

Nanoscale Heterogeneities in Monolayer MoSe₂ Revealed by Correlated Scanning Probe Microscopy and Tip-Enhanced Raman Spectroscopy

Kirby K. H. Smithe,^{†,○} Andrey V. Krayev,^{‡,○} Connor S. Bailey,[†] Hye Ryoung Lee,^{†,§} Eilam Yalon,^{†,○} Özgür Burak Aslan,^{||,⊥} Miguel Muñoz Rojo,^{†,○} Sergiy Krylyuk,[#] Payam Taheri,[#] Albert V. Davydov,[#] Tony F. Heinz,^{||,⊥} and Eric Pop^{*,†,§,▽,○}

[†]Department of Electrical Engineering, Stanford University, Stanford, California 94305, United States

[‡]Horiba Scientific, Novato, California 94949, United States

[§]Department of Materials Science & Engineering, Stanford University, Stanford, California 94305, United States

^{||}Department of Applied Physics, Stanford University, Stanford, California 94305, United States

[⊥]SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

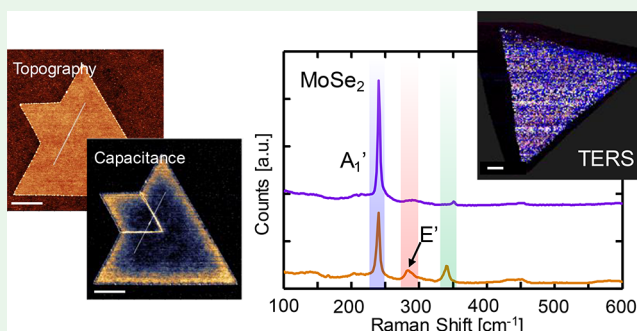
[#]Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

[▽]Precourt Institute for Energy, Stanford University, Stanford, California 94305, United States

Supporting Information

ABSTRACT: Understanding growth, grain boundaries (GBs), and defects of emerging two-dimensional (2D) materials is key to enabling their future applications. For quick, nondestructive metrology, many studies rely on confocal Raman spectroscopy, the spatial resolution of which is constrained by the diffraction limit ($\sim 0.5\ \mu\text{m}$). Here we use tip-enhanced Raman spectroscopy (TERS) for the first time on synthetic MoSe₂ monolayers, combining it with other scanning probe microscopy (SPM) techniques, all with sub-20 nm spatial resolution. We uncover strong nanoscale heterogeneities in the Raman spectra of MoSe₂ transferred to gold substrates [one near $240\ \text{cm}^{-1}$ (A_1'), and others near $287\ \text{cm}^{-1}$ (E'), $340\ \text{cm}^{-1}$, and $995\ \text{cm}^{-1}$], which are not observable with common confocal techniques and appear to imply the presence of nanoscale domains of MoO₃. We also observe strong tip-enhanced photoluminescence (TEPL), with a signal nearly an order of magnitude greater than the far-field PL. Combining TERS with other SPM techniques, we find that GBs can cut into larger domains of MoSe₂, and that carrier densities are higher at GBs than away from them.

KEYWORDS: tip-enhanced Raman spectroscopy, scanning probe microscopy, chemical vapor deposition, MoSe₂, heterogeneity



INTRODUCTION

Two-dimensional (2D) semiconductors, specifically the class of monolayer (1L) transition metal dichalcogenides (TMDs), have attracted significant attention in recent years due to their unique electrical, thermal, and optical properties. These include direct optical band gaps in the visible to near-infrared wavelengths,^{1–3} valley-specific circular dichroism,^{4–7} and strong excitonic interactions even at room temperature.^{8–12} Among 2D materials, monolayer MoSe₂ is known to have a direct optical band gap around 1.55 eV,^{13–17} and devices with mobility values somewhat higher than the more prevalently studied MoS₂ have been reported,^{18–20} making this material an attractive candidate for nano- and optoelectronic applications.

