Review

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Near-field optical imaging and spectroscopy of 2D-TMDs

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Abstract: Two-dimensional transition metal dichalcogenides (2D-TMDs) are atomically thin semiconductors with a direct bandgap in monolayer thickness, providing ideal platforms for the development of exciton-based optoelectronic devices. Extensive studies on the spectral characteristics of exciton emission have been performed, but spatially resolved optical studies of 2D-TMDs are also critically important because of large variations in the spatial profiles of exciton emissions due to local defects and charge distributions that are intrinsically nonuniform. Because the spatial resolution of conventional optical microscopy and spectroscopy is fundamentally limited by diffraction, near-field optical imaging using apertured or metallic probes has been used to spectrally map the nanoscale profiles of exciton emissions and to study the effects of nanosize local defects and carrier distribution. While these unique approaches have been frequently used, revealing information on the exciton dynamics of 2D-TMDs that is not normally accessible by conventional far-field spectroscopy, a dedicated review of near-field imaging and spectroscopy studies on 2D-TMDs is not available. This review is intended to provide an overview of the current status of near-field optical research on 2D-TMDs and the future direction with regard to developing nanoscale optical imaging and spectroscopy to investigate the exciton characteristics of 2D-TMDs.

Keywords: exciton; TEPL; TERS; TMD; two-dimensional materials.

1 Introduction

Since the discovery of graphene, two-dimensional (2D) materials have been the focus of extensive studies; however, optical applications of graphene and other metallic 2D materials have been limited due to the absence of a bandgap [1–5]. Transition metal dichalcogenides (TMDs) are semiconducting 2D materials with bandgaps that cover the visible and infrared ranges, and the number of layers can be controlled owing to the weak van der Waals interlayer interaction [6]. In addition, the effects of quantum confinement and low dielectric screening cause the binding energies of excitons in 2D-TMDs in a single layer to be very large, i.e., up to a few 100 meV [7, 8]. This has led to extensive research on various exciton-based optoelectronic applications [9–12].

Atomic force microscopy (AFM), scanning tunneling microscopy (STM), and transmission electron microscopy (TEM) can reveal structural properties such as surface roughness, height, defects, and lattice structure of 2D-TMDs with atomic resolution [13–15]. However, these microscopy techniques do not provide optical responses such as photoluminescence (PL), Raman scattering, and absorption spectra. Confocal optical microscopy facilitates the visualization of the spatial distribution of PL and Raman scattering at diffraction-limited spatial resolution and has been extensively used in the characterization of nanomaterials and devices [16–19]. However, the spatial resolution of confocal microscopy is limited to ~300 nm [20, 21], and the near-field scanning microscope is a good option for measuring the optical properties of 2D-TMDs [22–25] with a spatial resolution higher than 100 nm. Specifically, near-field scanning microscopy (NSOM), tip-enhanced PL (TEPL), and Raman spectroscopy (TERS) techniques have been highly effective in obtaining nanoscale optical images of 2D-TMDs [26–28].

To date, there have been a number of review papers on the use of near-field microscopy on low-dimensional materials [29–33], but no review has been dedicated to near-field optical studies of 2D-TMDs that has brought significant advances on understanding of local optical properties of 2D-TMDs. For instances, ultra-high spatial

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resolution of near-field optical imaging and spectroscopy have enabled the optical identification of nanoscale structural defects such as localized defects, grain boundaries, and wrinkles on 2D-TMDs, and visualized fine modulation of spatial distribution of local charge carriers [26, 34, 35], which are not normally probable by far-field optical imaging. Furthermore, in near-field systems using metallic probes, the optical responses of 2D-TMDs can be manipulated by locally tuning the strain or plasmon coupling [28, 36]. In this review, studies on the optical properties of 2D-TMDs performed by near-field microscopy are reviewed in terms of the specific interests of the studies such as the identification of defects and carrier densities or the effects of strain and plasmon resonances on the spectral and spatial characteristics of exciton emissions of 2D-TMDs.

2 Overview of development of near-field optical microscopes

The resolution of a conventional optical microscope is limited to the Rayleigh criterion given as $0.61 \times \lambda/\text{NA}$, where λ is the wavelength of light and NA is the numerical aperture of the lens. A confocal optical microscope integrated with a laser source and detection pinhole can provide a slightly better resolution; however, the spatial resolution is still limited by diffraction [17, 37, 38].

Near-field optical microscopy was developed to overcome the diffraction limit. In 1928, Synge proposed the concept of near-field optical microscopy using a nanoscale hole, where the spatial resolution was limited by the hole size rather than the diffraction or the wavelength of the light [39]. In his paper, Synge suggested that the sub-wavelength hole must be very close to the object in the “near-field” regime to facilitate the evanescence field. Ash and Nicholls demonstrated Synge’s proposal using microwaves in 1972 [40]. Lewis and Pohl first described an optical near-field application in 1984 [41, 42]. Betzig first designed aperture-type near-field scanning optical microscopy (a-NSOM) using a metallized pipette tip with an aperture size of ~ 100 nm and achieved a spatial resolution of $\sim \lambda/43$ [43, 44].

Another type of NSOM system designed by Keilmann is a scattering-type scanning near-field optical microscopy (s-SNOM) [45], where an apertureless tip instead of an aperture probe was used to locally scatter the light and the spatial resolution of s-SNOM was determined mostly by the apex size tip. Recently, the concepts of TERS and TEPL were developed by integrating s-SNOM with a plasmonic tip (AFM or STM tip made or coated with Au or Ag) to scatter

the near-field signal, and a high spatial resolution beyond the diffraction limit was achieved [27, 36]. Near-field optical microscopes can be categorized into two types: aperture and scattering. Figure 1 shows the schematics of the working principles of the confocal microscope, a-NSOM and s-SNOM.

