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Nonlinear optics of two-dimensional heterostructures

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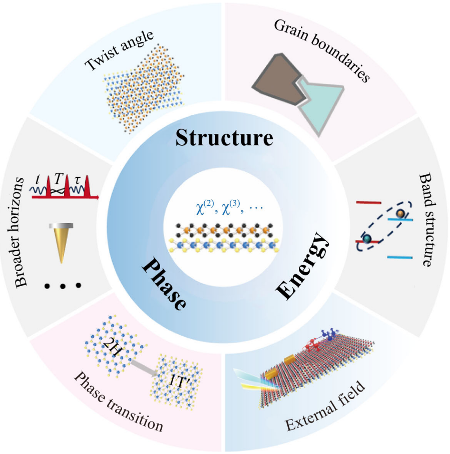
ABSTRACT

Two-dimensional (2D) materials exhibit exceptionally strong nonlinear optical responses, benefiting from their reduced dimensionality, relaxed phase-matching requirements, and enhanced light-matter interaction. With additional degrees of freedom in the modulation of the physical properties by stacking 2D layers together, nonlinear optics of 2D heterostructures becomes increasingly fascinating. In this perspective, we provide a brief overview of recent advances in the field of nonlinear optics of 2D heterostructures, with a particular focus on their remarkable capabilities in characterization and modulation. Given the recent advances and the emergence of novel heterostructures, combined with innovative tuning knobs and advanced nonlinear optical techniques, we anticipate deeper insights into the underlying mechanisms and more associated applications in this rapidly evolving field.



Keywords nonlinear optics, 2D heterostructures

1 Introduction

Two-dimensional (2D) materials, characterized by their atomic layer thickness and interlayer coupling through van der Waals forces, have attracted significant attentions in various research fields [1–4]. Compared to bulk materials, 2D materials exhibit significantly larger nonlinear optical responses, which make them highly appealing for the development of compact, multifunctional, and low-loss nonlinear optical devices [5, 6]. Extensive research efforts have been focused on understanding and harnessing the unique nonlinear optical effects in 2D materials, paving the way for future advances in areas such as ultrafast laser sources [7], all-optical signal processing [8, 9], and nonlinear photonics [10].

2D heterostructures, including both vertical and lateral heterostructures composed of several 2D crystals, have been highlighted in recent years [11, 12]. 2D heterostructures hold great importance in the realm of nonlinear optics, as they offer a multitude of degrees of freedom, including constituent materials, twist angle, and external field. This inherent versatility allows for the precise design of materials with customized properties, fueling significant advances in both fundamental science and industrial applications [1]. Within this context, the intriguing realms of moiré physics and optoelectronic devices have become a focal point in nonlinear optics of 2D heterostructures, offering rich exploration opportunities and immense practical potential. For instance, moiré superlattices [13, 14] in 2D heterostructures has unraveled fascinating phenomena, including emergent flat bands and correlated electronic phases [15–17], which promise exciting opportunities for the design of

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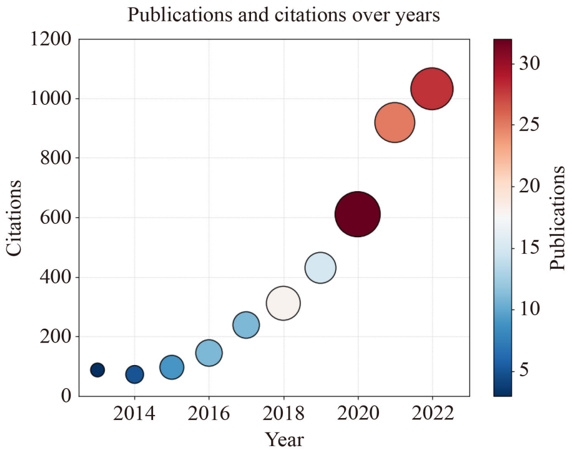

Fig. 1 Publications and citations about the nonlinear optical research on 2D heterostructures since 2013. Certain data included herein are derived from Clarivate Web of Science. Copyright © Clarivate 2023.

novel nonlinear optical devices. Nonlinear optical responses are widely applied in the characterization of 2D heterostructures, considering their sensitivity to crystal structure, quasiparticle energy and coherence. Meanwhile, the rich properties and remarkable tunability of 2D heterostructures facilitate the exploration and modulation of various nonlinear optical phenomena. These remarkable features lead to a surge of researches in this field, as evidenced by the soaring number of published articles and citations in nonlinear optical research pertaining to 2D heterostructures in Fig. 1. Despite the great promise of nonlinear optics of 2D heterostructures, a comprehensive outlook discussing its future development is in urgent need.

