential for use in the development of such optoelectronic devices. To date, SHG is identified in numerous such 2D crystals and several reviews are addressing their NLO properties [3]–[8].

Nonlinear optics encompasses a wide range of applications, including photon generation, manipulation, transmission, detection, and imaging. Nonlinear optical phenomena occur in the presence of intense light, and they have been a subject of intense study of numerous NLO effects. NLO plays a crucial role in various applications such as laser frequency conversion, ultrashort pulse laser generation, terahertz (THz) wave generation, optical switches, photodetectors, and optical modulators [9]–[13]. To facilitate these applications, the development of nonlinear optical materials is essential [14]. The bulk NLO materials exhibit issues with a low nonlinear coefficient and suboptimal conversion efficiency [11]. This limitation is crucial when...
integrating them into miniaturized photonic and optoelectronic devices.

Over the past few decades, there has been a growing interest in 2D materials as NLO materials [2]–[13]. For more than a decade, 2D materials have been a hot topic owing to their unique material features, ultra-thin scale, and outstanding linear and nonlinear optical capabilities that make them ideal for a wide variety of device applications. After discovering graphene in 2004, many efforts have been made to uncover the SHG physics in 2D materials. Continuous advancements in preparation methods and growth techniques for 2D materials have enabled high-quality and large-scale production, which provides favorable conditions for commercial use [14].

In 2009, the graphene’s exceptional saturable absorption characteristics were presented [15]. Since then, various research teams have experimentally confirmed the optical nonlinearity of 2D materials and demonstrated numerous impressive nonlinear optical devices based on 2D materials [2]–[13], [16]–[19]. In the last decade, transition metal dichalcogenides (TMDs) have gained significant attention because of their unique physical properties, such as high exciton binding energies [20], [21], direct bandgap in the visible and IR ranges [22], [23], and naturally occurring intrinsic valley polarization [24]. In 2013, researchers began to investigate SHG in TMDs [2]–[13]. The research of SHG is also conducted in various 2D materials. SHG in 2D materials is a result of confining electrons within an atomically thin plane, which induces a pronounced second-order nonlinear optical response. SHG research on TMDs attracted the attention of many researchers due to the following features. First, their 2D crystal structure is non-centrosymmetric enabling SHG processes, which is not the case in graphene [9]. Second, there are numerous possibilities for TMD homo- and heterostructures with strong and tunable SHG responses [2]–[13]. Last but not least, SHG in TMDs is a rapidly developing area with a lot of novel physics, such as valley selective SHG, controlling the SHG in bilayers by tuning the twist-angle, Moiré nanostructures and polaritons [2]–[13], [25]. Furthermore, it has been demonstrated that the excitonic states in TMDs are highly correlated with the SHG response delivered by TMDs and their heterostructures [26]. The integration of resonant nanostructures with TMDs has also attracted a great deal of attention as they enhance the SHG from TMDs [27]. In addition, several other factors, including strain, electric gating [25], excitonic resonance, unusual optical resonances [28], phase and edge modulation [29], also have been used to manipulate the SHG in TMDs.

Here, we review recent advancements in the polarization-resolved SHG (P-SHG) signals from such atomically thin crystals, placing emphasis on the fundamental unified theoretical framework of nonlinear optics for P-SHG measurements that is applied to the latest literature reports. In particular, we investigate recent advancements on how the P-SHG technique is used in two major classes of 2D materials, namely metal chalcogenides and perovskites, as an effective characterization method. Furthermore, first attempts to tune and control the SHG properties via nanophotonic schemes are presented and discussed.

2 Second harmonic generation in 2D transition metal dichalcogenides and 2D metal monochalcogenides

The field of 2D materials initiated in 2004, when Konstantin Novoselov and Andre Geim used Scotch tape to strip, for the first time, monoatomic thickness graphene from graphite [30]. Shortly after the discovery of graphene, the 2D materials family grew bigger with the introduction of the 2D transition metal dichalcogenides and the introduction of 2D metal monochalcogenides.

Group IV metal monochalcogenides, denoted by MX with M = Sn, Ge and X = S, Se, are a class of layered, orthorhombic (mm2 point symmetry group), semiconducting 2D materials attracting significant interest [31]–[33]. They are known as phosphorene analogues [31]–[34], since they share similar puckered or wavylattice structures with phosphorene, a 2D format of black phosphorus [35], [36]. The in-plane structural anisotropy of MXs, with puckered structure along the armchair direction [33] induces in-plane anisotropic physical properties [31]–[33], [37], [38]. A plethora of properties have been reported to exhibit in-plane anisotropic response, including carrier mobility [37], optical absorption, reflection, extinction, refraction [38] and Raman spectral behavior [31]. The in-plane anisotropic response is exhibited along the distinguished in-plane armchair and zig-zag crystallographic directions, offering an additional degree of freedom in manipulating their properties [31]–[33], [37], [38].

On the other hand, the 2D TMDs are direct bandgap semiconductors and they follow the formula MX2, where M is: Mo or W, and X counts for: S, Se, or Te. These 2D TMDs exhibit diverse band structures and demonstrate distinctive optical, electrical, and mechanical characteristics. They offer a basis for ongoing advancements across various fields of research and hold significant potential for the development of ultra-thin, low-power transistors [39].
Moreover, 2D TMDs show inequivalent valleys at the corners of the Brillouin zone, leading to new valley degree of freedom [40]–[42]. Additionally, the strong quantum confinement at the atomic level renders the SHG response of 2D TMDs highly sensitive to the number of layers, ranging from one single layer to the bulk form [43]–[45]. In 2D crystals the atoms are arranged into a periodic pattern that is described by various types of crystal symmetries [46]. The crystal symmetry is essential in determining the physical properties of materials. Therefore, a key objective in the study of 2D materials is to determine the crystal symmetry and identify the armchair direction of the crystal. In contrast to conventional X-ray diffraction (XRD) and transmission electron microscopy (TEM) methods, the all-optical second harmonic generation (SHG) offers minimally-invasive means to examine 2D materials, bypassing complex sample preparation processes (e.g. transfer in a TEM grid etc.). SHG is a second-order NLO process that occurs in non-centrosymmetric materials [47]. For example, TMD monolayers lack inversion symmetry and produce strong SHG signals [48], [49]. The TMD monolayers with in-plane threefold rotational symmetry, belong to the D$_{3h}$ crystal symmetry group. In Table 1 typical $\chi^{(2)}$ values are presented [2].

Quantifying and modelling the SHG signals intensity in 2D materials requires accounting for various physical phenomena. For example, the SHG intensity from 2D materials is affected by the boundary conditions, due to the confinement of electrons that can significantly alter the electronic states and, consequently, the nonlinear optical response. For example, grain boundaries may exhibit electronic and optical properties completely different from the rest of the material [9]. On the other hand, resonant enhancement of SHG can occur when the incident or second harmonic frequency matches the electronic or phononic resonances of the material. This resonance can lead to a substantial increase in SHG intensity. For example, SHG resonance at about 1,310 nm is observed on the atomic edges of monolayer MoS$_2$ [50]. The nonlinear optical susceptibility is significantly enhanced when the real energy level is in the vicinity of virtual states that are involved in the nonlinear optical process as density of states dramatically increase [25]. Additionally, the choice of substrate can affect the SHG signal due to changes in the local field enhancement and interference effects. For example, a significant enhancement of SHG can be achieved by placing a monolayer of 2D material on a photonic moiré superlattice made from dielectric materials. The local field enhancement at the resonance modes of the moiré superlattice can dramatically boost the SHG response. For instance, a MoS$_2$ monolayer on a photonic moiré superlattice showed an SHG conversion efficiency orders of magnitude larger than that from a monolayer on a flat dielectric slab [51]. The choice of substrate material affects the SHG signal. For example, an SHG enhancement was observed when comparing fluorine-doped tin oxide and glass as substrates. This indicates that the substrate’s optical properties can significantly influence the SHG intensities [52]. Additionally, metal nanostructures can enhance SHG through surface plasmon resonance. This enhancement occurs because the central symmetry at the interface of two centrally symmetric media is disrupted, leading to the generation of a second harmonic signal at the interface layer [53]. Moreover, the use of high numerical aperture (NA) objectives focuses the incident light into a tight spot, increasing the local field intensity and enhancing the SHG signal. However, high NA objectives can also introduce aberrations and distortions in the beam profile altering the field distribution and affecting the SHG measurement. These distortions can affect the uniformity and intensity of the SHG signal across the 2D material [54]. In summary, quantifying the SHG intensity in 2D materials requires a comprehensive understanding of the material’s properties and the experimental conditions.

SHG signals are coherent with well-defined polarizations, thus polarization-resolved measurements enable the extraction of additional information than SHG intensity only measurements [55], [56]. In particular, P-SHG measurements provide information about the direction of the crystal armchair direction and crystal homogeneity [49], [57]–[63] grain boundaries [48], [64] stacking sequence and twist-angle [65], [66], number of layers [59], [62] in plane

<table>
<thead>
<tr>
<th>2D Material</th>
<th>Crystal symmetry</th>
<th>$\chi^{(2)}$ ($10^{-12}$ m/V)</th>
<th>SHG wavelength</th>
<th>Substrate</th>
<th>Thickness</th>
<th>Fabrication method</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnS</td>
<td>mm$^2$</td>
<td>1.37</td>
<td>450 nm</td>
<td>MgO</td>
<td>~30 nm</td>
<td>MBE</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>D$_{3h}$</td>
<td>105</td>
<td>405 nm</td>
<td>SiO$_2$/Si</td>
<td>1L</td>
<td>Exfoliation</td>
</tr>
<tr>
<td>MoSe$_2$</td>
<td>D$_{3h}$</td>
<td>50</td>
<td>810 nm</td>
<td>SiO$_2$/Si</td>
<td>1L</td>
<td>CVD</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>D$_{3h}$</td>
<td>4500</td>
<td>415 nm</td>
<td>SiO$_2$/Si</td>
<td>1L</td>
<td>Exfoliation</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>D$_{3h}$</td>
<td>100</td>
<td>775 nm</td>
<td>SiO$_2$/Si</td>
<td>1L</td>
<td>Exfoliation</td>
</tr>
<tr>
<td>MoTe$_2$</td>
<td>D$_{3h}$</td>
<td>2500</td>
<td>775 nm</td>
<td>SiO$_2$/Si</td>
<td>1L</td>
<td>Exfoliation</td>
</tr>
</tbody>
</table>
anisotropy [67], valley polarization [68], [69] and strain [70], [71].