3 Identification of exciton profiles around structural defects

3.1 Exciton emissions affected by defect formation

TMDs are composed of the chemical formula MX_2 , where M is a transition metal and X is a chalcogen atom and one transition metal is vertically sandwiched by two chalcogenide atoms [46]. 1L-TMDs display extremely stable formations of bound excitons consisting of electrons and holes even at room temperature with a large exciton binding energy owing to the strong Coulomb interaction, suggesting many promising exciton devices [7, 8]. Depending on the growth methods or physical parameters such as local structural defects and carrier concentration of TMDs, 1L-TMDs show spatially different exciton distributions. Various exciton species such as excitons (bright or dark), trions (positive or negative), and biexcitons (coupled with two exciton) and defect-state excitons lead to complex optical responses [6, 47–49]. Although the structural properties of 1L-TMDs have been characterized by AFM, STM, and TEM [13–15], in order to investigate the variations in the optical responses such as PL and Raman scattering

Figure 1: Schematics of confocal, a-NSOM, and s-SNOM microscopes applied to optical investigation of 2D-TMDs. a-NSOM: aperture-type near-field scanning optical microscopy. s-SNOM: scattering-type scanning near-field optical microscopy. Δx represents typical size of spatial resolution achievable by respective methods. λ : light wavelength; NA: numerical aperture of objective lens. Red spots represent excitation area of 2D-TMDs and green shadow represents laser illumination.

affected by variations in structural properties, one needs optical tools with a high optical resolution.

Because grain boundaries (GBs) and local defects of 1L-TMDs generated during the growth process with nanoscale dimensions are responsible for the spatial nonuniformity of 1L-TMDs [14, 50], optical investigations using far-field optical microscopy provide limited understanding of the local behavior of exciton complexes in nonuniform 1L-TMDs requiring the use of near-field imaging combined with PL or Raman spectroscopy. In this section, we focus on the characterization of 1L-TMDs through near-field imaging using NSOM, TERS, or TEPL for nanoscale profiling of exciton emissions of 1L-TMDs.

3.2 Grain boundary

PL variation in GBs of 2D-TMDs has been reported to occur as either a PL reduction or increase [50–52]. Near-field PL images clearly showed the PL variation around the GBs and structural defects such as add-layer and line defects [26]. Figure 2a shows confocal and near-field images of CVD-grown 1L-MoS₂ with spatial resolutions of ~400 and ~100 nm, respectively. Unlike the confocal PL image, the near-field PL image clearly shows distinguishable GBs. In addition, the reduction in PL intensity due to physical damage is consistent with previous data [53, 54]. Similar work on PL imaging around GBs was performed by Bao et al. [55], who investigated the near-field spectral characteristics of CVD-grown 1L-MoS₂ using

a campanile tip, an apertureless-type tip that produced ~60 nm spatial resolution, as shown in Figure 2b. From near-field spectral imaging, the PL emission of the CVD-grown 1L-MoS₂ was found to consist of excitons (1.84 eV) and trions (1.81 eV) [56, 57], and PL intensity quenching was observed at the edges and GB regions. This can be explained by the n-doping effect near the edge, and GBs coming from the sulfur vacancies tend to reduce the PL intensity [58, 59].

By contrast, in the case of 1L-MoSe₂, the PL intensity was stronger at the GBs and edge sites, as shown in Figure 2d, which was conducted by TEPL [60]. Because tip-induced plasmon enhancement can generate excess carriers in 1L-MoSe₂ and cause the doping effect by oxidation, the exciton species of 1L-MoSe₂ are mostly biexcitons and trions, as shown in Figure 2c, which is consistent with the previous result [28, 61]. Near-field PL images of trions and biexcitons show that the GBs and edge sites exhibit stronger PL signals both by trions and biexcitons than in other regions. This was attributed to the electron tunneling occurring on GBs and edges owing to the lower dielectric constant and the plasmon coupling [62]. Smithe et al. also performed TERS of CVD-grown 1L-MoSe₂, as shown in Figure 2e [63].

Figure 2e shows the TERS image and three representative Raman spectra obtained at the resonance (orange), nonresonance (purple) excitation, and GB regions (black). Raman spectra indicate that the A₁' mode (240 cm⁻¹) is strong at the nonresonant excitation, and the E' mode (287 cm⁻¹) and at 340, 460, and 550 cm⁻¹ are strong at the

Figure 2: Near-field images of 1L-TMDs.

(a) Confocal (left panel) and near-field (right panel) PL images of 1L-MoS₂. Reproduced with permission from ref. [26]. Copyright 2015, Royal Society of Chemistry. (b) Illustration (left panel) and near-field PL image (right panel) of 1L-MoS₂ using the Campanile tip. Inset: representative deconvoluted averaged spectra obtained by near-field image. Reproduced with permission from ref. [55]. Copyright 2015, Nature Publishing Group. (c) Representative deconvoluted averaged PL spectrum of 1L-MoS₂. (d) Near-field PL images of trion (left panel) and biexciton (right panel). Reproduced with permission from ref. [60]. Copyright 2020, Nature Publishing Group. (e) TERS image (left panel) and averaged TERS spectra (right panel). Reproduced with permission from ref. [63]. Copyright 2018, American Chemical Society. (f) Simulated optical field profile at sample plane for tilted ($\theta_{\text{tip}} = 35^\circ$) and ($\theta_{\text{tip}} = 90^\circ$) tip orientations. (g) Near-field second harmonic generation (SHG) image. (h) Far-field SHG images measured parallel and perpendicular to the excitation direction configuration. Reproduced with permission from ref. [69]. Copyright 2018, American Chemical Society.

resonant excitation [64]. In particular, the Raman spectrum near 995 cm^{-1} , known as the out-of-plane molybdenyl bond ($\alpha\text{-MoO}_3$), was observed using TERS measurements [64, 65]. The nanoscale domain of MoO_3 was created during growth. The TERS image shows only the background signal at the GB regions owing to the lack of MoSe_2 flakes in the GBs. In general, second harmonic generation (SHG) can identify structural features such as defects, crystal orientation, and stacked angle for bilayers through the nonlinear optical response [66–68]. Park et al. performed SHG near-field imaging of 1L- MoS_2 with control of the tip orientation [69]. Far-field SHG images showed the typical change in SHG intensity depending on the laser polarization and the orientations of MoS_2 grains, as shown in Figure 2h [68]. By contrast, the near-field SHG image obtained with 35° tilted tip showed the uniform SHG contrast regardless of the MoS_2 grain orientation, as shown in Figure 2g. It is because the near-field tip with tilted configuration ($\theta_{\text{tip}} = 35^\circ$) produces both the out-of-plane and in-plane optical fields unlike the normal ($\theta_{\text{tip}} = 90^\circ$) tip that preferentially produces the out-of-plane fields [26, 55, 60, 63], whereas far-field SHG imaging uses mostly the in-plane illumination that are the most efficient to induce SHG signal [68]. It was observed that near-field SHG intensity obtained at a 35° tilted tip was 10 times higher than at 90° normal tip, as shown in Figure 2f.