This perspective starts from reviewing the recent progresses on the characterization and modulation of nonlinear optics in 2D heterostructures (including homostructures). Based on the brief review, we aim to propose several exciting research directions that can facilitate our comprehension and exploration of nonlinear optics and 2D heterostructures. By delving into the exciting advances in this field, our endeavor seeks to shed light on the promising prospects and groundbreaking discoveries that lie ahead.

To begin with, nonlinear optical responses provide researchers with deep insights into 2D materials [18], benefiting from their sensitivity to structure, energy and phase as depicted in Fig. 2. Compared to characterization techniques such as electronic microscopy and linear optical spectroscopy, nonlinear optics offers a more accessible, efficient, and non-invasive method for characterizing and examining crucial parameters of 2D materials, including crystal axes, grain boundaries, stacking orders, dynamics and external couplings for 2D materials and 2D heterostructures [5]. As a well-established example, second harmonic generation (SHG) is widely applied to determine the layer number and crystal axis of 2H-stacked transition metal dichalcogenides (TMDCs), where SHG vanishes with even layer number due to the appearance of spatial inversion symmetry [19], and the crystal axis of TMDCs can be unveiled through the polarization-resolved SHG. This sensitivity lies the foundation for the applications of nonlinear optical responses in the investigation of 2D heterostructures. On the other hand, the highly tunable light–matter interaction within 2D heterostructures introduces a promising avenue for innovative nonlinear optical applications [5]. As summarized in Fig. 2 and elaborated in the following paragraphs, we discuss the physical insights and modulation strategies through the combination of nonlinear optical responses and 2D heterostructures.

2 Twist angle

As preparation techniques evolve, vertically stacked 2D heterostructures can be fabricated either through conventional mechanical exfoliation and stacking methods, or by directly growing multiple 2D layers on a substrate [20–23]. In the research of these 2D heterostructures, twist angles between neighboring layers play a significant role on novel phenomena such as quasiparticle band reconstruction, interlayer excitons, and moiré physics. Consequently, unambiguous determination of the crystal axis of 2D materials becomes critical in the investigation of vertical heterostructures. The crystal axis sensitive SHG in 2D materials provides a non-invasive, accurate and simple way for the determination of the twist angles. In case of heterostructures like the $\mathrm{WSe_2/WS_2}$, the twist angles are determined with an accuracy better than 0.1° through the polarization-resolved SHG pattern [24]. Moreover, researchers demonstrated that the SHG response from a bilayer heterostructure is a coherent superposition of the SHG response from each composing layer, with intensity being dependent on the twist angle [25]. Nowadays, polarization resolved SHG has become a standard test method to characterize twist angles, including in the study of moiré physics within 2D heterostructures.

Conversely, by precisely adjusting the stacking order and twist angles, a remarkable control of nonlinear optical responses from 2D heterostructures was realized, driven by the modification of system symmetry and band structure. In 2021, Yang *et al.* [26] demonstrated the twist angle tunable SHG in twisted bilayer graphene due to the inversion symmetry breaking. Yao *et al.* [27] reported similar highly twist-angle dependent SHG in vertically stacked h-BN homostructures with multiple interfaces, which paves the way for the realization of highly efficient and *in-situ* tunable nonlinear optical device architectures. Moreover, twist angle modifies the band alignment between composing layers [28], enabling the further modulation of nonlinear optical response,