2.1 Layer-dependent SHG in 2D transition metal dichalcogenides

The MX₂ crystal comprises two honeycomb sublattices – one comprising M atoms and the other X atoms – shifted relative to each other; therefore, in its bulk form, the 2H-MX₂ crystals are inversion symmetric (for an even number of layers), belonging to the D₆h symmetry group, characteristic of the Bernal-stacked trigonal prismatic structure (Figure 1(a)) [60]. However, this symmetry is broken for an odd number of layers due to stacking termination along the c-axis, resulting in non-centrosymmetric unit cell (3R stacking Figure 1(b) [60]) that give rise to SHG. In the case of odd layers unit cell, an individual layer of M atoms with threefold symmetry is hexagonally packed between two trigonal atomic layers of X atoms, resulting in a hexagonal honeycomb lattice, where the M and X atoms are located at alternate corners of the hexagon (Figure 1(c) [62]). Therefore, the MX₂ monolayer belongs to the D₃h point symmetry group, with broken inversion symmetry along the armchair direction (Figure 1(d) [62]). The lack of inversion symmetry in the monolayer

Figure 1: Layer-dependent SHG in 2D TMDs. (a) Schematic of the crystal structure of 2H-MoS₂ (two-layer unit cell). The side projection shows the flipped orientation of each layer and the anti-parallel orientation of the SHG dipoles that cancel the SHG. (b) Crystal structure of 3R-MoS₂ (three-layer unit cell). The layers are oriented in such a way that the dipoles are parallel allowing for production of SHG. (c) Schematic representation of the structure of 3R-TMDs, containing three sublattices, with a plane of metal atoms being hexagonally packed between two planes of chalcogen atoms. (d) Top view where the armchair and zig-zag directions are drawn. Non-centrosymmetry and thus the production of SHG originates from the interchange of halogen/metal atoms in the armchair crystal direction. (e) Optical image of the 3R-MoS₂ crystal, where the number of layers are seen on top of the corresponding areas and mapping of the produced SHG. (f) SHG intensity of the 3R and 2H-MoS₂ normalized to the respective single-layer intensity. The dependence of the SH intensity is squared with relation to the layer number in the 3R crystal, while it oscillates with number of layers in the 2H crystal. (a), (b), (e), (f) are reprinted with permission from [60]. Copyright 2016. Springer Nature. (c), (d) are reprinted with permission from [62]. Copyright 2020. Institute of Optics and Electronics, Chinese Academy of Sciences.
results in SHG when an intense field is incident on the crystal [57] (Figure 1(e)). For nanoflakes with even layer number, the SHG signals from adjacent layers are cancelled out. Hence, high contrast of SHG intensity between odd and even numbers can be used to characterize parity of number of layers. For odd layers of MX₂ with finite SHG, the exact layer number is further identified by intensity variation of SHG with number of layers [60] (Figure 1(f)). In particular, the induced non-linear dipoles allow for constructive interference of SHG, resulting in quadratic dependent SHG intensity with the number of layers [60] (Figure 1(f)). On the other hand, in 1T’ phase form, the layer dependency of SHG is opposite to that in 2H phase, i.e. even layers of 1T’ crystal produce significant SHG while odd layers with inversion symmetry show negligible SHG [61]. Therefore, the stacking sequence of 2D materials plays an important role in the SHG intensity.

2.2 Pixel-wise mapping of 2D TMDs armchair directions; polarization-resolved SHG and raster-scanning

Polarization-resolved SHG (P-SHG) establishes a relation with the direction of the 2D material armchair crystallographic axes [58]. The optical setup for P-SHG measurements is based on controlled excitation polarization and controlled detection of the polarization of the SHG signals, while raster-scanning is performed using galvanometric mirrors (Figure 2(a)) or moving piezoelectric stages [2]–[8].

In order to describe the interaction of an excitation field with a 2D MX₂ and the subsequent production of SHG, we use the following formalism [59], [62].

Two coordinate systems are schematically shown in Figure 2(b): the laboratory frame (X, Y, Z) and the crystal coordinates (x, y, z), where z \( \equiv Z \). The laser is normally incident on the crystal, and linearly polarized along the sample plane, at an angle \( \phi \) with respect to X laboratory axis. By rotating the half-wave plate, we vary the orientation of the excitation linear polarization, and record the SHG emerging from the sample as function of the polarization angle \( \phi \). The x axis is taken parallel to the armchair direction of the crystal and at an angle \( \theta \) from X (Figure 2(b)).

The excitation field after passing the half-wave retardation plate can be expressed in laboratory coordinates by the vector \( \begin{pmatrix} E_0 \cos \varphi \\ E_0 \sin \varphi \end{pmatrix} \), where \( E_0 \) is the amplitude of the electric field. The expression of this vector in the coordinates system of the 2D crystal can be derived by multiplying the excitation field with the rotation matrix

\[
\begin{pmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta
\end{pmatrix},
\]
giving

\[
E' = \begin{pmatrix} E_0 \cos(\varphi - \theta) \\ E_0 \sin(\varphi - \theta) \end{pmatrix}.
\]

As we saw above, the 3R TMD monolayers MX₂ belong to the D₃h symmetry group [48], [49], [57]–[64] and their intrinsic second-order nonlinear susceptibility tensor, \( \chi^{(2)}_{\text{int}} \) features the following non-zero elements [49], [57]:

\[
\chi_{xxx} = -\chi_{xyy} = -\chi_{xzy} = \chi^{(2)}_{\text{int}}.
\]

As a result, the 2nd order induced polarization is expressed as [59], [62]:

\[
\begin{pmatrix}
p_{x}^{\text{2o}} \\
p_{y}^{\text{2o}}
\end{pmatrix} = \epsilon_0 \chi^{(2)}_{\text{int}} \begin{pmatrix} E^2_x - (E^2_y)^2 \\ 2E_x E_y \\ 2E_x E_z \end{pmatrix},
\]

where, \( \epsilon_0 \) is the permittivity of the free space. Considering that the pump laser beam is polarized along the sample plane, i.e., \( E^2_z = 0 \), Eq. (1) is reduced to:

\[
\begin{pmatrix}
p_{x}^{\text{2o}} \\
p_{y}^{\text{2o}}
\end{pmatrix} = \epsilon_0 \chi^{(2)}_{\text{int}} \left( \begin{pmatrix} E_x^2 - (E_y^2)^2 \\ 2E_x E_y \\ 2E_x E_z \end{pmatrix} \right) = \epsilon_0 \chi^{(2)}_{\text{int}} \left( \begin{pmatrix} \cos 2\theta - \sin 2\varphi \\
\sin 2\theta + \cos 2\varphi
\end{pmatrix} \right).
\]

We then transform Eq. (2) back to laboratory coordinates by multiplying with the rotation matrix

\[
\begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta
\end{pmatrix},
\]

obtaining:

\[
\begin{pmatrix}
p_{x}^{\text{2o}} \\
p_{y}^{\text{2o}}
\end{pmatrix} = \epsilon_0 \chi^{(2)}_{\text{int}} \begin{pmatrix} \cos(3\theta - 2\varphi) \\ \sin(3\theta - 2\varphi)
\end{pmatrix}.
\]

By using a rotating polarizer in front of the detector, we collect the components of the SHG field, described by multiplying with the matrix

\[
\begin{pmatrix} \cos^2 \zeta & \sin \zeta \cos \zeta \\ \sin \zeta \cos \zeta & \sin^2 \zeta
\end{pmatrix}.
\]

Here, \( \zeta \) is the angle of the transmission axis of the polarizer with respect to X-axis.

Then, the intensity of the SHG field is described by [59], [62]:

\[
I^{\text{2o}} = A \cos^2(\zeta - 3\theta + 2\varphi),
\]

where \( A \) is a multiplication factor depending on \( \chi^{(2)}_{\text{int}} \) and the amplitude of the excitation field.

For rotating polarizer with an angle \( \zeta = \varphi \), i.e. rotating polarizer always parallel to the direction of the excitation polarization \( \varphi \), the SHG intensity reads [49], [57]:
Figure 2: Pixel-wise mapping of 2D TMDs armchair directions identifies 2D crystal imperfections. (a) Typical raster-scanning P-SHG experimental setup; HWP, half-waveplate; GM, galvanometric mirrors; L1,2, lenses; D or M, dichroic (for epi detection) or mirror (for forward detection); O, objective lens; SP, sample plane; C, condenser; M, mirror; SPF, short-pass filter to cut-off the laser; BPF, bandpass filter for SHG; LP, linear polarizer; PMT1,2, photomultiplier tubes. The excitation linear polarization is rotated with an angle \( \varphi \), while the linear polarizer is rotated with \( \zeta = \varphi \) (6 lobes polar diagrams) or is fixed, e.g. at \( \zeta = 0^\circ \) or \( \zeta = 90^\circ \) (4 lobes polar diagrams). (b) Coordinate system describing the experimental measurements and introducing relevant angles with respect to the laboratory frame \((X,Y,Z)\); \( \varphi \): angle between excitation linear polarization \( E^\omega \) and \( X \)-laboratory axis; \( \theta \): angle between armchair direction \( \rightarrow x \) and the \( X \)-lab axis; \( \zeta \): angle between linear polarizer axis and \( X \)-axis. The crystal structure and armchair direction of a TMD crystal are shown (top view). (c) Experimental P-SHG data from a MoS\(_2\) monolayer for \( \zeta = \varphi \) (6 lobes polar diagram) and fitting using Eq. (6). Top view of the MoS\(_2\) crystallographic orientation with respect to the incident laser polarization. (d) SHG image of CVD grown WSe\(_2\) 2D flakes. Four pixels of interest (POIs) are marked. (e) Experimentally retrieved P-SHG polar diagrams from the four POIs. The rotation of the polar diagrams corresponds to different armchair directions \( \theta \). (f) Mapping of armchair orientations \( \theta \) over a large sample area. The POIs shown correspond to the same positions as in (d). (g) Magnified view of ROI-A SHG intensity. (h) The mapping of armchair directions reveals grains of different crystal orientations, not seen in the SHG intensity image. (i) Image histograms showing the distribution of armchair orientations inside ROIs-A1-4. The crystal quality is reflected in the standard deviation (\( \sigma \)) of the mean armchair direction, \( <\theta>\). Small \( \sigma \) values are indicative of good crystal quality. (a), (b), (d), (e), (f), (g), (h), (i) are reproduced with permission from [59]. Copyright 2018. Springer Nature. (c) is reprinted with permission from [57]. Copyright 2013. American Physical Society.
\[ I^{2\omega} = A \cos^2 3(\varphi - \theta). \] (5)

The above experimental configuration provides 6 lobes P-SHG polar diagrams (Figure 2(c)) [57], that rotate for different armchair orientations \( \theta \).