3.3 Local defects

Local defects in 2D-TMDs occur for several reasons. For example, structural defects such as atomic vacancies and

line defects such as wrinkles can be created under fluctuating growth conditions or transfer processes [14, 59, 70, 71]. Local defects cause 2D-TMD to be spatially nonuniform and may reduce the quantum yield (QY), which can significantly affect the efficiency of optoelectronic devices. Therefore, precise near-field imaging with a high spatial resolution has been used to determine the roles of local defects. In this section, we focus on the near-field imaging of local defects in 1L-TMDs to study the relationship between optical responses and local defects.

Lee et al. performed near-field imaging of CVD-grown 1L- WS_2 using an aperture type with $\sim 70\text{ nm}$ spatial resolution [34]. Figure 3a displays the near-field excitons, trions, and defect-bounded exciton profile images. In this study, researchers observed the presence of localized defect state excitons at room temperature, which were not identified by confocal microscopy owing to the large detection volume. In addition, they found that exciton emission spreads uniformly along the line defects, while trion emission is reduced there. This can be explained by the smaller population of excess electrons on the wrinkles or the different behaviors of diffusion of excitons and trions. Defect-bounded excitons were mostly detected around the line defects, which is consistent with the nature of defect-bound excitons [72, 73].

On the other hand, TERS imaging of 1L-TMDs has also provided spatial information about local defects in 1L-TMDs, which is not usually detected by far-field optical microscopy. TERS images with high spatial resolution and enhanced Raman signals identified the local defect regions [74–76]. In particular, Lee et al. first observed defect-related Raman modes from CVD-grown 1L- WS_2 at room

Figure 3: Near-field images of CVD grown 1L-TMDs.

(a) Near-field PL images of exciton, trion, and local defect exciton of 1L- WS_2 , respectively. Reproduced with permission from ref. [34]. Copyright 2017, Royal Society of Chemistry. (b) Line profile of TERS intensity (upper panel) and TERS spectrum of 1L- WS_2 (lower panel). (c) TERS images of A_{1g} peak area intensity and peak position, respectively (upper panel) and D peak and D' intensity, respectively (lower panel). Reproduced with permission from ref. [27]. Copyright 2018, American Chemical Society.

temperature using a TERS system; the results are shown in Figure 3c and d [27]. Owing to the plasmonic enhancement occurring between the tip and substrate and the ~ 45 nm spatial resolution, defect-related Raman modes D and D' peaks, referred to as B_{1u} , were observed only in the bilayer WS_2 , as shown in Figure 3c [77, 78]. Figure 3d shows the separated near-field TERS peak position images of the A_{1g} , D, and D' modes and the intensity of the A_{1g} mode. The intensities of the D and D' modes are spatially correlated with the red-shifted A_{1g} peak position, whereas they are anticorrelated with the intensity of the A_{1g} mode, perhaps owing to the increased sulfur vacancies at local defect regions.

4 Exciton emission modulated by charge transfer

4.1 Near-field imaging of local charge distribution

Carrier density is a critical factor that determines the PL spectral weights of the exciton species, as well as the overall PL intensity. Near-field imaging techniques provided nanoscale optical imaging of carrier density profiles of 2D-TMDs [34, 79]. Figure 4a displays near-field PL images of ratio of trion emission to exciton emission of 1L- WS_2 at 6 and 20 mW laser power. Figure 4b shows the representative PL spectra obtained at 6 and 20 mW laser power.

Figure 4a and b both indicate that as the laser power was increased, trion spectral weight increased. Because the energy difference between exciton and trion energy peak represents the trion dissociation energy (E_{ds}) that is the sum of the trion binding energy and the Fermi level (E_F) as schematically depicted in Figure 4c. Thus, the map of E_{ds} would represent the local distribution of Fermi level (E_F) assuming the constant value of trion binding energy (estimated to be ~ 20 meV [80]) or the amount of accumulated charges. Figure 4d shows near-field images of E_{ds} at 6 mV and 20 mW. At 20 mW laser power, the regions of high E_F are spatially correlated with the line defects, which suggest the local charge population around the line defects. Figure 4e displays near-field PL images of 1L- MoS_2 obtained at 1.83 and 1.87 eV corresponding to trion (upper side of Figure 3b) and exciton emission (lower side of Figure 3b), respectively [56, 57]. In both images, PL is lower along the line defects but more distinctively in exciton emission, which means the ratio of trion to exciton is higher along the line defects. This observation suggests that the electron density is high at defect sites and grain edges, which tend to be populated with sulfur vacancies [50, 58, 81, 82].

4.2 Charge exchanges in TMD heterostructures

Near field imaging can capture the spatial and spectral changes of PL emission caused by the charge transfer and

Figure 4: Local charge population of 1L- WS_2 .

(a) Near-field image of the ratio of trion emission to exciton emission at 6 and 20 mW, respectively. (b) Representative near-field PL spectra. (c) Schematic energy band diagram to explain the relation between trion dissociation energy (E_{ds}), trion binding energy (E_b) and Fermi level (E_F). (d) Near-field images of E_{ds} or the estimated E_F assuming E_b of 20 meV at 6 and 20 mW. Reproduced with permission from ref. [34]. Copyright 2018, Royal Society of Chemistry. (e) Near-field PL images of trion and exciton of 1L- MoS_2 , respectively. Reproduced with permission from ref. [79]. Copyright 2018, Royal Society of Chemistry.