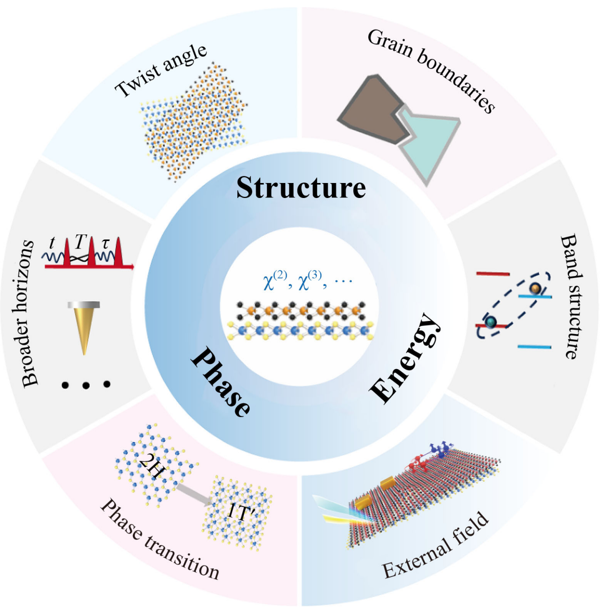

Fig. 2 Recent progresses in the field of nonlinear optics of 2D heterostructures. Owing to their sensitivity to structure, energy, and phase, nonlinear optical responses are demonstrated offering unique insights into the abundant degrees of freedom of 2D heterostructures, such as twist angles, grain boundaries, band structure, external field, phase transition, and beyond, as well as their underlying physics. Conversely, modulations of nonlinear optics become feasible by tweaking these degrees of freedom in 2D heterostructures.

which will be discussed in detail later.

In 2D heterostructures, twist angle and lattice mismatch lead to the formation of moiré superlattices, which has become one of the most exciting topics in condensed-matter physics in recent years [29]. Unveiling the physical mechanisms behind the emergent properties resulting from the formation of moiré patterns in 2D materials is of significant scientific interest and of great importance for various applications. Notably, these properties have been directly linked to phenomena such as superconductivity [30], ferromagnetism [31], and current findings in atomic reconstruction [32]. Further researches in this direction are essential for advancing our understanding of these unique phenomena and exploring their potential implications. Considering the twist angles significantly modify the size and depth of the periodic moiré potentials, the modified localization by moiré potentials provides an ideal platform for the investigation of numerous novel physical phenomena, such as moiré excitons, emergence of mini flat bands, and correlated electronic phases [33–35]. In this case, optical resonances in moiré superlattices also show exceptional sensitivity to the interlayer twist angle.

We anticipate the systematic investigation to the moiré physics by nonlinear optical approaches will unveil more intriguing physics and bring in novel functionalities, as depicted in Fig. 3(a). For instance, how the novel physics in moiré superlattices, e.g., the emergence of correlated electronic phases at specific carrier doping levels, modulates the nonlinear optical responses remains an open question. On the other hand, nonlinear optical responses, as an optical process involving multiple photons, are promising to shed light on the investigation of correlated physics and many-body effects in this system. Overall, there is still plenty of room in this direction, waiting for future explorations.

3 Grain boundaries

The 2D lateral heterostructure is a crucial component for constructing single-layer p–n junctions [36, 37]. Second-order nonlinear optical response greatly depends on the local symmetry of the crystal, making it a suitable tool for characterizing the 2D lateral heterostructures. Through SHG microscopy, the epitaxial growth of MoS_2 in the CVD grown MoS_2/WSe_2 lateral heterostructure has been unveiled, where MoS_2 aligns with the internal crystal orientation of WSe_2 [36]. Furthermore, in these heterostructures where multiple 2D crystals are stitched together, besides the determination of crystal axes, the characterization of grain boundaries between different crystalline domains is crucial but challenging, particularly in lateral homostructures. In 2015, Cheng *et al.* [38] demonstrated the precise determination of the grain boundaries due to SHG interference between neighboring domains. Based on this discovery, a comprehensive investigation into the intricate CVD growth dynamics was made possible. In general, nonlinear optical characterizations offer a noninvasive, rapid, and precise approach for comprehensively studying and monitoring the growth and formation of lateral heterostructures. Along with advances of the CVD growth techniques in recent years [39], we expect that nonlinear optical characterizations hold significant potential in gaining deeper insights into the nature of lateral heterostructures. This can be achieved by enabling real-time monitoring of the dynamics of CVD growth and the distribution of strain. At the same time, the ability to fabricate high-quality 2D heterostructures on a large area by CVD growth provides a critical prerequisite to the application of 2D heterostructures in next-generation nonlinear optoelectronic devices.