For \( \zeta = 0^\circ \) or \( \zeta = \pi/2 \) i.e. fixed analyzer parallel to X or Y laboratory axes, respectively, the SHG intensity reads [59], [62]:

\[ I_N^{2\omega} = A \cos^2 [3\theta - 2\varphi] \] (6)

and

\[ I_N^{2\omega} = A \sin^2 [3\theta - 2\varphi]. \] (7)

The result of the experimental configuration described by Eq. (6) (fixed analyzer at \( \zeta = 0^\circ \)) demonstrates a four-lobe polar diagram (Figure 2(e)), that rotates for different armchair orientations \( \theta \). The armchair directions differing by 60\(^\circ\) produce the same polar diagrams (that is, the armchair direction can be determined modulo 60\(^\circ\)), reflecting the threefold rotational symmetry of the MX\(_2\) crystal (that is, the fact that there are three equivalent armchair axes).

By fitting pixel-by-pixel the P-SHG experimental data (Figure 2(d)) to Eq. (6), the armchair direction \( \theta \) for every point of the 2D crystals is acquired (Figure 2(f)) [59]. This pixel-wise mapping of the armchair directions provides the means for evaluating crystal homogeneity and thus crystals quality. By choosing a region of interest (ROI) in the crystal (Figure 2(g) and (h)), the armchair directions distribution is acquired, described by its mean and standard deviation \( \sigma \) (Figure 2(i)). Then \( \sigma \) is used as a quality criterion [59]. A broad distribution of armchair directions in the ROI indicates the presence of defects that affect the crystal structure and homogeneity, while a narrow distribution indicates a uniform crystal structure. Thus, the narrower the distribution of armchair directions is, the better the crystal quality is [59].

### 2.3 Polarization-resolved SHG measurements of twist-angles in artificial TMD homo/heterobilayers and multi-layer structures

Apart from single materials, the atomically thin 2D layers can stack into van der Waals heterostructures [72]. Nowadays, 2D heterostructures can be designed with arbitrary angles hence result in large variance of symmetries [73], [74]. Such variety leads to engineering of materials’ properties. For example, the band structure and optical properties of twisted bilayer MoS\(_2\) vary with the twisted angle [75]. Thus, it is of great importance to identify and precisely control the interlayer stacking angles of heterostructures [76].

Considering the fabrication of a 2D heterostructure with specific requirement of stacking angle, the knowledge of crystal orientation is required. Designed vertical stacking of TMDs heterostructures with specific twist-angles creates new material system with tailored properties [77], [78].

Given the atomic phase-matching condition, SHG from the 2D heterostructure can be regarded as a coherent superposition of the SHG fields from the individual layers [65], [66], [79], with a phase difference depending on the stacking angle (Figure 3(a)) [65]. A recent work on modeling twist-angle in MoS\(_2\) was demonstrated with an open source package [80].

Hsu et al. [65] studied the SHG interference from artificially stacked TMD bilayers and showed that the total intensity \( I_N^{2\omega} \) recorded in the bilayer region can be expressed as:

\[ I_N^{2\omega} = \left| \sum_{i=1}^{N} I_i^{2\omega} \right|^2 = \sum_{i=1}^{N} I_i^{2\omega} + \sum_{i \neq j} \sqrt{I_i^{2\omega} I_j^{2\omega}} \cdot \cos(3\delta_{ij}), \] (8)

with \( I_i^{2\omega} \) the intensity of the \( i \)th layer, and \( \delta_{ij} \) the twist-angle between layers \( i \) and \( j \). \( \delta_{ij} = \theta_i - \theta_j \).

For \( N = 2 \), the SHG intensity of the bilayer (BL) is given by [65]:

\[ I_{(BL)}^{2\omega} = I_1^{2\omega} + I_2^{2\omega} + 2 \sqrt{I_1^{2\omega} I_2^{2\omega}} \cdot \cos(3\delta). \] (9)

Furthermore, for layers of equal SHG intensity \( I_i^{2\omega} = I_1^{2\omega} = I_{M\_L} \) at zero twist-angle \( (\delta = 0) \), we obtain, \( I_{(BL)}^{2\omega} = 4I_{M\_L} \), i.e. the well-known result that SHG intensity scales quadratically with layer number (Figure 3(b)).

The above analysis [65] is based on SHG intensities measurements only (Figure 3(a)), i.e. at a fixed excitation polarization and without the use of an analyzer. Using Eq. (9) two intensity measurements, one in the monolayer and one in the bilayer regions can provide twist-angle values modulo 60\(^\circ\).

Nevertheless, it is demonstrated that P-SHG measurements, i.e. rotation of the excitation linear polarization, provides a more detailed description than the intensity only measurements and reveals the twist-angle values modulo 120\(^\circ\) [66], [79].

In the P-SHG experimental scenario, as before, the measurement utilizes rotation of linear excitation polarization in an angle \( \varphi \) with respect to the X lab axis (Figure 3(c)).

The SHG of \( N \) number of such one-armchair layers, built with a stacking angle \( \delta_{ij} \), for the case of fixed analyzer at \( \zeta = 0^\circ \) and rotating linear polarization in an angle \( \varphi \), is then described by [66], [79]:
Figure 3: Twist-angle mapping in 2D TMD bilayers. (a) CCD image (up) and SHG intensity mapping (down) of MoS$_2$ bilayers with different stacking angles of $\theta = 2^\circ$, $30^\circ$ and $54^\circ$. (b) Schematic representation of the top view in the atomic configuration of a 2D WS$_2$ bilayer, for the AA stacking sequence. Atoms of W–W or S–S are on top of each other and the SHG signals depend quadratically on the number $N$ of the monolayers, (SHG $\sim N^2$). In the atomic configuration for the AB stacking sequence (twist-angle $= 60^\circ$) the alternating W–S atoms are on top of each other and the SHG signals cancel (SHG = 0), because centrosymmetry is restored. (c) Coordinate system of the experimental configuration used for P-SHG imaging. $\theta_1$ and $\theta_2$ denote the armchair directions of monolayer (ML) −1 and ML −2, respectively. $\phi$ indicates the direction of the excitation linear polarization and $\zeta$ the axis of the analyzer. In our experiments $\zeta$ is fixed to $0^\circ$ which greatly simplifies the experimentally retrieval of the P-SHG polar diagrams. (d) Numerical simulation showing the effect of twist-angle in the polar diagrams of P-SHG. (e) Experimental extraction of $\theta_{\text{eff}}$ from the bilayer region. 

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\[ I^{2\omega}_{\text{N}} = \left| \sum_{i=1}^{N} A_i \cos(3\theta_i - 2\phi) \right|^2, \quad (10) \]

where $\theta_i$ are the armchair directions of each individual flake. In the case of two monolayers ($N = 2$) reduces to [66], [79]:

\[ I^{2\omega}_{(AB)} = \left[ A_1 \cos(3\theta_1 - 2\phi) + A_2 \cos(3\theta_2 - 2\phi) \right]^2, \quad (11) \]

where $\theta_1$ and $\theta_2$ are the armchair directions of each individual flake.

One can therefore employ Eq. (11) to deduce the real armchair orientation of a second layer that resulted to the total SHG from both layers.

Assuming $A_1 = A_2$ (layers of equal SHG i.e. WS$_2$/WS$_2$ homobilayer) in Figure 3(d) are presented the theoretical P-SHG modulations of the two monolayers, as well as the SHG modulation of the product of their interference in their overlapping region, for several armchair twist-angles $\delta$ [79].

The effective armchair direction $\theta_{\text{eff}}$ in the overlapping region of the two TMD monolayers that describes the total SHG intensity produced by the 2 monolayers is given by [66], [79] as:
\[ I_{\text{SHG}}^{2\omega} = \left| A_{\text{eff}} \cos(3\theta_{\text{eff}} - 2\varphi) \right|^2 \]

where
\[ A_{\text{eff}} = 2 \cos \frac{3}{2} \delta, \]

where \( \delta = \theta_1 - \theta_2 \) is the twist-angle, between the monolayers and
\[ \theta_{\text{eff}} = \frac{\theta_1 + \theta_2}{2}. \]

This means that the P-SHG modulation emerging from a bilayer region consisting of two TMD monolayers, at twist angle \( \delta = \theta_1 - \theta_2 \), behaves as if it was the P-SHG modulation of a single monolayer with armchair direction \( \theta_{\text{eff}} \). The \( \theta_{\text{eff}} \) is extracted experimentally from the P-SHG polar obtained from the bilayer region [66, 79].