Nonetheless, most research on 2D TMDs to date has focused on characterization techniques that measure properties on the scale of microns or larger, including X-ray photo-

emission spectroscopy (XPS), far-field photoluminescence (PL) and confocal Raman spectroscopy, as well as micro-electronic device measurements. However, devices in modern electronics tend to be smaller than $\sim 100\ \text{nm}$, and as such it is critical to employ techniques that allow for (preferably nondestructive) characterization on the order of tens of nanometers.²¹

Imaging with tip-enhanced Raman spectroscopy (TERS) is a natural choice for comprehensive nanoscale characterization technique for 2D materials, because it combines the advantages of strong enhancement of the Raman signal by a plasmonic structure located at the apex of a scanning probe microscope tip

Received: October 24, 2017

Accepted: December 26, 2017

Published: December 26, 2017



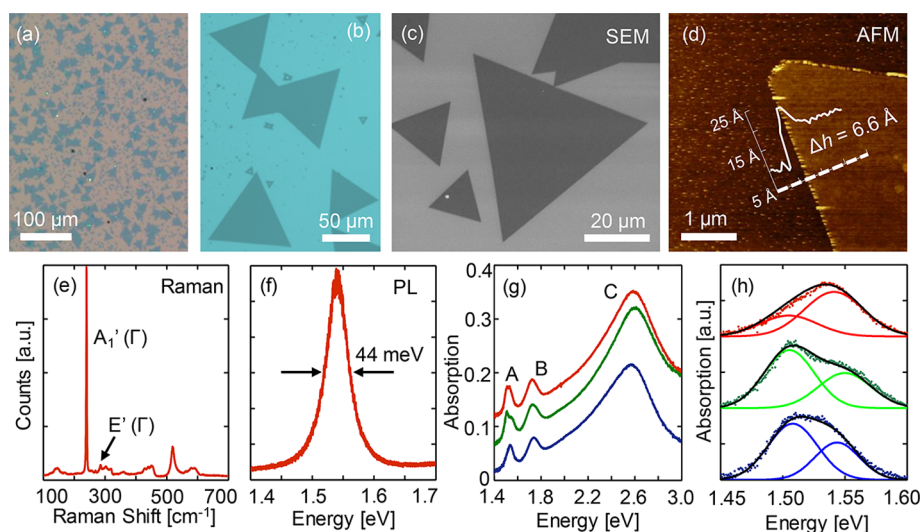


Figure 1. (a, b) Optical images of large-grain, single crystal, monolayer MoSe₂ grown by CVD on SiO₂/Si substrates. (c) SEM image of similar MoSe₂ single crystals. (d) AFM scan on the edge of a flake, demonstrating a monolayer step height $\Delta h < 7$ Å and RMS roughness on the crystal surface of 1.6 Å. (e) Confocal Raman spectrum of 1L MoSe₂, taken with a 532 nm laser, with the characteristic A₁' peak at 239 cm⁻¹ and overtones at higher energies. (f) Far-field PL of monolayer MoSe₂, showing a direct optical band gap of 1.53 eV and full-width at half-maximum (fwhm) of 43.8 meV. (g) Three absorption spectra on different areas of a similar MoSe₂ crystal grown directly on quartz and adjusted to reflect absorption for free-standing samples (offset for clarity). (h) Zoomed-in view of absorption around the A exciton with background subtracted, emphasizing the broadening and splitting of this feature. Two Gaussian curves are required to fit each feature, indicating spatial inhomogeneity in regions smaller than a few hundred nanometers.

with high spatial resolution (down to a few nm) of both the hyperspectral Raman maps and multiple scanning probe microscopy (SPM) channels such as topography, phase shift, surface potential, conductivity, etc. Recent advances in development of efficient SPM systems with dedicated TERS imaging modes²² have enabled nanoscale characterization of novel 2D materials, both carbon-based^{23–25} and TMDs, first for nanoscale tip-enhanced PL (TEPL) imaging^{26–28} and then for TERS imaging of mono-to-few-layer MoS₂^{29–31} and WS₂.³² Many of these initial studies revealed interesting nanoscale inhomogeneities in the optical and vibrational properties of 2D materials which could not be observed or properly characterized with conventional techniques.

To this end, we perform TERS measurements of 1L polycrystalline MoSe₂ films synthesized by chemical vapor deposition (CVD) and transferred to gold substrates. Optical spectroscopy, Raman scattering, photoluminescence (PL), contact potential difference (CPD), and $\partial^2 C/\partial z^2$ (capacitance) measurements are all performed with a resolution below 20 nm. We demonstrate that cross-correlating the results provided by scanning Kelvin probe microscopy (SKPM) and these other tip-enhanced techniques can yield important information on the unexpected spatial distributions of grain boundaries in polycrystalline MoSe₂ flakes. On one hand, we observe increased capacitance at the grain boundaries of MoSe₂ as-grown on SiO₂/Si, but a sharply decreased capacitance and TERS signal at the grain boundaries of flakes transferred to Au substrates. Based on the observations, we argue that the concentration of the charge carriers in these boundaries is increased compared to the interior of the as-grown monolayer crystals, but that exposure to base solutions for transferring etches the crystal at the grain boundaries. We also find that, even in monocrystalline flakes, there exist small (20–100 nm) domains with Raman signatures different from the rest of the transferred flake, with the TERS spectra in the nanoscale regions implying the presence of MoO₃. This work highlights

the importance of nanoscale characterization of 2D materials and also demonstrates the capability of simultaneous combined scanning probe techniques to meet this need.