4 Band structure

2D heterostructures show distinct band structures and valley alignments through the combination of different constituent materials and twist angles. In general, 2D heterostructures form type-II band alignment that facilitate efficient electron–hole separation and induce fascinating physical phenomena, such as the formation of interlayer excitons and ultrafast interlayer charge transfer. Through the enhanced nonlinear optical responses corresponding to optical resonance in 2D heterostructures, it becomes feasible to reveal the band structures through nonlinear optical approaches. In twisted bilayer $\mathrm{MoS_2}$, researchers employ nonlinear optical responses to reveal the band structure of the system through the SHG enhancement in resonance with A/B excitons and interlayer excitons [40, 41].

Intriguingly, nonlinear optical responses are demonstrated applicable to the investigation of interlayer charge transfer. Interlayer charge transfer in 2D heterostructures, such as $\mathrm{MoS_2/WS_2}$ heterostructure, was observed to occur within an ultrafast timescale (~50 fs in $\mathrm{MoS_2/WS_2}$ heterostructure) [42], which provides a novel approach for the miniaturized light-harvesting devices [43]. Notably, related studies indicate the intensity of SHG in heterostructures positively correlates with the built-in electric field due to interlayer charge transfer, which reveals the dynamics of interlayer charge transfer [44]. Recently, SHG arising from interlayer charge transfer in $\mathrm{ReS_2}$/graphene heterostructure was reported as well [45], introducing SHG in centrosymmetric materials.

Moreover, alteration of the constituent materials in 2D heterostructures, resulting in distinct band structures, automatically leads to the modifications of nonlinear optical responses. SHG from 2D heterostructures formed between monolayer graphene and 2/4/6 layers $\mathrm{MoS_2}$ was investigated [46], wherein the highest SHG signal was observed in heterostructure with bilayer $\mathrm{MoS_2}$, while the lowest SHG signal was observed in heterostructure with 6 layers $\mathrm{MoS_2}$. Additionally, different 2D materials typically have different lattice structures and lattice constants. When they form heterostructures, lattice mismatch results in interface strain and the formation of lattice defects such as wrinkles and domains. These distortions and structural defects notably influence the physical properties of charge carriers, thereby impacting the nonlinear optical response of 2D heterostructures [18].

In general, nonlinear optical responses serve as an efficient all-optical approach to explore the novel physics in 2D heterostructures, including interlayer charge transfer and the formation of interlayer excitons, in which we anticipate abundant underlying mechanisms to be explored in the future. Additionally, band structure related physical phenomena such as interlayer excitons and interlayer charge transfer are sensitive to external fields, especially electric field, across the layers owing to the modified band alignment between composing layers, providing abundant tuning knobs for nonlinear optical responses as elaborated in following paragraphs.

5 External field

One of the most fascinating features of 2D heterostructures lies on its sensitivity to external fields, which enables the fine tuning of the band structure and band alignment, which consequently enables the modification to light-matter interaction and modulation of nonlinear optical responses. For instance, in 1L graphene/2L $\mathrm{MoS_2}$ heterostructure, external electrical field controlled interlayer charge transfer was discovered to significantly modulate SHG intensity [46]. This behavior is attributed to the altered charge transfer between the composing layers due to the applied gate voltages, which alters nonlinear polarization of the system. Similar to the doping-dependent THG and four-wave mixing (FWM) in monolayer graphene [47], gate-tunable nonlinear optical phenomena are anticipated to exist in 2D heterostructures as well. These findings pave the way for the future development of gate-tunable nonlinear optical responses in 2D heterostructures.