Additionally, as it is noted in Figure 3(c), the SHG signals originating from the bilayers regions with twist-angles of 10(°) and 110(°), 20(°) and 100(°), 30(°) and 90(°), and 40(°) and 80(°), are of equal SHG intensities. Nevertheless, the P-SHG interference polar diagrams from the bilayers’ regions (red lines in Figure 3(d)) for the twist-angles of 10 (°) and 110 (°), 20 (°) and 100 (°), 30 (°) and 90 (°), and 40 (°) and 80 (°), are different, thus P-SHG is able to identify and discriminate twist-angles that produce equal SHG intensities from the bilayer regions. Since \( \theta_1, \theta_2 \in [0°, 60°] \) (i.e. modulo 60°) we have that \( \delta \in [-60°, 60°] \) (i.e. modulo 120°) and \( \theta_{\text{eff}} \in [0°, 60°] \) (i.e. modulo 60°) [66]. From Figure 3(d) it is evident that by using P-SHG measurements and by controlling the twist-angle between two monolayers allows for full control of intensity and polarization of the produced SHG from the bilayer region.

2.4 Single-scan calculation of twist angle in 2D TMD heterobilayers

In the case of TMD monolayers the armchair direction \( \theta \) could also be determined by combining the Eqs. (6) and (7), as [62, 63]:
\[ \theta = \frac{1}{3} \left( 2 \varphi + \tan^{-1} \sqrt{\frac{I_{\text{SHG}}^{2\omega}}{I_X}} \right). \]

It was demonstrated experimentally that by fixing the excitation linear polarization parallel to X-axis (\( \varphi = 0° \) in Eq. (15)) and by performing two SHG intensity measurements \( I_{\text{SHG}}^{2\omega} \) for parallel (\( \zeta = 0° \)) and \( I_X^{2\omega} \) for perpendicular (\( \zeta = 90° \)) to X-axis SHG detection, the armchair direction can be calculated in the range [0–30°] [63]. In (Figure 4(a)) [63] the application of Eq. (15) and the resulted mapping of the armchair crystal orientations for a big area is presented [63].

In the case of 2D TMD heterobilayers, in the overlapping region, the SHG signals of the two different TMD monolayers interfere and the overall produced SHG is governed by their vectorial addition. For polarizer parallel to X-axis (i.e. \( \zeta = 0° \)), the SHG from \( N \) stacked TMD monolayers is described by \( \langle \varphi = 0° \rangle \) [81]:

![Figure 4: Single-scan extraction of twist-angle in 2D TMD heterobilayers. (a) Individual grains and as seen under a conventional microscope. (b) The color-mapped armchair direction image was produced by two SHG scans. Scale bar indicates 250 µm. (c) Illustration of the experimental configuration for single-scan calculation of twist-angle in 2D TMD heterobilayers. The linear polarization of the laser beam is parallel to X-axis (\( \varphi = 0° \)) and a polarization beam-splitter cube is placed in front of two detectors. Simultaneously, during a single-scan, the detector-1 records the \( I_X^{2\omega} \) and the detector-2 records the \( I_Y^{2\omega} \) component of the SHG. (d) CCD image of a WS₂/MoS₂ heterobilayer. The regions of WS₂ monolayer, MoS₂ monolayer, and their overlapping region are denoted. (e) SHG intensity image of the WS₂/MoS₂ heterobilayer, for the parallel to X-axis SHG component, \( I_X^{2\omega} \) and (f) for the perpendicular component, \( I_Y^{2\omega} \). (g) The resulted twist-angle \( \delta \) of the WS₂/MoS₂ heterobilayer, after application of Eq. (20), using a single-scan. (a) and (b) are reproduced with permission from [63]. Copyright 2015. AIP publishing. (c)–(g) are reproduced with permission from [81]. Copyright 2021. IOP Publishing Ltd.](image-url)
Recently, Higashitarumizu et al. performed also supported by another theoretical work by Panday and Fregoso [82], while Zhu et al. and Maragkakis et al. reported polarized SHG spectroscopy on a micrometer-size mono-anisotropic SHG in few-layer SnS [67], [85].

2.5 Polarization-resolved SHG in 2D metal monochalcogenides

The 2D MXs belong to the non-centrosymmetric, orthorhombic point group $C_{2v}$ [67], [83]. Thus, they have five independent, nonzero SHG susceptibility tensor elements, namely:

$$
\chi^{(2)}_{xzy} \cdot \chi^{(2)}_{yzy} \cdot \chi^{(2)}_{yzz} \text{ and } \chi^{(2)}_{yyx} = \chi^{(2)}_{xyy} \text{ and } \chi^{(2)}_{yyz} = \chi^{(2)}_{yyz}.
$$

As a result, the nonlinear polarization can be written in matrix form as [67]:

$$
\begin{bmatrix}
I^{(2)}_x \\
I^{(2)}_y \\
I^{(2)}_z
\end{bmatrix} = \varepsilon_0 E_0 \begin{bmatrix}
\chi^{(2)}_{yyx} \\
\chi^{(2)}_{yyy} \\
\chi^{(2)}_{yzy}
\end{bmatrix} \begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}.
$$

Given that the excitation field is polarized along the sample plane, i.e. $E_x = 0$, the SHG equation is reduced to:

$$
I^{(2)}_{y} = \varepsilon_0 E_0 \begin{bmatrix}
\chi^{(2)}_{yyx} \sin^2(2\varphi - \theta) \\
\chi^{(2)}_{yyy} \sin^2(\varphi - \theta) + \chi^{(2)}_{yzy} \sin^2(\varphi + \theta)
\end{bmatrix}.
$$

This expression back to laboratory coordinates and for fixed polarizer before the detector at $\zeta = 0^\circ$, results in [67]:

$$
I^{(2)}_{xy} \sim \frac{1}{16} \begin{bmatrix}
2(\chi^{(2)}_{yxx} + \chi^{(2)}_{zyy}) \sin \theta + (2\chi^{(2)}_{yxy} - \chi^{(2)}_{zyx} + \chi^{(2)}_{yyz}) \\
2\chi^{(2)}_{yxy} - \chi^{(2)}_{yyz} + \chi^{(2)}_{yyz}
\end{bmatrix} \sin(\theta - 2\varphi) \\
\times \sin(3\theta - 2\varphi) \right|^2.
$$

The above Eq. (23) can be expressed in terms of dimensionless $\chi^{(2)}$ tensor elements ratios, obtaining [67]:

$$
I^{(2)}_{xy} \sim a[2(b + 1) \sin \theta + (2c - b + 1) \sin(\theta - 2\varphi)]^2,
$$

where

$$
b = \chi^{(2)}_{yxx} / \chi^{(2)}_{zyy}, \ c = \chi^{(2)}_{yxy} / \chi^{(2)}_{yyz}, \text{ and } a = \varepsilon_0 E_0 / \left[16 \left(\chi^{(2)}_{yyz}\right)\right].
$$

(25)

is a multiplication factor. The SHG intensity can also be expressed in the equivalent form, which is used to fit the P-SHG experimental data [67]:

$$
I^{(2)}_{xy} = a[2(b + 1) \sin \theta + (b - 1) \left[(e - 1) \sin(\theta - 2\varphi) + (e + 1) \sin(3\theta - 2\varphi)\right]]^2.
$$

(26)
Figure 5: In-plane anisotropic P-SHG in 2D metal monochalcogenides. (a) Schematic of the crystal structure of orthorhombic 2D MXs, as seen from the top (left) and the side (right). (c) SHG imaging of 2D SnS flakes. (b) Numerical simulations of the theoretical P-SHG intensity produced by a 2D MX, described by Eq. (23). (d) Experimentally retrieved polar diagrams of the P-SHG intensity taken inside each ROI are depicted in (c). By fitting with Eq. (26) the armchair and the zig-zag crystallographic directions as well as the tensor element parameters $b$ and $e$, for each ROI could be calculated [67]. The changes in the polar-diagrams for different flakes, is the signature of differences in their in-plane anisotropy. Figure is reproduced with permission from [67]. Copyright 2022. Wiley VCH.
where
\[ e = 2c/(b - 1). \]  

(27)

In Figure 5(b), is presented the numerical simulation of the \( I_{\text{SHG}} \) modulation, described by Eq. (24), in polar plots, as a function of the orientation of the linear polarization of the excitation field, \( \varphi \), for fixed values of \( b \), \( c \), and for different armchair directions, [67]. Three possible shapes are obtained: one with four symmetric lobes, one with four lobes symmetric in pairs, and one with two symmetric lobes.

The changes in the shape of the P-SHG polar diagrams, shown in Figure 5(b), reflect the in-plane anisotropy of the orthorhombic MXs. The origin of this shape change is described by Eq. (24), where the SHG intensity depends on four parameters, i.e., \( a \), \( b \), \( c \), and \( \theta \). It is therefore established a direct link between the P-SHG intensity modulation and the in-plane anisotropy of orthorhombic MXs through these four parameters. In particular, the shape of the theoretically predicted P-SHG polar diagrams shown in Figure 5(b) is determined by the corresponding armchair direction \( \theta \) and the tensor elements ratios \( b \) and \( c \). The parameters \( b \) and \( c \) denote the relative contribution of different directions to the SHG signals. Experimental demonstration of the effect of the in-plane anisotropy of orthorhombic SnS in the P-SHG measurements is presented in Figure 5(b) and [67].

In contrast to the monolayer TMDs where the armchair direction can be calculated modulo 60° (due to their threefold rotational symmetry i.e., the fact that they have three equivalent armchair axes), in the case of 2D MXs, the armchair direction is unique. This is readily reflected in the SHG polar diagrams of MXs which are the same every 180° in the armchair direction (i.e. modulo 180°) [67].