SAMPLE FABRICATION

We synthesize 1L MoSe₂ crystals by chemical vapor deposition (CVD) using a 2 in. tube furnace system from planarTECH. (A diagram, photograph, and specific preparation steps are presented in the Supporting Information section A.) The MoSe₂ is grown with the aid of a perylene-3,4,9,10 tetracarboxylic acid tetrapotassium salt (PTAS) solution³³ distributed over the surface of SiO₂/Si substrates in a manner very similar to that in ref 34. The growths are initially characterized by optical and scanning electron microscopy (SEM), which reveal grain sizes ranging from a few μm to 100 μm on an edge (see Figure 1a–c) and grown covering an area of several cm². We also initially confirm the 1L nature of the crystals with atomic force microscopy (AFM), shown in Figure 1d. It is worth noting that, in addition to a measured step height of ~ 0.66 nm, the root-mean-square roughness of the flake is merely 0.16 nm, suggesting that the surface is atomically smooth.

Further characterization is performed by room-temperature confocal Raman and far-field PL measurements using a 532 nm laser with ~ 1 μm spot size, shown in Figure 1e,f. Similar to previous reports,^{13,16} we observe a strong A₁' peak at 239.4 cm⁻¹, as well as many other weaker peaks and overtones at higher wavenumbers. The prominent PL peak, indicative of a direct band gap in monolayer TMDs,³⁵ is centered at 1.53 eV with a line width of 43.8 meV. We also characterize our as-grown films with X-ray photoelectron spectroscopy (XPS, see the Supporting Information section B), and find the Mo 3d_{3/2} and 3d_{5/2} peaks to be centered at 232 and 229 eV, indicating that all the Mo is bonded as Mo⁴⁺ (these peaks blueshift by ~ 4 eV for Mo⁶⁺).^{18,36} Analogous peaks for Se are also shown as the doublet centered around 55 eV.

Finally, we perform optical absorption measurements of MoSe₂ grown directly on quartz (Figure 1g), which reveal three strong excitonic features near 1.53, 1.73, and 2.59 eV, respectively, corresponding to the A, B, and C excitons. The 200 meV splitting of the A and B excitons is consistent with previous reports.³⁷ It is worth noting that the PL and absorption peaks are slightly redshifted

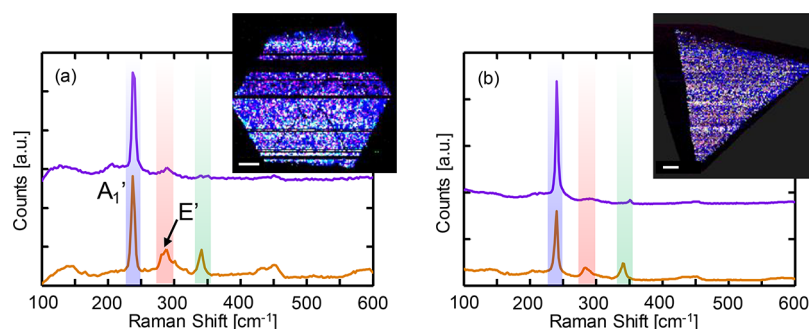


Figure 2. (a) Combined TERS spectra of a polycrystalline monolayer MoSe₂ flake transferred to gold, collected with a shorter focal distance Raman spectrometer (XPlora). Intensity of three different peaks are illustrated by color: ~ 240 cm⁻¹ (blue), ~ 287 cm⁻¹ (red), and ~ 340 cm⁻¹ (green). Two distinct types of Raman spectra are observed: nonresonant (purple) with a single dominant peak at 240 cm⁻¹; and resonant (orange) with significant intensity of peaks at 287 and 340 cm⁻¹ as well as broad overtones between 400 and 600 cm⁻¹. Inset: TERS map of the polycrystalline flake. The horizontal dark lines in the TERS image are the result of the probe picking up some contamination and losing the enhancement as a consequence; however, even with these imperfections, the pattern of the grain boundaries (GBs) is clearly discernible. (b) Similar combined TERS spectra of a monocrystalline monolayer MoSe₂ flake on gold collected with a LabRam-EVO Raman spectrometer. Inset: TERS map of the monocrystalline flake. Scale bars are 1 μ m.

relative to reports for exfoliated flakes due to the CVD-grown films experiencing tensile strain during cooling after synthesis.³⁸ For absorption spectra taken at different locations, we observe slightly different relative values of splitting and broadening in the excitonic peaks, emphasized with peak fitting in Figure 1h. Given that our laser spot size is several hundred nm for these measurements, we can conclude that nanoscale domains with differing properties exist on the scale of a few hundred nm; however, detailed characterization of these domains requires further measurement techniques coupled with scanning probe microscopy, as detailed below.