Strain field shows profound impacts on the physical properties of 2D materials. In the study of nonlinear optics in 2D materials, strain modulation holds importance due to the high sensitivity of SHG to strain effects. In a study by Li *et al.* [48], monolayer $\mathrm{MoS_2}$ was deposited onto $\mathrm{TiO_2}$ nanowires to form a $\mathrm{MoS_2/TiO_2}$ heterostructure. By manipulating the twist angle between the nanowires and the monolayer $\mathrm{MoS_2}$, the $\mathrm{MoS_2}$ experienced uniaxial strain with different orientations, thereby achieving control over the polarization dependent SHG intensity of $\mathrm{MoS_2}$. The experimental results demonstrated a significant enhancement in the SHG intensity within the heterostructure region. By comparing the polarized SHG intensity of the heterostructure region with that of the monolayer $\mathrm{MoS_2}$, the researchers were able to further extract the strain fields distribution inside heterostructures. Moreover, in comparison to bulk materials, vertical heterostructures possess inherent robustness against heterostructure strains, making strain engineering of 2D materials remarkably prominent. Overall, nonlinear optical responses hold immense promise in precisely characterizing and evaluating strains within these materials [49, 50].

By manipulating light field, e.g., phonon energy, field strength, polarization, interaction between light and 2D heterostructures can be directly controlled. For instance, with the presence of silicon substrate, when the photon energy is tuned resonant with the intralayer and interlayer excitons of bilayer $\mathrm{MoS_2}$, SHG intensity undergoes considerable enhancement [41], showing comparable intensity to the non-resonant case in monolayer $\mathrm{MoS_2}$. At the same time, the SHG signal away from the exciton resonance in bilayer $\mathrm{MoS_2}$ remains orders of magnitude smaller than that from the monolayer $\mathrm{MoS_2}$. Furthermore, under the influence of strong light field, numerous novel light-induced phenomena, such as Floquet states and light induced topological phases, provide a grand avenue to further modulate nonlinear optical responses of 2D materials and heterostructures [51].

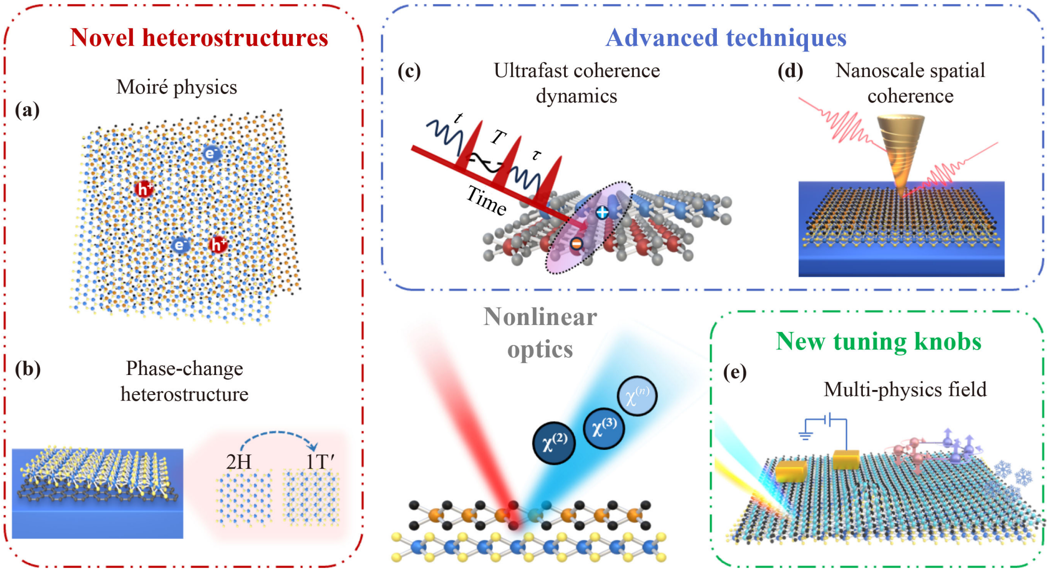

Fig. 3 Directions for future research on the nonlinear optics of 2D heterostructures. We anticipate the future endeavors will mainly focus on three aspects: **(a, b)** exploration of nonlinear optics in novel heterostructures, like moiré superlattice (a) and phase change heterostructure (b); **(c, d)** unveiling of deeper physical insights by advanced techniques such as 2DCS (c) and adiabatic plasmonic nano-focusing technique (d); **(e)** modulation of nonlinear optics via tuning the properties of 2D heterostructures by various tuning knobs.