### 2.6 Layer dependent SHG in 2D metal monochalcogenides

To describe the SHG intensity generated from a noncentrosymmetric orthorhombic 2D MX, with \( N \) number of layers, the interference model introduced for 2D TMDs [66], [79] is used. For example, SnS has been reported to exhibit two possible stacking sequences, the non-centrosymmetric AA and the centrosymmetric AB staking [82]. Experimental evidence has been provided that all ultrathin SnS flakes below a critical thickness, including the even-number layers, show SHG signals [82]. In any case, neglecting propagation effects, from an ultrathin noncentrosymmetric MX crystal which produces optical SHG, the second harmonic field arising will have the form of vector superposition:

\[ E^{(2)} = E_1^{(2)} + E_2^{(2)} + \ldots + E_N^{(2)}, \]  

(28)

where the indices denote the second harmonic signal from the corresponding layers. The total SHG intensity produced by the N-layer structure, will then be [67]:

\[ I_N^{(2)} = |E_1^{(2)}|^2 + |E_2^{(2)}|^2 + \ldots + |E_N^{(2)}|^2 \]

\[ = 2E_1^{(2)}E_2^{(2)} + \ldots + 2E_{N-1}^{(2)}E_N^{(2)} \]

(29)

\[ I_N^{(2)} = I_1^{(2)} + I_2^{(2)} + \ldots + I_N^{(2)} + 2\sqrt{I_1^{(2)}I_2^{(2)}\cos \delta_{1,2} + \ldots} \]

\[ + 2\sqrt{I_{N-1}^{(2)}I_N^{(2)}\cos \delta_{N-1,N}} \]

(30)

where \( \delta_{ij} \), \( i, j = 1, 2, \ldots, N \) denote the relative angle between layers \( i \) and \( j \) i.e., the twist-angles. If for simplicity is assumed that the SHG intensity from the individual layers is equal \( (I_1^{(2)} = I_2^{(2)} = \ldots = I_N^{(2)} = I_{\text{ML}}^{(2)}) \) and that the three layers are aligned (i.e., all twist-angles are zero), is found that [67]:

\[ I_N^{(2)} = N I_{\text{ML}}^{(2)} \]  

(31)

\[ I_N^{(2)} = N^2 I_{\text{ML}}^{(2)}. \]  

(32)

This is the same with the previous result for TMD flakes with zero twist-angle, that the SHG intensity scales quadratically with the number of layers.

Polarized SHG has been widely used to characterize the crystal orientation for odd layers of 2H phases. While for other crystal forms of 2D materials belonging to different space groups, two-fold or four-fold pattern are employed as indicators of crystal orientation [86].

### 2.7 Polarization-resolved SHG probes valley polarization

Traditional optoelectronics relies on using light to control the movement of electronic charge, facilitating tasks such as information transmission, storage, and retrieval. In electronic setups featuring degenerate minima in their band structures – known as valleys – a supplementary parameter, the valley index, can function as a distinct carrier of information, marking these minima. This concept has paved the way for a novel domain in electronics called valleytronics. Valleytronics offers the potential to process extra information within the confines of the same physical area [87]–[89].

The underlying physical principle is the population imbalance between different valleys. This is reasonable considering that polarization and transport effects are associated with charge separation and local variations in the chemical potential, respectively. Hence, they directly reflect the crystal symmetries in both real and momentum space.
Figure 6: P-SHG probes valley polarization in 2D TMDs. (a) Top view of monolayer TMD with transition metal atoms in red and chalcogen atoms in blue. The lattice vectors $a_1$ and $a_2$ and first-neighbor vectors $\delta_1$, $\delta_2$, and $\delta_3$ are also shown. The region bounded by dashed lines corresponds to the primitive cell. (b) First Brillouin zone (shaded) of monolayer TMD showing the high symmetry points $\Gamma$, $K$, and $K'$. The reciprocal lattice vectors $b_1$ and $b_2$ are also depicted. (c) Schematic of monolayer TMD dispersion. The paraboloids represent valence and conduction bands at $K$ (purple) and $K'$ (cyan) points. The white dashed lines indicate the chemical potential at different valleys for the case of population imbalance. (d) Experimental demonstration of temperature dependence of the P-SHG polar diagram due to valley population imbalance. With decreasing temperature, the SHG intensity increases due to the valley-induced contribution. A rotation of the polar diagram away from the main crystallographic axis is clearly seen [68]. (e) Optical image of a WS$_2$ flake consisting of monolayer, few layer and bulk regions. (f) SHG intensity mapping of the WS$_2$ flake at 78 K. (g) Mapping of valley population imbalance in terms of the dimensionless parameter $\delta\mu$ at 78 K. (h) Measurement of valley polarization at room temperature by changing the ellipticity $\gamma$ of the excitation field and measuring the rotation $\Delta\gamma$ of the produced SHG elliptical polar diagram. (a)–(g) are reproduced with permission from [68]. Copyright 2021, Springer Nature. (h) is reproduced with permission from [69]. Copyright 2020, American Chemical Society.

In real space, the charge is locally accumulated around the atomic positions, whereas in momentum space, the carriers occupy states in the vicinity of high symmetry points within the hexagonal Brillouin zone [68]. Both polarization and transport effects are studied by analyzing the second-order nonlinear optical response of atomically thin crystals [68], [69], [90], [91].

Recent studies suggest that the second-order optical response is a useful tool to probe the electronic configuration of 2D crystals [90], [92], [93]. This is possible due to the symmetry characterizing the hexagonal Brillouin zone in momentum space. Similarly, to the alternating atoms at the corners of the hexagon in real space, characterized by the $D_{3h}$ symmetry (Figure 6(a)), in momentum space the alternating $K$ and $K'$ points also result in $D_{3h}$ symmetry, reflecting the trigonal warping of electrons in the vicinity of high symmetry points (Figure 6(b)) [68]. A direct consequence is the capability for such crystals to produce valley-induced SHG, additionally to the intrinsic second-order response. As a result, in the presence of population imbalance between the two valleys additional elements in the second-order nonlinear optical susceptibility tensor become nonzero [68], [94]:

$$\chi^{(2)}_{yy} = -\chi^{(2)}_{yxx} = -\chi^{(2)}_{yxy} = \chi^{(2)}_{vpi}$$

where $\chi^{(2)}_{vpi}$ is the nonzero element of the valley population imbalance (VPI)-induced second order susceptibility tensor.

Notably, since the VPI defines the difference between the valley populations,

$$\delta n = n_K - n_k,$$

it also reflects the chemical potential difference, $\delta\mu$, between the two valleys (Figure 6(c)). Hence, in the presence of imbalance, the additional valley-induced contribution to the SHG that is intrinsically generated by the TMD crystal, can be estimated as [68]

$$I_{SHG}^{VPI} \sim \delta n^2 \sim \delta\mu^2$$

with the corresponding contribution to the second-order nonlinear susceptibility being proportional to the chemical potential difference, $\delta\mu$ [68]. Accordingly, local variations in the chemical potential affect the SHG induced by the VPI and thus can be probed by nonlinear optical experiments [68]. More importantly, and in contrast to the intrinsic nonlinear optical response of 2D TMDs, the valley-induced SHG is sensitive to temperature variations. Based on this, by varying the temperature of a 2D TMD crystal and the corresponding changes in the SHG intensity are used to probe the intervalley chemical potential difference and therefore the VPI [68].

An experimental SHG measurement of VPI was first proposed by Hipolito and Pereira [90], in which a quarter-wave plate is placed before the sample with its fast axis at an angle $\alpha$. Experimentally the above concept was utilized by
Mouchliadis et al. [68] using a half-wave plate to control the orientation \( \varphi \) of the fundamental linear polarization, while a linear polarizer placed before the detector at an angle \( \zeta \), selects suitable SHG components. The linear polarization of the excitation changes to elliptical as the beam passes through the quarter-wave plate whose axis has an offset of 5° with respect to the polarization axis. Such a configuration provides the means for an asymmetric population of the two valleys [68], [69], [91].

Application of nonlinear optics for a crystal with \( D_{3h} \) symmetry in the presence of VPI yields the SHG field emerging from the crystal as [68]:

\[
\begin{align*}
\left( \frac{p_{20}^{\text{vpi}}}{p_{20}^{\text{int}}} \right) & \sim \left( \chi_{\text{int}}^{(2)} \right)^2 \left( E_{x}^{\text{vpi}} \right)^2 - 2 \chi_{\text{vpi}}^{(2)} E_{x}^{\text{vpi}} E_{y}^{\text{vpi}} - \left( \chi_{\text{int}}^{(2)} \right)^2 \left( E_{x}^{\text{int}} \right)^2 - 2 \chi_{\text{int}}^{(2)} E_{x}^{\text{int}} E_{y}^{\text{int}},
\end{align*}
\]

(35)

Here \( \chi_{\text{int}}^{(2)} \) and \( \chi_{\text{vpi}}^{(2)} \) correspond to the intrinsic and induced due to VPI contributions to the second-order response, respectively.

This means that the SHG intensity reaching the detector depends on four angles, namely \( \varphi, \theta, \alpha, \zeta \), corresponding to the effects of excitation linear polarization, crystal orientation, quarter-wave plate, and analyzer, respectively. In this case, the detected SHG intensity is given by [68]:

\[
I^{\text{vpi}} = A \left[ \cos(2\alpha + \zeta - 3\theta) - \kappa \sin(2\alpha + \zeta - 3\theta) \right]^2 + \sin^2(2\alpha - \varphi) \left[ \kappa \cos(2\alpha + \zeta - 3\theta) + \sin(2\alpha + \zeta - 3\theta) \right]^2,
\]

(36)

where \( \kappa \) denotes the magnitude of VPI-induced to intrinsic susceptibility ratio [68], [69], [91],

\[
\kappa = \frac{\chi_{\text{vpi}}^{(2)}}{\chi_{\text{int}}^{(2)}},
\]

(37)

and \( A \) is a multiplication factor that depends on the amplitude of the field and the intrinsic second-order susceptibility.

The ratio \( \kappa \) which indicates the contribution of VPI to the P-SHG modulation can be extracted upon fitting the experimentally measured P-SHG intensity with Eq. (36) [68]. In this experimental configuration, \( \varphi = \zeta \) that gives rise to a six-petal pattern for the P-SHG intensity (Figure 6(d)). Temperature dependent mapping of \( \kappa \) parameter in monolayer, few layer and bulk of exfoliated WS\(_2\) crystal has been presented by Mouchliadis et al. [68]. In another experimental configuration the degree of valley polarization is calculated at room temperature by changing the ellipticity \( \gamma \) of the excitation field (thus exciting with elliptical polarization) and measuring the rotation \( \Delta \) of the produced elliptical SHG polar diagram. This is done by rotating a linear polarizer before the detector (Figure 6(h)) [69], [91].