exchanges. 1L-TMDs can be vertically stacked to form a vertical heterostructure owing to the weak van der Waals interaction between 2D-TMD layers. Generally, 2D-TMD heterostructures often form a type II band alignment, facilitating the separation of electrons and holes; further, they can host the interlayer exciton, which has a long lifetime [83–85]. The unique characteristics of the heterostructure have been widely utilized in optoelectronic, photodetector, and light-harvesting applications [86–88]. However, in the case of vertical TMD heterostructures, we found only two papers using near-field imaging techniques, probably because of the low intensity of the heterostructure PL due to charge transfer across the heterostructure interface [89, 90]. TEPL imaging of a vertical $\text{WSe}_2/\text{MoSe}_2$ heterostructure [89] revealed the intralayer and interlayer exciton dynamics (further discussion on this work is given later in the 5.2 plasmon resonance section). In another study, TEPL imaging of vertical heterostructures of $\text{WSe}_2/\text{MoS}_2$ and $\text{MoS}_2/\text{WSe}_2$ [90]. In this study, the blisters and nanobubbles showed different PL signals (more discussion is given in Section 5.1). On the other hand, lateral heterojunctions (HJs) between different kinds of 1L-TMDs have been fabricated, where two domains of different TMDs form a lateral HJ with atomically sharp interfaces [91–93]. Because physical properties such as the formation of interface width and optical properties such as exciton behavior at the interface are of key interest for application in optoelectronic devices [94, 95], it is important to optically investigate lateral HJ formation with nanoscale spatial resolution.

Figure 5 shows the results of the near-field PL imaging of lateral $\text{MoSe}_2/\text{WSe}_2$ HJ [96–98]. Figure 5a shows the TEPL imaging of the multijunction lateral HJ of $\text{MoSe}_2/\text{WSe}_2$ synthesized by a water-assisted CVD growth process [99, 100]. For the TEPL measurements, they used an Au-coated Ag tip, and the spatial resolution was estimated to be ~ 40 nm. In this image, the bright and dark regions correspond to WSe_2 and MoSe_2 , respectively. Interestingly, two types of smooth (~ 230 nm) and sharp (~ 40 nm) interfaces existed, as shown in the inset of Figure 4a, which were caused by the gas switching during the CVD growth [99, 101]. Figure 5b also displays the TEPL image of the lateral HJ of $\text{MoSe}_2/\text{WSe}_2$ grown by CVD under variable temperature conditions [96]. The interface width of HJ was ~ 150 nm, and they further investigated the varying plasmonic effects of the interface region while adjusting the tip-sample distance, which is discussed in detail in Section 5.2. Near-field PL imaging using an aperture-type probe with an aperture size of ~ 90 nm was also utilized for the investigation of lateral HJ, as shown in Figures 4d and 5c [98]. PL quenching at the interface was observed with a spatial

width of ~ 370 nm, which originated from the exciton charge separation due to the type II band alignment between the MoSe_2 and WSe_2 monolayers [102]. For the quantitative analysis, a plot of the trion/exciton ratio versus lateral distance across the interface was provided. While approaching the interface, the trion/exciton ratio of MoSe_2 , which represents the density of excess charge, increased, while that of WSe_2 decreased. These results directly indicate that exciton separation occurs at the interface of the lateral HJ.

Several groups have focused on the role of aging effects that result in exciton suppression in lateral TMD HJs. Figure 6a shows the TEPL images obtained after 2 weeks of growth, where the nanoparticles were generated due to the aging effect [97]. No nanoparticles were observed in the fresh samples, as shown in Figure 5a. Aging-induced nanoparticles prevented the tip-induced enhancement of the near-field PL signal and quenched the PL intensity. In addition, the PL peak position of the nanoparticles exhibited a 2–4 nm red-shift because of the strain at the localized nanoparticle sites. Another group also performed TEPL imaging of MoS_2/WS_2 HJ, as shown in Figure 6b [103]. The heterostructure consists of WS_2 in the outer region and MoS_2 in the inner region, forming an HJ width of ~ 100 nm. Figure 6b shows near-field PL images obtained at 1.94 eV (WS_2 excitons) and 1.81 (MoS_2 excitons) with time ranges of 1–103 days. The WS_2 and MoS_2 regions displayed different degradations of PL intensity. The PL intensity of WS_2 showed spatially inhomogeneous degradation, the rate of which rapidly decreased after a few days. By contrast, the MoS_2 regions maintained almost the same PL intensity for up to 103 days. This distinct difference could be explained by the fact that the density of sulfur vacancies, which leads to degradation by oxidation, is higher along the edge regions than in the inner regions [104]. In addition, the HJ interface may have blocked oxidation propagating from the edge to the inner regions. Because the formation of $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ alloy is known to be thermodynamically stable [105], the presence of HJ may have prevented oxidation of the inner region.

4.3 Effects of chemical doping and passivation

Chemical doping and defect passivation can modulate the carrier density of 1L-TMDs. Chemical doping by molecular adsorption has been extensively used to transfer charges to 1L-TMDs. For example, the PL intensity of n-type 1L-TMDs, such as MoS_2 , MoSe_2 , and WS_2 , was significantly enhanced by chemical p-doping, which was attributed to the

Figure 5: Near-field images of lateral HJ of WSe₂/MoSe₂.

(a) TEPL image. Inset: the line profile obtained along the white dash lines in the TEPL image. Reproduced with permission from ref. [97]. Copyright 2019, Optical Society of America. (b) TEPL image. Inset: the line profile highlighted white dashed line in TEPL image. Reproduced with permission from ref. [96]. Copyright 2018, American Physical Society. (c) Near-field PL image. Inset: the line profile highlighted black dash in near-field PL image. (d) Plot of the trion/exciton ratio of WSe₂ (upper) and MoSe₂ (lower). Inset: the band alignment of MoSe₂/WSe₂ lateral HJ. Reproduced with permission from ref. [98]. Copyright 2019, Optical Society of America.

Figure 6: TEPL images that show the aging effect of TMD HJ (a) TEPL intensity (upper panel) and peak position (lower panel) images. Squares display the location of nanoparticles formed by aging effect. Reproduced with permission from ref. [97]. Copyright 2019, Optical Society of America. (b) TEPL images obtained at 1.94 eV (upper) and 1.81 eV (center) and interface (lower). Reproduced with permission from ref. [103]. Copyright 2021, American Chemical Society.

reduction of charge screening and Auger recombination [19, 57]. On the other hand, several studies have reported that local defects in 1L-TMDs can be repaired by chemical treatment, greatly increasing the PL emission. Amani et al. showed that exfoliated 1L-MoS₂ and 1L-WSe₂ treated with bis(trifluoromethane)-sulfonimide (TFSI) showed near-unity QYs [106]; however, mechanism of the PL modulation by chemical treatment is not clear. This is because chemical treatments tend to have concurrent effects on both doping and defect repair. Therefore, in order to understand the exact mechanism, a precise investigation that can spatially and spectrally distinguish the defect and clean regions of 1L-TMD is required. In this section, we discuss the near-field images obtained before and after chemical treatment of 1L-MoS₂.