In addition to the aforementioned modulation strategies by external field, coupling 2D materials with micro-nano structures, such as microresonators, metasurfaces, quantum dots and nanowires (NWs), to form mixed-dimension heterostructures allows for further enhancement and manipulation of nonlinear optical responses. In 2019, Hu *et al.* [52] reported on the utilization of metasurface to control the incident light phase, combined with the valley selective optical transitions in 2D TMDCs, enabling researchers to enhance and steer nonlinear valley-locked chiral emission at room temperature. Subsequently, in 2021, by exploiting the capability of gold nanoribbons to enhance the electric field of incident beam and the graphene plasma emission, researchers realized a significant enhancement of THG from monolayer graphene [53]. In the same year, Hong *et al.* [54] reported that by coating a 200 nm thick layer of quantum dots film onto 2D materials can significantly enhance nonlinear optical response, with an enhancement exceeding three orders of magnitude. There are also studies on the modulation of nonlinear optical responses generated through coupling with NWs. In 2022, Shafi *et al.* [55] reported the preparation of high-quality InP nanowires on MoS_2. They observed significant nonlinear optical responses in the NW/MoS_2 heterostructures. Another example is the heterostructure comprising 2D InSe and 1D AlGaAs NWs. Through this approach, the engineering of the in-plane dipole moment in InSe is achieved, the SHG enhancement factor of this system is estimated to be about 12 [56]. These preliminary advances based on monolayer 2D materials pave the way for future high performance nonlinear optoelectronic devices based on 2D heterostructures.

Combining with electric, strain, optical and other external fields like thermal field and magnetic field, researchers expect an efficient modulation of nonlinear optical responses. However, it is noteworthy that the extent of research conducted thus far remains preliminary, which leaves plenty of room for future research and applications. Especially, by implementing multi-physics fields jointly as depicted in Fig. 3(e), the precise control, deep modulation and novel phenomena of the nonlinear optical responses in 2D heterostructures are anticipated, which will facilitate the design and optimization of innovative nonlinear optoelectronic devices, and potentially open up new avenues in quantum information and optoelectronic applications [57].

6 Phase transition

The characterization and manipulation of diverse phases constitute a fundamental undertaking in the field of condensed matter physics. Thus far, a plethora of phase transitions in 2D materials have been reported, ranging from structural phase transition to magnetic phase transition. The dynamic phase transitions in 2D heterostructures can be driven by various factors: chemical reaction, temperature, strain, laser irradiation, doping levels, electric field, magnetization, and so on [58]. Transition between different phases usually involves intricate physics, such as lattice and layer interactions, as well as interactions among strongly correlated electrons. By virtue of their sensitivity to both structural and electronic phases, nonlinear optical approaches have been extensively applied to characterize phase transitions in 2D materials. These techniques offer several advantages, including non-invasiveness and real-time visualization. For instance, a plethora of methods were demonstrated to induce phase transitions in the 2H-MoTe$_2$, including laser ablation, thermal treatment, and local strain. The experimental results show a transformation of SHG polarization pattern from the original six-fold symmetry to two-fold symmetry in the induced region [59], indicating a transition from the 2H phase (D_{3h}^1 space group), which exhibits semiconductor properties, to the 1T' phase (C_s^1 space group) with metallic properties.