### 2.8 Polarization-resolved SHG maps strain

The properties of 2D materials can be strongly influenced by strain making them promising candidates for stretchable and flexible electronics [95]. For flexible device design using 2D materials, it is of significant importance to engineer their properties in a controllable way. Currently, strain engineering represents a very efficient and powerful route for this purpose [95], [96], benefiting from the flexibility of 2D materials. Accordingly, the development of suitable techniques to precisely characterize both the amplitude and direction of the local strain vector is a prerequisite for future applications [70], [71].

Thus, it is essential to figure out the strain tensor distribution in 2D materials. The direct impact of strain on 2D materials is lattice deformation and symmetry variations. As we saw above, the second-order nonlinear susceptibility \( \chi_{\text{int}}^{(2)} \) is sensitive to crystallographic direction, therefore strain will change the lattice structure and thus the optical susceptibility of the material. The second order nonlinear susceptibility after the application of strain reads [70], [71]:

\[
\chi_{\text{st}}^{(2)} = \chi_{\text{int}}^{(2)} + p_{ijklm}u_{lm},
\]

where \( p_{ijklm} \) is the photoelastic tensor and \( u_{lm} \) is the strain tensor. The \( \chi_{\text{st}}^{(2)} \) describes the second-order nonlinear susceptibility of the unstrained crystal. The parameters of \( p_{ijklm} \) and \( \chi_{\text{st}}^{(2)} \) can be obtained by applying different levels of uniaxial strain combined with P-SHG signals, and finally the strain tensor is accessed [70], [71].

For TMD monolayer, in the P-SHG measurements the linear polarized incident electric field is under angle \( \varphi \) and the SHG signal is analyzed with same polarization, i.e. \( \zeta = \varphi \). The SHG under strain is then given by [71]:

\[
I^{\cos(\varphi)} = \frac{1}{4} \left[ A \cos(3\varphi) + B \cos(2\theta + \varphi) \right]^2,
\]

(38)

where,

\[
A = (1 - \nu)(p_1 + p_2)(\varepsilon_{xx} + \varepsilon_{yy}) + 2\chi_{\text{int}}^{(2)}
\]

(39)

and

\[
B = (1 + \nu)(p_1 - p_2)(\varepsilon_{xx} - \varepsilon_{yy}) + 2\chi_{\text{int}}^{(2)}
\]

(40)

The \( p_1 \) and \( p_2 \) are the photoelastic parameters, \( \varepsilon_{xx} \) and \( \varepsilon_{yy} \) denote the principal strains, \( \theta \) is the principal strain orientation and \( \chi_{\text{int}} \) the nonlinear susceptibility parameter of the unstrained crystal lattice.
The applied uniaxial tensile strain (Figure 7(a)) alters the shape and intensity of P-SHG patterns (Figure 7(b) and (c)) from which parameters in the photoelastic tensor as well as the strain tensor can be extracted by fitting Eq. (38). Based on this, it is convenient to visualize the strain field of a certain area combined with the P-SHG mapping (Figure 7(d)) [71]. The inset of Figure 7(d) shows the scanning electron microscopy (SEM) image of the MoS$_2$ monolayer lying on a lithographically defined structure. The MoS$_2$ membrane undergoes inhomogeneous strain tensor distribution across the grids. Figure 7(d) shows the strain mapping by arrows after the pixel-by-pixel fitting of the P-SHG experimental data to Eq. (38).

3 Second harmonic generation in 2D perovskites

Halide perovskites are generally defined as a network of corner-sharing [BX$_6$]$^-$ octahedra that crystallize with a general ABX$_3$ (or equivalent) stoichiometry, where A and B denote cations, and X represent halide anions [97]. They have attracted significant attention from the scientific community due to their superior optical properties, ability to tune bandgaps by varying the composition, and ease of synthesis methods. Recently, in addition to 3D perovskites, layered 2D perovskites have also started to attract research attention. From a purist’s perspective, the notion of a 2D perovskite presents an inherent paradox. The very definition of a perovskite structure necessitates a three-dimensional framework of corner-sharing [BX$_6$]$^-$ octahedra extending infinitely [97]. However, the terminology “2D perovskite” has become so ubiquitous in the scientific community that we shall adhere to this convention for the purposes of this review. The advantages of 2D materials compared to 3D analogues are that they have more ability to tune properties by widely changing the functional organic cations or increasing the thickness of the perovskite layer [98]. Their unique structure, leading to strong quantum confinement and excitonic effects, can lead to significant enhancement of nonlinear optical properties (and second harmonic generation in particular) compared to their 3D counterparts [99], [100].

Therefore, 2D organic–inorganic hybrid perovskites are promising materials with many potential applications in light-emitting, sensing and other optical devices. In this review we will focus on their application for SHG.
3.1 General properties of 2D perovskites

Generally, 2D layered perovskites are multiple quantum well (MQW) structures, where a 2D layer of $[B X_6]^{4-}$ octahedra functions as a quantum well and layers of bulk organic anions act as a barrier. In the chemistry of layered perovskites, two main phases are defined in the following way: the Dion–Jacobson (DJ) phases $A'_n A_{n-1} B_n X_{3n+1}$ (Figure 8(b)) have one interlayer cation $A'$ per formula unit, while the Ruddlesden–Popper (RP) phases $A'_2 A_{n-1} B_n X_{3n+1}$ (Figure 8(a)) have two interlayer cations $A'$ per formula unit. The main structural feature of RP and DJ inorganic layered perovskites is the displacement of adjacent perovskite layers in $(a, b)$ layer plane. In RP phases, a shift $(a + b)/2$ is observed (where $a$ and $b$ are in-plane parameters corresponding to the length of one octahedron) as a result of the capped square anti-prismatic coordination of cations in the interlayer space. In DJ phases, displacement of neighboring perovskite layers relative to each other in the plane of layers $(a, b)$ does not occur, since the interlayer cations adopt cubic type coordination [101]. Additionally, ACI (alternating cation in the interlayer space) phase of 2D perovskites is often mentioned [102], which consists of two different alternating cations in the interlayer space. In this work we also consider perovskite-like structures, which cannot be attributed to the above phases (for example, R/S-(MPEA)$_{1.5}$PbBr$_{3.5}$(DMSO)$_{0.5}$ [103], Figure 8(d)), but have the main features of 2D perovskites.

Table 2 presents chemical composition and strength of second order nonlinear effects for 2D perovskites and perovskite-like structures, described in the literature.

\[
\chi^{(2)} \text{ of materials calculated from the following expression:}
\]

\[
\chi^{(2)}_S = \frac{\left| I_S(2\omega) \right|}{I_S(2\omega)}^{1/2}
\]

During the calculations, the following values were used as reference [127]:

\[
\chi^{(2)}_{\text{KDP}} = 0.88 \text{ pm/V(1064 nm)}; \]
\[
\chi^{(2)}_{\text{\alpha-\text{quartz}}} = 0.67 \text{ pm/V(1064 nm)}
\]

3.2 Formation of second order nonlinearity

It needs to be noted that the majority of 2D perovskites do not exhibit second order NLO due to the structure symmetry. Therefore, for SHG signal to be present centrosymmetry should be broken. Thus, here we discuss the influence of composition on the structural properties and symmetry breaking in 2D perovskites $A'_n A_{n-1} B_n X_{3n+1}/A'_2 A_{n-1} B_n X_{3n+1}$. 
Table 2: Reported 2D perovskite materials for SHG.