Figure 7 displays near-field images of CVD-grown 1L-MoS₂ obtained before and after TFSI and 7,7,8,8-tetracyanoquinodimethane (TCNQ) that acted as chemical doping [79]. Before chemical treatment, exciton emission was weak at line defects, while trion was relatively strong. This effect more clearly appeared in the trion/total emission ratio image (A^-/A^{Total}). CVD-grown 1L-MoS₂ was known to be n-type and trions are populated at line defects, as

shown in Figure 4e, which are in good agreement with previous results [50, 58, 81, 82]. After chemical treatment, total PL emission increased and the exciton and trion emission also followed the trend of total emission. However, the trion/total emission ratio was reduced. This result indicates that the electron depletion by TFSI is more distinct at line defects. On the other hand, in the case of chemical doping by TCNQ, the PL was enhanced in the defect-free region, as shown in Figure 7b. This means the p-doping by TCNQ was conducted uniformly, whereas electron depletion or p-doping effects by TFSI was prominent at the defect sites.

5 Effects of strain and plasmon resonances

5.1 Strain

Strain engineering of 2D-TMDs can modulate their electronic, optical, and excitonic properties. For example, exciton funneling of 1L-WSe₂ can be controlled by the

Figure 7: Near-field PL images of 1L-MoS₂ by two different chemical treatment.

(a) Near-field PL images of total, exciton, trion, and trion/total ratio 1L-MoS₂ before (upper panel) and after TFSI-treatment (lower panel). (b) Near-field PL images of total, exciton, trion, and trion/total ratio of 1L-MoS₂ before (upper panel) and after TCNQ-treatment (lower panel). Reproduced with permission from ref. [79]. Copyright 2018, Royal Society of Chemistry.

formation of topographic wrinkles [107], and the exciton-phonon coupling of 1L-TMDs can be modulated by mechanical strain [108], and the band gap can be tuned by the strain gradient in bilayer MoS_2 [109]. Strain on 2D-TMDs can be present on bubbles, blisters, and wrinkles that are naturally formed during the growth or transfer process [90, 110] or artificially made by substrate deformation, thermal expansion, and AFM tip contact [107, 111, 112]. Both natural and artificial structures can produce switchable and tunable optical properties of 2D-TMD [113–115]. However, because the strain in 2D-TMDs made by the above-mentioned methods is locally generated at the nanoscale, strain effects can hardly be directly observed with far-field optical microscopy. In this section, we discuss how strain effects can affect 2D-TMD, as revealed by near-field imaging.

Bubbles and wrinkles generated by the growth or transfer process can induce strain on 2D-TMDs [90, 110]. Near-field studies on wrinkles were performed using TERS and TEPL, as shown in Figure 8 [76, 116]. Figure 8a shows the TERS image of the wrinkles with a spatial resolution of ~ 20 nm. Wrinkles were well identified by AFM and showed strong TERS intensity. The authors explained that the increase in the TERS signal at the wrinkle is due to the folding of the layers. TEPL imaging of wrinkles was also performed by Rodriguez et al., as shown in Figure 8b [116]. Large and small wrinkles are observed in the TEPL intensity and energy maps in Figure 8b. These different sizes of wrinkles showed different energy peak shifts, which were red-shifted at large wrinkles and blue-shifted at small wrinkles. These phenomena can be explained by the fact that large wrinkles combine the effects of energy funneling and the tensile strain effect [117], while small wrinkles result in a

compressive strain effect [118]. Another investigation on wrinkles was performed by Koo et al. [35]. They performed TEPL measurements near the wrinkle, which showed the variation of different shapes and intensities, as shown in Figure 8c. At the apex of the wrinkle, the TEPL intensity was stronger, and the peak position was more red-shifted than that at the ground regions. The spectra from the slope regions showed different intensities depending on the distance to the apex or the ground of the wrinkle. They performed TEPL imaging near the wrinkles, as shown in Figure 8d. From the TEPL and AFM images and as indicated by the dashed line in the TEPL and AFM images, it was found that the peak position was red-shifted and linewidths were reduced in the apex region due to tensile strain, and the region between the slope and the ground showed a lower PL intensity and increased linewidths. This result can be explained by exciton funneling, where the excitons tend to move toward the lower bandgap region. Therefore, the results obtained from the TEPL images were explained by the concurrent effects of tensile strain and funneling [117].

Nanobubbles generated by the transfer process have also been studied using near-field optical techniques. Darlington et al. performed near-field imaging of nanobubbles of 1L- WSe_2 with ~ 34 nm spatial resolution [119]. The localized exciton state emission (~ 1.56 eV) within the nanobubbles was observed by spatial mapping of the local exciton intensity, and the corresponding AFM image is shown in Figure 9a. In general, the low-energy emission of 2D-TMDs occurs in the case of thermal broadening [120] and plasmonic coupling with the tip [121]. Recently, the observation of localized exciton emission in the nanobubble region of 1L- WSe_2 was attributed to a single-photon

Figure 8: Near-field optical images of wrinkles in 1L-TMDs.