Meanwhile, transition between different phases of 2D materials provides a promising way to realize high performance optoelectronic devices, including memristors and nonlinear optical devices [60], owing to the potential of changing 2D heterostructure properties fundamentally due to reshaped band alignment, proximity effect, etc., through phase transition by external factors. Specifically, considering the structural phase transition of few layer MoTe$_2$ within 2D heterostructures from 2H semiconducting phase to 1T' metallic phase, we anticipate observing a significant modification in nonlinear optical responses from these 2D heterostructures. Moreover, the transition between magnetic phases, e.g., different nematic orders in the antiferromagnet FePS$_3$, offers great opportunities for the magnetic tuning of nonlinear optical responses in composing heterostructures [61]. Overall, phase-change 2D heterostructures hold the great promise to further advance nonlinear optical applications, as summarized in Fig. 3(b), paving the way for novel functionalities and applications in optoelectronic and photonic domains.

7 Broader horizons

In contemporary times, the characterization and modulation of nonlinear optical responses within 2D heterostructures are extending their influence to a broader sphere of impact. For instance, nonlinear optical responses, which offer advantages including high sensitivity, rapid imaging speed, extensive detection area, and non-invasiveness, are suitable for the real-time monitoring of chemical reaction process, including oxidation effects. By employing a combination of SHG and FWM techniques, both structural and electronic imaging can be performed, enabling the real-time observation of oxidation kinetics in bilayer MoS$_2$. As demonstrated by Li *et al.* [62], the central region of the bilayer MoS$_2$ progressively undergoes a transition into a complete monolayer MoS$_2$ with prolonged annealing time in atmosphere. We expect diverse potential applications based on nonlinear optical responses within 2D heterostructures are on their way in the future.

Applications of novel nonlinear optical techniques are expected to provide deeper insights into the study of 2D heterostructures. SHG, sum-frequency generation (SFG) and FWM are demonstrated as a powerful tool to unveil the profound exciton interactions and dynamics in monolayer TMDCs, which are expected to provide deeper insights in 2D heterostructures [63, 64]. Employing a Raman-like FWM process, two-dimensional coherent spectroscopy (2DCS) is involved recently to probe and manipulate the quantum dynamics of 2D materials. By virtue of the 2DCS technique, the coherence dynamics and many-body effects of exciton families in 2D heterostructures can be unequivocally extracted, shedding light on the intricate mechanisms that govern novel physical phenomena [65]. 2DCS has successfully detected exciton families and their associated dynamics in MoSe$_2$/WSe$_2$ and WS$_2$/MoS$_2$ heterostructures [65, 66]. Potential research directions for 2DCS experiments in 2D heterostructures include a wide array of topics, such as the quantum coherence between interlayer excitons and other quasiparticles, many-body effects of interlayer excitons, and quantum dynamics of moiré excitons [67, 68]. Besides, the evolution of near-field optical microscopies, notably exemplified by the adiabatic plasmonic nano-focusing technique and tip-enhanced scanning probe microscopy [69], has illuminated a pathway towards the study of nonlinear optical responses such as SHG and FWM within 2D heterostructures at the nanoscale, breaking the diffraction limit of nonlinear optical responses [70]. The near-field nano-imaging of the nonlinear optical responses is made possible by the nano-confined light field at the tip apex, which provides a microscopic way to unveil the underlying physics of the interaction between 2D materials and nanophotonic structures, including plasmonic structures, photonic cavities, metamaterials, and aligns seamlessly with ultrafast spectroscopy techniques. Overall, the involvement of novel nonlinear optical techniques is expected to provide profound insights into the 2D heterostructures, which in turn holds the potential to catalyze progress in diverse fields including sensors, optoelectronics, and energy conversion.

8 Summary

In summary, although significant progress has been made in the field of nonlinear optics, the investigation into nonlinear optics of 2D heterostructures remains at a preliminary stage, due to the inherent complexity arising from their distinctive low-dimensional characteristics and abundant degrees of freedom. Along with the opportunities and challenges therein, we anticipate a rapid growth in this burgeoning field. As depicted in Fig. 3, through the investigation of novel 2D heterostructures like moiré superlattice and phase-change heterostructures, coupled with new modulation approaches exemplified by the multi-physics field joint modulation and novel nonlinear optical techniques, such as near-field optics and 2DCS, we expect to gain further insights into the research and applications of nonlinear optics in 2D heterostructures in the near future.

Declarations The authors declare that they have no competing interests and there are no conflicts.

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