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Phase</th>
<th>$\chi^{(2)}$, pm/V</th>
<th>$\chi_{max}^{(2)}$, pm/V</th>
<th>$\lambda_{exc}$, nm</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n-butylammonium)₂CsPb₂Br₇</td>
<td>R-P</td>
<td>0.62</td>
<td>0.70</td>
<td>1,064</td>
<td>[106]</td>
</tr>
<tr>
<td>[n-butyrammonium]₂(methyleneammonium)Pb₂Br₇</td>
<td>R-P</td>
<td>0.56</td>
<td>0.64</td>
<td>1,064</td>
<td>[107]</td>
</tr>
<tr>
<td>(n-butylammonium)₂[ethylenammonium]PbI₁₂</td>
<td>R-P</td>
<td>0.56</td>
<td>0.64</td>
<td>1,064</td>
<td>[108]</td>
</tr>
<tr>
<td>R/S-(β-methylphenethylamine)₁₂PbBr₁₂(DMSO)₂₅</td>
<td>–</td>
<td>1.36</td>
<td>1.55</td>
<td>850</td>
<td>[109]</td>
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<tr>
<td>[R/S-1-(4-chlorophenyl)ethylammonium]₁₂PbI₄</td>
<td>–</td>
<td>0.62</td>
<td>0.70</td>
<td>1,064</td>
<td>[109]</td>
</tr>
<tr>
<td>(isoamylammonium)₂[ethylammonium]PbI₁₀</td>
<td>R-P</td>
<td>0.51</td>
<td>0.58</td>
<td>1,300</td>
<td>[110]</td>
</tr>
<tr>
<td>(p-bromobenzylammonium)₁₂PbI₁₀</td>
<td>R-P</td>
<td>0.92</td>
<td>1.05</td>
<td>1,340</td>
<td>[111]</td>
</tr>
<tr>
<td>(N-methyl-iodopropylation)₄PbI₄</td>
<td>R-P</td>
<td>5.73</td>
<td>6.51</td>
<td>1,580</td>
<td>[112]</td>
</tr>
<tr>
<td>(3-(aminomethyl)pyridinium)GeI₄</td>
<td>D-J</td>
<td>0.69</td>
<td>0.78</td>
<td>1,064</td>
<td>[114]</td>
</tr>
<tr>
<td>(4-(aminomethyl)pyridinium)GeI₄</td>
<td>D-J</td>
<td>0.68</td>
<td>0.77</td>
<td>1,064</td>
<td>[114]</td>
</tr>
<tr>
<td>(3-(aminomethyl)pyridinium)methylammonium)Ge₂I₇</td>
<td>D-J</td>
<td>0.74</td>
<td>0.84</td>
<td>1,064</td>
<td>[114]</td>
</tr>
<tr>
<td>(4-(aminomethyl)pyridinium)methylammonium)Ge₂I₇</td>
<td>D-J</td>
<td>0.65</td>
<td>0.74</td>
<td>1,064</td>
<td>[114]</td>
</tr>
<tr>
<td>[2-fluorobenzylammonium]₂PbCl₄</td>
<td>D-J</td>
<td>0.83</td>
<td>0.94</td>
<td>1,064</td>
<td>[115]</td>
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<tr>
<td>(4-(aminomethyl)piperidinium)AgBiBr₈</td>
<td>–</td>
<td>0.88</td>
<td>1.00</td>
<td>1,064</td>
<td>[116]</td>
</tr>
<tr>
<td>(4-(aminomethyl)piperidinium)₄AgBiBr₈·H₂O</td>
<td>–</td>
<td>0.51</td>
<td>0.58</td>
<td>1,064</td>
<td>[116]</td>
</tr>
<tr>
<td>(n-butylammonium)₂(formamidinium)GeI₄</td>
<td>R-P</td>
<td>17.5</td>
<td>19.9</td>
<td>850 to 930</td>
<td>[117]</td>
</tr>
<tr>
<td>(n-butylammonium)₂(formamidinium)SnI₄</td>
<td>R-P</td>
<td>0.63</td>
<td>0.72</td>
<td>850 to 930</td>
<td>[117]</td>
</tr>
<tr>
<td>(n-butylammonium)₂(formamidinium)PbI₄</td>
<td>R-P</td>
<td>0.19</td>
<td>0.22</td>
<td>850 to 930</td>
<td>[117]</td>
</tr>
<tr>
<td>(n-butylammonium)₂(formamidinium)PbI₄</td>
<td>R-P</td>
<td>0.05</td>
<td>0.06</td>
<td>850 to 930</td>
<td>[117]</td>
</tr>
<tr>
<td>(methylhydrazinium)₂PbBr₄</td>
<td>R-P</td>
<td>0.28</td>
<td>0.32</td>
<td>1,300</td>
<td>[118]</td>
</tr>
<tr>
<td>(n-butylammonium)₂(methyleneammonium)₁₂PbI₁₀</td>
<td>R-P</td>
<td>0.067</td>
<td>0.08</td>
<td>1,800</td>
<td>[119]</td>
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<tr>
<td>(R/S-1-(4-chlorophenyl)ethylamine)₁₂PbI₁₀</td>
<td>–</td>
<td>3.80</td>
<td>4.32</td>
<td>2060</td>
<td>[120]</td>
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<tr>
<td>(R-1-(1-naphthyl)ethylammonium)₁₂PbI₁₀</td>
<td>–</td>
<td>0.60</td>
<td>0.68</td>
<td>1,064</td>
<td>[121]</td>
</tr>
<tr>
<td>(4,4-difluorocyclohexylammonium)₂PbBr₄</td>
<td>–</td>
<td>1.14</td>
<td>1.3</td>
<td>1,064</td>
<td>[122]</td>
</tr>
<tr>
<td>(2-Methyl-1,5-diaminopentaneH₂)PbBr₄</td>
<td>R-P</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[123]</td>
</tr>
<tr>
<td>[(phenylethylammonium)₂]PbCl₄</td>
<td>R-P</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[105]</td>
</tr>
<tr>
<td>(R/S-1-(4-chlorophenyl)ethylamine)₁₂PbI₁₀</td>
<td>R-P</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[120]</td>
</tr>
<tr>
<td>(phenylethylammonium)₄PbI₄, RNH₃⁺ = PEA</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[113]</td>
<td></td>
</tr>
<tr>
<td>(2-thiophenemethylammonium)₄PbI₄, n = 2,3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[124]</td>
<td></td>
</tr>
<tr>
<td>[4-Bromo-2-fluorobenzylammonium]₂CsGeI₄</td>
<td>R-P</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[125]</td>
</tr>
<tr>
<td>[Methylhydrazinium]₂PbCl₄</td>
<td>R-P</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[126]</td>
</tr>
</tbody>
</table>

3.2.1 A'-site cation influence

Although the optical properties of 2D perovskites are mostly dependent on the inorganic layer, the steric effect of the organic cation can induce distortion in the crystal lattice. One of the main ways to introduce second-order nonlinearities (and therefore SHG) in 2D perovskites is the use of chiral spacer A'-site cations, which can lead to the formation of non-centrosymmetric 2D perovskite structures due to intrinsic centrosymmetry breaking in chiral structures. Recently, several works have been published that raise this topic [103], [109], [112], [120]. However, enantiomeric pure chiral ammonium cations can be expensive due to problems associated with asymmetric synthesis and chiral resolution techniques [113].

Alternatively, R. Chakraborty et al., in an article devoted to the design of non-centrosymmetric hybrid halide perovskites, developed the approach for obtaining non-centrosymmetric structure by using achiral spacer cations through lowering the rotational symmetry at both ends of the spacer cation A', which should lead to heterogeneous hydrogen-iodine and iodine-iodine interactions at the organic-inorganic interface of 2D perovskites, which break the local inversion symmetry of Pb-I octahedra [113]. In this work, the authors demonstrated the synthesis of a non-centrosymmetric 2D perovskite (MIPA)₂PbI₄ (where MIPA is N-methyl-iodopropylammonium), the break of the central symmetry of which arose due to the substitution of a –H (in –NH₃⁺) with –CH₃ group and substitution of a –H...
in the hydrocarbon skeleton) with –I, leading to a significant change in hydrogen bond interactions (Figure 9(a), Table 3).

### 3.2.2 A-cation influence

In case of 2D perovskites with number of layers \( n \geq 2 \) in addition to interlayer spacer A’ cations, smaller different A-cations located between \( n \) layers of octahedra may also be present. Xinyu Li et al. studied the influence of the organic A cation on the structural properties of 2D perovskites \((BA)_2(A)Sn_2I_7\) \[117\]. They demonstrated that as the size of cation A increases, the average Sn–I bond length and volume of the perovskite cage also generally increases, and elongation of the Sn–I bond length increases the tendency of B-cation displacement from the center. Displacement of the B cation breaks the central symmetry and allows second-order nonlinear optical effects (Figure 9(b), Table 3).

### 3.2.3 B-cation influence

Varying B-cation in \((BA)_2(MA)B_2I_7\) 2D perovskites, Xinyu Li et al. \[117\] demonstrated the increased lone-pair expression in following order of B cations: \(Pb^{2+} < Sn^{2+} < Ge^{2+}\), that has two origins. First, in the \(Pb^{2+} < Sn^{2+} < Ge^{2+}\) trend, the covalent interaction between the B cations and the p-orbitals of the halide anions increases as a result of the relativistic contraction of the ns\(^2\) orbital. Second, as the radius of the B-cation decreases, i.e., \(Pb^{2+} > Sn^{2+} > Ge^{2+}\), the methylammonium (MA) cation becomes too big for the corresponding metal halide framework; this expands the perovskite cage. As a result, increasing the B–I bond length increases the tendency of the B-cation off-center displacement (Figure 9(b), Table 3).

### 3.2.4 X-anion influence

The size and polarizability of the X anion also have a major influence on the overall symmetry of the perovskite crystal lattice. Larger halogen anions distort the crystal lattice more than smaller ones, and this distortion can break central symmetry. Furthermore, recent findings \[128\] demonstrate that methylhydrazine’s nitrogen atoms can participate in coordination with lead atoms, alongside halides. This interaction activates a previously stereo-inactive electron pair, leading to significant alterations in the system’s symmetry.

<table>
<thead>
<tr>
<th>Tuning parameter</th>
<th>Material</th>
<th>Result</th>
<th>Figure</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A’-cation</td>
<td>(IPA)(_2)PbI(_4) (MIPA)(_2)PbI(_4)</td>
<td>(IPA)(_2)PbI(_4): centrosymmetric (MIPA)(_2)PbI(_4): (\chi^{(2)} = 5.73) pm/V</td>
<td>Figure 9(a)</td>
<td>[113]</td>
</tr>
<tr>
<td>A-cation</td>
<td>(BA)(_2)(MA)Ge(_2)I(_7)</td>
<td>(BA)(_2)(MA)Ge(_2)I(_7): (\chi^{(2)} = 13.1) pm/V (BA)(_2)(FA)Ge(_2)I(_7): (\chi^{(2)} = 17.5) pm/V</td>
<td>Figure 9(b)</td>
<td>[117]</td>
</tr>
<tr>
<td>B-cation</td>
<td>(BA)(_2)(FA)B(_2)I(_7)</td>
<td>(BA)(_2)(FA)B(_2)I(_7): (\chi^{(2)} = 17.5) pm/V (BA)(_2)(FA)Sn(_2)I(_7): (\chi^{(2)} = 0.63) pm/V</td>
<td>Figure 9(b)</td>
<td>[117]</td>
</tr>
<tr>
<td>Layer thickness</td>
<td>([(C(_6)H(_5)CH(_2)NH(_3)(_2))PbCl(_4)]</td>
<td>(d_{21}/d_{22}) ratios are, respectively, 1.46 and 1.17 for the 92.2 and 18.8 nm nanosheets</td>
<td>Figure 9(c)</td>
<td>[105]</td>
</tr>
</tbody>
</table>
3.2.5 Layer thickness influence

The thickness of the multilayer structure formed by 2D perovskites also has a major influence on the resulting nonlinear optical properties. Wen-Juan Wei et al. studied the influence of van der Waals interactions on the SHG response of 2D perovskite \([\text{Cs}_2\text{NH}_{3}\text{PbCl}_4]\) [105]. They found that the induced second-order polarization occurs predominantly due to cations \((\text{Cs}_2\text{H}_2\text{NH}_{3})^+\); and these organic amine cations form significantly reorganized conformations with decreasing nanosheet thickness due to weakening van der Waals interactions. Since the orientation of organic components at the interface determines their electrical properties and, in particular, dipolar susceptibility, the difference in resulting structure leads to dramatic changes in the SHG properties. Results, presented by Wen-Juan Wei et al. show that the SHG intensity of these nanosheets increases with increasing layer thickness, while their in-plane anisotropy shows the opposite trend (Figure 9(c), Table 3).

3.3 Tuning of SHG response

Tuning the SH signal is an important task for many nonlinear photonics applications. Control of a nonlinear optical signal can be achieved by many different methods, including the use of electrical, thermal, optical, or other signals.