(a) AFM image (upper panel) and TERS intensity image (lower panel) of 1L- MoS_2 . Reproduced with permission from ref. [76]. Copyright 2019, American Institute of Physics. (b) TEPL intensity image (upper panel) and peak energy image (lower panel) of 1L- MoS_2 . Reproduced with permission from ref. [116]. Copyright 2019, WILEY-VCH. (c) Topography of a wrinkle in WSe_2 (upper panel) and TEPL spectra obtained at wrinkle (lower panel). (d) TEPL images of peak energy, FWHM, intensity obtained at 1.62–1.68 eV and 1.70–1.74 eV, and topography image. Reproduced with permission from ref. [35]. Copyright 2021, WILEY-VCH.

emitter state coupled to a plasmonic cavity at low temperature [110, 122]. Therefore, the strong low-energy emission originating from the localized state in the nanobubbles was induced due to enhancement by the plasmonic tip. To further analyze the exciton characteristics of nanobubbles, AFM images and corresponding TEPL images of the nanobubbles were obtained, as shown in Figure 9b. The spatial distribution of the low-energy state exhibited a doughnut-like pattern, and the peak energy was the lowest at the nanobubble periphery, and the PL intensity was strong in the center region. This can be explained by the exciton funneling effect occurring at the central region of the nanobubbles [123], whereas the PL variation at the periphery was dominated by the strain effect. The TEPL investigation of nanobubbles and blisters of vertical TMD heterostructures (i.e., $\text{WSe}_2/\text{MoS}_2$ on h-BN) was performed by Rodriguez et al. [90]. In their work, the blisters and nanobubbles of $\text{WSe}_2/\text{MoS}_2$ were identified by TEPL imaging, as shown in Figure 9c. The strain in the blister and nanobubbles was estimated to be 0.5 and 0.9% by TEPL measurements, respectively. Interestingly, they found that the strain effects of nanobubbles changed depending on the vertical order of the two layers in the heterostructure. Figure 9d shows the TEPL mapping images of nanobubbles in vertical $\text{WSe}_2/\text{MoS}_2$ and $\text{MoS}_2/\text{WSe}_2$ heterostructures. When WSe_2 was placed on top, the PL of only WSe_2 was redshifted, as shown in Figure 9c, and the

PL of MoS_2 was stronger in the surrounding region of the nanobubble. When MoS_2 was placed on top, both layers exhibited PL red-shift due to the strain in the center of the nanobubble, as shown in the spectra in Figure 9d.

We can also control the local strain by artificially manipulating the surface of 1L-TMDs. One simple method is to use an AFM tip to apply the contact force to the sample. Park et al. controlled the local strain by adjusting the contact force between the tip and sample [36]. Figure 10a shows the TEPL spectra of 1L- WSe_2 obtained in an irreversible and reversible state under tip-sample force interaction. The tensile strain in the transferred 1L- WSe_2 was estimated to be $\sim 0.98\%$ [124]. When the contact force was sufficiently large, the TEPL intensity increased, and the spectral shift was blue-shifted by ~ 48 meV. Eventually, the strain relaxation becomes irreversible. By contrast, a small force corresponding to a blue shift of ~ 24 meV was able to reversibly release the strain. This study revealed that the strain can be manipulated by adjusting the tip-sample contact force. The other method was to fabricate a metal-patterned substrate [125]. AFM imaging and corresponding TERS imaging of exfoliated MoS_2 transferred onto Au nanotriangles were performed by Rahaman et al., as shown in Figure 10b. The Raman signal was strong at the corner of the Au triangle owing to the plasmonic enhancement between the Au nanotriangles and the Au tip. To quantitatively analyze the strain distribution of MoS_2 on the Au substrate, they

Figure 9: Near-field images of bubbles in 2D-TMDs.

(a) Upper panel: AFM and TEPL images of 1L- WSe_2 . Lower panel: representative TEPL spectra obtained at flat (blue) and nanobubble (green) regions. Inset: far-field spectrum of 1L- WSe_2 . (b) AFM (upper panel) and TEPL peak energy (lower panel) images of a nanobubble. Reproduced with permission from ref. [119]. Copyright 2020, Nature Publishing Group. (c) Upper panel: TEPL image includes flat (#1), blister (#2), and nanobubble (#3) regions of vertical $\text{WSe}_2/\text{MoS}_2$ heterostructure. Lower panel: TEPL spectra of blisters and nanobubbles. (d) Upper panel: TEPL intensity maps of nanobubbles in (left panel) $\text{WSe}_2/\text{MoS}_2$ and (right panel) $\text{MoS}_2/\text{WSe}_2$ heterostructures. Lower panel: TEPL spectra of the $\text{MoS}_2/\text{WSe}_2$ nanobubble obtained from TEPL image of $\text{MoS}_2/\text{WSe}_2$. Reproduced with permission from ref. [90]. Copyright 2021, IOP Publishing.

Figure 10: Strain controlled by artificial methods.

(a) Left panel: TEPL spectra of 1L-WSe₂ with increasing compressive force induced by the tip (upper panel). For comparison, as-grown and transferred 1L-WSe₂ is presented (lower panel). Right panel: reversibly controllable TEPL spectra under control of the tip force. Reproduced with permission from ref. [36]. Copyright 2016, Nature Publishing Group. (b) AFM topography (upper) and TERS image (lower) (c) second order derivative image of AFM image (upper) and Raman peak position at the numbered locations indicated by circles (lower). Reproduced with permission from ref. [125]. Copyright.

obtained the second derivative of the AFM image and displayed the Raman shift corresponding to all 11 different locations selected from the AFM image, as shown in Figure 10c. The bright regions are believed to originate from the high curvature formed owing to the relatively larger strain. Because the Raman shifts of A_{1g} and E_{2g} are related to doping and strain, respectively [126, 127], no noticeable change in the A_{1g} peak position indicates a negligible strain, whereas a large shift of the E_{2g} mode by 4.2 cm⁻¹ compared to the flat surface indicates ~1.4% strain [127].

5.2 Plasmon resonance

Plasmonic effects can be utilized to control the light-matter interaction and to enhance the electric field and light-harvesting efficiency [128, 129]. Thus, plasmonic structures combined with 2D-TMDs can not only enhance their respective optical properties, but also create new ones. For example, plasmonic hot electrons in 2D-TMDs can modulate the carrier density [130], and the coupling between excitons and plasmonic nanocavity can greatly enhance the PL of 2D-TMDs [131, 132]. Measurements with high spatial resolution are advantageous for investigating plasmonic effects. In this section, we focus on near-field plasmon effects studied by near-field imaging.