### 3.3.1 Temperature-induced switching

Several works [110], [121], [122], [126] have demonstrated switching of the SHG signal through a reversible thermal phase transition. Yingjie Zhao et al. realized a reversible SHG switch without material degradation based on the transition between glassy and crystalline states in two-dimensional arrays of chiral \((\text{R-NPB})_2\text{PbBr}_4\) perovskite microwires [121]. Ming-Yang Wang et al. also demonstrated temperature control of the SHG signal with minimal loss during a reversible phase transition process near the high Curie temperature \((T_c \sim 409 \text{ K})\) for polar 2D perovskite \((4,4\text{-DCA})_2\text{PbBr}_4\) (Figure 10(d) and (e)) [122]. The combination of efficient SHG with reversible phase transitions and relative durability makes 2D perovskites promising materials for temperature sensors.

### 3.3.2 Electric field-induced switching

Another way to tune the SH signal is to modulate the material properties with an electric field. Ferroelectricity, which is one of the most important properties of materials, is inseparable from asymmetry and is usually accompanied by second-order NLO effects [129]. Yu Ma et al. presented improper ferroelectric of 2D multilayered perovskite \((\text{IA})_2(\text{EA})_2\text{Pb}_3\text{Br}_{10}\) (where IA is isoamylammonium and EA is ethylammonium), which exhibits ferroelectricity with a
high $T_c = 371$ K and biaxial $P_s \approx 2.2 \mu$C cm$^{-2}$ (Figure 10(a)) [110]. Authors demonstrated tuning of SHG response by applying the polarized light, closely involving with intrinsic in-plane electric polarization. The maximum SH response is achieved when the direction of polarized light is parallel to $P_s$, and the minimum appears in the vertical direction (Figure 10(b) and (c)). The strong SHG anisotropy provides an extremely high dichroism ratio of $\approx 12$, while the biaxial nature of ferroelectricity provides an ideal platform for tuning SHG properties through the polarity switching.

### 3.3.3 Water-induced switching

Additionally, SH modulation can be implemented in two-dimensional perovskite materials by other methods, such as the structural symmetry breaking induced by water molecules in two-dimensional (2D) double perovskite (Cs$_8$H$_{16}$N$_2$)$_2$AgBiBr$_8$ presented by Jiang-Feng Hong et al. [116]. Authors demonstrated reversible conversion of centric (Cs$_8$H$_{16}$N$_2$)$_2$AgBiBr$_8$ with complete absence of SHG activity to acentric (Cs$_8$H$_{16}$N$_2$)$_2$AgBiBr$_8$·0.5H$_2$O with $\chi^{(2)} = 0.51$ pm/V (Figure 10(f)).

Basing on the previous examples, one can conclude that the high values of second-order nonlinear susceptibility, as well as the ability to widely tune SH properties depending on composition and external stimulation, make 2D perovskites excellent materials for nonlinear optical applications such as sensing, imaging, polarization-based optoelectronic devices, ultrafast modulators, etc.

### 4 Nanophotonics for SHG and manipulation

Even though the nonlinear optical response of 2D materials per unit thickness is exceptionally strong, the brief interaction between light and matter poses a significant challenge for achieving high nonlinear conversion efficiency in technological applications. Graphene and transition metal dichalcogenides (TMDs) are easily combined with various photonic and nanostructures, such as fibers [130], [131], waveguides [132]–[135], microrings [136], and nanowires [137] as well as in such planar systems as photonic crystals and metasurfaces offering a valuable means to boost light–matter interactions (see Figure 11). This section outlines potential strategies to tackle this challenge and highlights recent developments in this area with the help of nanophotonics and meta-optics.

In one of the first works [138], a photonic crystal supporting 170-folds SHG enhancement on monolayer MoS$_2$ with a 1D photonic crystal compared to a bare monolayer MoS$_2$ on SiO$_2$ was demonstrated (Figure 11(a) and (b)). However, currently, wider used approach to enhance light–matter interaction in 2D materials is to combine them with nanostructured substrates such as resonant dielectric and plasmonic metasurfaces [138], [140], [142]–[145]. By gradually tuning the groove depth in a plasmonic metasurface, an enhanced SHG signal in the entire visible range was obtained [139] (Figure 11(c)). Indeed, plasmonic nanostructures and metasurfaces have also been used to enhance SHG in TMDs [146]. Shi et al. achieved a $\approx 400$-fold enhancement of SHG in a monolayer WS$_2$ incorporated onto a silver nanogroove grating that was finely tuned to match the resonant energy of the C exciton [146]. A three orders of magnitude SHG enhancement was observed in a monolayer WS$_2$ transferred onto a gold film with sub-20 nm-wide trenches [147], as well as in a monolayer MoS$_2$ on a suspended silver film patterned with a square nanohole array [148]. These hybrid samples exhibited modified SHG patterns due to directional enhancement and efficient polarization modulation. In the work [149], an elaborate metasurface of a monolayer WS$_2$ on a plasmonic vortex metalens, which not only enhanced SHG but also generated a giant SHG circular dichroism was developed.

Recently, high-Q all-dielectric metasurfaces were also applied for SHG enhancement from 2D materials. In the work [140], it was demonstrated a three orders of magnitude second harmonic generation (SHG) enhancement in transition metal dichalcogenides (TMDs) by combining a monolayer of WS$_2$ with an engineered asymmetric silicon substrate that supports high-Q modes (Figure 11(d)). Löchner et al. achieved a 35-fold SHG conversion efficiency enhancement by combining a monolayer TMD with a metasurface of periodic arrays of silicon nanoresonators that support a Fano resonance [145].

In addition to metasurfaces, an alternative approach for enhancing second harmonic generation (SHG) using localized plasmons was proposed in the work [150]. They achieved approximately a 300-fold enhancement in a monolayer (1L) WS$_2$ coupled to a plasmonic nanocavity composed of silver nanocubes (with a length of approximately 75 nm) on a silver film, separated by a 10 nm Al$_2$O$_3$ layer. The enhancement in SHG was driven by the amplification of the local field, with theoretical analysis indicating that the enhancement is proportional to the square of the local field intensity within the nanocavity under the interaction between the SH dipole in the 1L TMD and the electric quadrupole in the nanocavity.

In the work [141], the authors showcased the ultrafast manipulation of wavefronts through an advanced
Figure 11: Nanophotonics for SHG and manipulation. (a) A schematic of second harmonic wave generation from a MoS$_2$ monolayer placed on the top of a photonic crystal (PC). (b) SHG Spectrum profile of bare MoS$_2$ and MoS$_2$ on the PC. The spectrum from bare MoS$_2$ is manually magnified by 10 times for better visibility. Inset: calculated near-field distribution on the resonant mode. Reproduced with permission [138]. Copyright 2020, Elsevier Publishing Group. (c) Design of the broadband tunable metasurface integrated with a 1L WSe$_2$. Reproduced with permission [139]. Copyright 2021, Wiley-VCH GmbH. (d) Schematic of SHG from a 1L WSe$_2$ placed on top of a Si metasurface composed of a square array of bar pairs. Adapted with permission [140]. Copyright 2020, American Chemical Society. (e) Schematic representation of the operating principle of the cascaded TMD-metasurface structure for ultrafast wavefront shaping [141].

A meta-optical setup involving a monolayer TMD, a quarter-wave plate, and a silicon metasurface (Figure 11(e)). Through detailed spatially resolved pump-probe experiments, they illustrate the feasibility of achieving rapid transformations such as second harmonic beam deflection, transitioning from Gaussian to vortex beams, and altering topological charges on a femtosecond time scale. Notably, leveraging the polarization-selective nature of metasurfaces to encode complex spatial phase profiles opens up possibilities for seamless switching between diverse wavefronts with customizable intensity profiles and ultrafast dynamics. These findings hold promise for driving innovation in high-speed communications, remote sensing, ultrafast optics, and holographic applications.

5 Conclusions and future outlook

To summarize, recent advancements in the effective characterization of the SHG properties of 2D metal chalcogenide and perovskite atomically thin crystals has been presented and discussed. A unified theoretical framework of nonlinear optics for P-SHG measurements, that is applied to the latest literature reports, has been particularly demonstrated. It can be concluded that all-optical minimally invasive SHG and P-SHG are proven to be a powerful tool to unveil the physical properties of such 2D crystals and probe crystal orientation, number of layers, various types of defects, grain boundary, interlayer stacking, stacking angle, in-plane anisotropy, valley polarization and strain. Despite the rapid
progress of SHG applied in 2D crystals, there is still a lot of room for further exploring the physics of 2D materials. Among potential capabilities, P-SHG could be potentially exploited to precisely determine the susceptibility tensor elements in 2D crystals. Furthermore, P-SHG can be combined with pump–probe spectroscopy in order to probe the ultrafast carrier dynamics under non-linear excitation conditions. In addition, P-SHG could provide a new platform to explore the unexplored physics behind valley polarization and dark excitonic phenomena.

Furthermore, first attempts to tune and control the SHG properties via nanophotonic schemes are presented and discussed. The overview of modern nanophotonic approaches has shown a great potential for enhancement and manipulation of SH from 2D materials like TMDs. Indeed, intensity, polarization, and beam-shape control has been demonstrated during last several years. However, this powerful nanophotonic platform has not been applied for SHG from 2D halide perovskites yet. There were reports on odd (3rd and 5th) harmonics generation from perovskite metasurfaces [151], as well as multiphoton photoluminescence enhancement [152]–[154]. On the other hand, halide perovskite family of materials with second-order nonlinearity can be also nanostructured or integrated with non-perovskite metasurfaces to enhance or tailor their SHG. Recently, strong spectrally tunable SHG signal enhancement was demonstrated for lead-free germanium halide perovskite nanoparticles via coupling of incident light with Mie-type resonances [155]. For multilayer TMDs materials, SHG similarly can be improved or controlled by their direct patterning [156]. Therefore, we envision that the direct nanopatterning of 2D materials for SHG manipulation is an emerging and rapidly developing field of research during next several years.

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References