Figure 11a and b presents gap-plasmon TERS imaging of 1L-MoS₂ placed on a periodic array of Au nanostructures [133]. In general, when excited with 785.3 nm, the A_{1g} mode

is suppressed because the A_{1g} mode can only be excited via an electron-phonon exchange [134]. However, under the same excitation wavelength, the A_{1g} mode was remarkably enhanced and the E_{2g} mode vanished, as shown in Figure 11c. This is because the strong plasmonic coupling between MoS₂ and the Au nanostructure can easily generate hot electrons, leading to strong electron-phonon coupling [52, 135], or the perpendicular orientation between the Au tip and the sample surface enhanced the out-of-plane mode (A_{1g}) [136]. Additionally, the A_{2u} mode, referred to as the infrared-active mode, appeared because of the electric field gradient effect occurring between the angled tip and the metal substrate [137]. Furthermore, the Raman spectra obtained by TERS in Figure 11b show a strong signal due to the heating effect, the plasmonic enhancement, and the red-shifted peak position due to the strain effect at the edges of the Au nanocluster. In addition, the observation of the Raman mode at 335 cm⁻¹, characteristic of the 1T phase of MoS₂, strongly indicates that the phase transition from 2H to the 1T phase may have occurred at the edge site because the injected hot electrons made the 2H lattice unstable [52].

On the other hand, many researchers have focused on the effects of the plasmonic mode in the subnanometer gap ($d < \sim 0.5$ nm) between the tip and 2D-TMD surface. In general, tip-enhanced signals are known to enhance the electric field by localized surface plasmon resonances using Au or Ag-coated nanotips at certain distances ($1 < d < 20$ nm) from the sample surface. By contrast, under the van der Waals

Figure 11: Plasmon resonance effect of 1L-MoS₂ on an Au nanocluster array. TERS images of intensity (a) and peak position (b). (c) Representative TERS spectrum (red) and far-field spectrum (black). (d) TERS spectra obtained at (b) locations, 1 to 5 marked by a white circle in (b). Reproduced with permission from ref. [133]. Copyright 2018, Royal Society of Chemistry.

(vdW) contact, where $d < \sim 0.5$ nm, the quantum plasmonic effect of the charge tunneling between the tip and the sample surface tends to suppress the near-field enhancement [138–140]. Zhang et al. first demonstrated the TERS of few-layer MoS₂ on a gold substrate under vdW contact between the tip and sample ($d < \sim 0.36$ nm), called the quantum coupling region, as shown in Figure 12a [141]. At a tip-sample distance of $2 < d < 10$ nm, which is called the classic coupling region, the PL and Raman signals increase owing to the near-field enhancement. By contrast, in the quantum region, both the PL and Raman signals were saturated at a

certain distance and then gradually decreased. Here, the authors explained that the quenched signal was due to a decrease in the electric field in the gap, which occurred because the tunneling between the Au tip and MoS₂ reduced the charge accumulation at the apex of the tip.

He et al. performed TEPL imaging of 1L-WSe₂ by approaching the tip to sample the vdW distance [142]. Figure 12b displays the exciton and trion spectral images in the far-field and near-field. Far-field images of excitons and trions showed that excitons and trions have similar distributions of excitons and trions, while near-field profile images

Figure 12: Plasmon resonance effect by metallic tip.

(a) Few-layer MoS₂ PL and Raman intensity depending on tip-sample distance (left) and the illustration of tip-induced plasmon resonance (right). Reproduced with permission from ref. [141]. Copyright 2016, Nature Publishing Group. (b) Upper panel: TEPL images of 1L-WSe₂ of exciton (left) and trion (right). Lower panel: exciton (left) and trion (right) images obtained by far-field imaging. Reproduced with permission from ref. [142]. Copyright 2019, American Association for the Advancement of Science. (c) Upper panel: TEPL intensity of WSe₂ (left) and MoSe₂ (right) depending on tip-sample distance. Lower panel: TEPL intensity of lateral WSe₂/MoSe₂ HJ in depletion region of WSe₂ (left) and MoSe₂ (right) depending on tip-sample distance. Reproduced with permission from ref. [96]. Copyright 2018, American Physical Society. (d) Fitted TEPL intensity profiles WSe₂ (red), MoSe₂ (gold), and interlayer exciton peaks (green) versus tip-sample distance obtained from vertical WSe₂/MoSe₂. Blue lines display the shear-force feedback amplitude. Reproduced with permission from ref. [89]. Copyright 2021, Nature Publishing Group.

have different distributions because the tip-induced quantum plasmonic effect can convert excitons to trions in certain spatial locations. The interconversion of excitons into trions could be a useful application for novel nanoscale light-matter interactions. Tang et al. also focused on the tip-sample distance in the depletion region of the lateral WSe₂/MoSe₂ heterostructure, as shown in Figure 5b [96]. In the quantum coupling region, the TEPL intensity of pure WSe₂ increased with decreasing tip-sample distance, whereas in the case of MoSe₂, the PL intensity showed no significant change, as shown in the upper panel of Figure 12c. Because the CVD-grown WSe₂ exhibited p-type behavior, which means that the hole concentration in WSe₂ was larger than that of electrons, hot electrons injected into WSe₂ by the tunneling effect can combine with holes of WSe₂ within the vdW distance, leading to PL enhancement [143]. By contrast, CVD-grown MoSe₂, n-type, which lacks holes that can couple with the hot electrons, showed no enhancement of the PL signal [144]. However, this trend shows the opposite behavior in the depletion region, as shown in the lower panel of Figure 12c. The hot-electron accumulation in the WSe₂ region of HJ was suppressed owing to the type-II band alignment. Charge transfer across the depletion region caused the overall PL intensity of the WSe₂ to be quenched [84, 85].

By contrast, the PL signal of MoSe₂ increased in the depletion region, and the authors explained that an

increase in the number of hot electrons in MoSe₂ due to tunneling and charge transfer may increase the recombination rate. However, the Purcell effect by nanocavity may have contributed to this. More recently, May et al. performed TEPL measurements of a vertical WSe₂/MoSe₂ heterostructure on h-BN, as shown in Figure 12d [89]. TEPL signals also showed different behaviors depending on the tip-sample distance. The near-field region ($5 < d < 25$ nm) showed a continuous increase in the PL signal, regardless of the exciton type. In the ($1 < d < 5$ nm) region, two effects of PL intensity increase due to near-field enhancement and the decrease due to quantum tunneling competing with each other. In the $d < 1$ nm region, owing to the competing effects of the Purcell effect and quantum tunneling, the authors observed the enhancement of intralayer PL and a decrease in the interlayer excitons of the vertical WSe₂/MoSe₂ heterostructure. Interestingly, the TEPL of WSe₂ in the lateral (Figure 12c) or vertical (Figure 12d) heterostructures showed opposite behaviors in the quantum region. Therefore, a study of the quantum plasmonic region between the tip and the sample still needs to be conducted to understand the integrated plasmonic effects.

Park et al. also observed the dark exciton of 1L-WSe₂ using TEPL spectroscopy in a room temperature [28]. In general, the dark excitons generated from the spin-flip

Table 1: Summary of experimental details of the near-field optical studies of 2D-TMDs.

Target of the study	Sample type		Probe type	Optical response	
Grain boundaries	1L-MoS ₂		Apertured [26], scattering type [55], [62]	PL, Raman, SHG	
	1L-MoSe ₂		Scattering type [60], [61]	PL, Raman	
Local defects	1L-MoS ₂		Apertured [79]	PL	
	1L-WSe ₂		Apertured [34], scattering type [27]	PL, Raman	
Heterostructures	Vertically stacked	WSe ₂ /MoSe ₂	Scattering type [89]	PL	
		WSe ₂ /MoS ₂	Scattering type [90]		
	Lateral junction	WSe ₂ /MoSe ₂	Apertured [98], scattering type [96, 97]		
		MoS ₂ /WS ₂	Scattering type [103]		
Effect of chemical doping and passivation	1L-MoS ₂		Apertured [79]	PL	
Strain	Wrinkles	1L-MoS ₂	Scattering type [76, 116]	PL, Raman	
		1L-WSe ₂	Scattering type [35]	PL	
	Bubbles	1L-WSe ₂	Scattering type [119]	PL	
		Vertically stacked (WSe ₂ /MoS ₂)	Scattering type [90]	PL	
		AFM tip contact	1L-WSe ₂	Scattering type [36]	PL
	Plasmon resonance	Au nanotriangle	1L-MoS ₂	Scattering type [125]	Raman
		1L-MoS ₂		Scattering type [133]	Raman
Few-layer MoS ₂			Scattering type [141]	PL, Raman	
1L-WSe ₂			Scattering type [142]	PL	
Lateral junction (WSe ₂ /MoSe ₂)			Scattering type [96]	PL	
Vertically stacked (WSe ₂ /MoSe ₂)			Scattering type [89]	PL	
	1L-WSe ₂		Scattering type [28]	PL

Figure 13: Applications of near-field imaging of 2D-TMDs.

(a) AFM image and microwave near-field images of 1L-MoS₂ with -6 V and -11 V tip bias. Reproduced with permission from ref. [150]. Copyright 2015, Nature Publishing Group. (b) Schematic of MoS₂-gated 1L-graphene device (left) and near-field-infrared amplitude image (right). Reproduced with permission from ref. [153]. Copyright 2021, Nature Publishing Group.

process cannot be normally observed [145, 146]. Recently, observation of dark excitons was conducted using an in-plane magnetic field [147], SPP coupling [148], and polarized detection from the sample edge [149], which requires measurements at low temperatures. Therefore, to meet the demands for selective excitation and out-of-plane transition dipole moments, researchers constructed the required near-field system. The authors observed that the emission of dark exciton from 1L-WSe₂ changed with the distance between the Au tip and the sample. The intensity of out-of-plane optical field gets stronger than that of the in-plane mode at very near distance. Thus, the portion of neutral exciton having in-plane dipole moment decreased as the distance decreased while the emission of dark exciton with out-of-plane dipole moment increased at near distance [147–149]. Therefore, the emissions of dark excitons versus, neutral excitons can be controlled by adjusting the tip-sample distance. Finally, we summarize the experimental details of near-field optical studies of 2D-TMDs in Table 1.

6 Outlook

To date, near-field imaging has provided information about optical responses and allows for the precise investigation of 2D-TMDs. However, near-field imaging techniques require specific environments regarding substrates, tips, and temperatures to obtain a high spatial resolution. Nevertheless, if near-field imaging can be combined with other measurement systems, it would be of great help to understand the unique 2D-TMD properties and their applications. One possibility is the use of a different light source, as shown in Figure 3e.

Berweger et al. performed microwave near-field imaging of 1L-WSe₂, as shown in Figure 13a [150]. This work demonstrated the ways to measure electrical properties such as conductivity and capacitance [151, 152]. The charge

carrier density of WSe₂ can be controlled by adjusting the tip bias. In addition, Sunku et al. performed near-field imaging of graphene-based heterostructures using an infrared light source, as shown in Figure 13b [153]. Near-field imaging showed a pattern showing the propagation of plasmons. In this work, bilayer MoS₂ was used as the top-gate metal. Although MoS₂ exhibited a weaker efficiency of top-gate displacement than monolayer graphene, it is meaningful in that they first performed near-field IR imaging of 2D-TMDs.

Moiré patterns in TMD heterostructures have recently become a popular topic. Although we have already covered the near-field studies of heterostructures of 2D-TMD interlayer excitons, the moiré exciton states depending on stack angles remain an interesting subject that can be investigated by near-field imaging. Theoretical studies have shown that moiré potentials in TMD heterostructures can have a significant effect on optical properties [154]. Many researchers have experimentally observed moiré exciton states in WSe₂/WS₂ heterostructures and observed intervalley excitons in MoSe₂/WSe₂ heterostructures at low temperatures [155, 156]. Although the interlayer twist offers an additional degree of freedom to regulate moiré excitons, the study of the interlayer exciton dynamics of TMD heterostructures remains a challenging and attractive topic. We expect that a near-field imaging system with ~2 nm spatial resolution can optically identify the moiré pattern. In addition, the valley polarization of 2D-TMD is a unique property of 2D-TMDs that could open new applications [157–159]. Many studies have already investigated valley effects on 2D-TMDs using circular polarization [160, 161]. However, there have been no near-field studies of valley polarization of 2D-TMDs that require experimental environments such as low temperature, proper excitation sources, and magnetic fields. We expect that valley-resolved near-field optical imaging will provide critical information for the further development of 2D-TMD valleytronics.

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