NANOSCALE CHARACTERIZATION

Nanoscale characterization of synthesized monolayer MoSe₂ films was performed with scanning probe microscopy (SPM) and tip-enhanced optical spectroscopy (TEOS), which includes TERS and TEPL. (A diagram of our instrumentation is given in the Supporting Information section C.) Due to the extreme focusing of incoming optical fields by a plasmonic structure at the apex of a TEOS-active SPM microscope (typically several nm and only fundamentally limited by the size of the surface plasmon³⁹), the spatial resolution of Raman and PL maps is dramatically improved, far beyond the diffraction limit of conventional confocal microscopy. Additionally, when a full spectrum is collected in every pixel of a scanned map (<20 nm/pixel in most of the TEOS maps presented here), the hyperspectral nature of TEOS imaging permits one to perform detailed analysis of the intensity distribution of any observed feature, as we demonstrate below.

In order to significantly enhance the various TEOS signals, measurements are performed in the gap-mode,⁴⁰ whereby a sample is sandwiched between a plasmonic tip and a matching plasmonic substrate (typically silver or gold).^{41,42} To enable this type of measurement, MoSe₂ samples are transferred from the SiO₂ growth substrates to substrates coated with 50 nm of gold, using hot NaOH and a rigid PMMA layer to avoid cracking or wrinkling of the MoSe₂ during transfer. (The details of this transfer process can be found in the Supporting Information section D.) SPM and TEOS measurements were performed using an OmegaScope-R (formerly AIST-NT, now Horiba Scientific) coupled either to an XPlora or a LabRam-EVO Raman spectrometer (both from Horiba Scientific), with a laser excitation, respectively, at 638 or 632.8 nm and with power of ~ 75 μ W. OMNI-TERS probes (APP Nano) were

used in all the experiments for both the SPM and TEOS analysis.

We performed TERS measurements on both poly- (Figure 2a) and monocrystalline (Figure 2b) MoSe₂ in order to explore possible differences in these morphologies. In both cases, our measurements reveal two distinct types of TERS spectra: a nonresonant spectrum, with a single dominant peak at 240 cm⁻¹ (the A₁' mode); and a much more abundant resonant spectrum, where in addition to the 240 cm⁻¹ peak, reasonably intense peaks at 287 cm⁻¹ (E' mode) and 340 cm⁻¹ as well as complex broad peaks at ~ 430 and 585 cm⁻¹ (overtone peaks) are present. All observed peaks are in good agreement with ref 43 except for that at 340 cm⁻¹, which appears to be unreported in the literature for MoSe₂. The TERS maps (insets in Figure 2a,b) show that the ratio of the intensities of contributing peaks, represented by color, changes across the sample, implying the presence of nanoscale heterogeneity, discussed further below.

The presence of both types of spectra in the maps is not a mere temporal fluctuation of TERS response and can be reproduced across multiple scans, even though the domains with corresponding type of Raman response were fairly small, on the order of few tens of nanometers across (see the Supporting Information section E). The size of the areas with nonresonant spectra, rarely over 150 nm, makes it essentially impossible to detect such heterogeneity with conventional Raman microscopy, since the observed heterogeneity would be averaged over the laser spot size. The subdiffraction spatial resolution of TERS allows one to see differences in adjacent nanoscale domains in MoSe₂ monolayers and reveals significant inhomogeneity where more commonly used confocal Raman microscopy would see a uniform distribution of spectra.

Although both the poly- and monocrystalline TERS maps show both the resonant and nonresonant spectra, the polycrystalline TERS map (inset of Figure 2a) also shows lines running parallel to the crystal edges where the TERS intensity drops dramatically (the horizontal black lines are the result of the probe picking up some contamination and losing the enhancement as a consequence). To further investigate these features, similar measurements were performed with a sharper SPM tip on a cleaner flake. Shown in Figure 3a–c are concurrently taken topography, CPD, and $\partial^2 C/\partial z^2$ (obtained from frequency-modulated SKPM measurements) maps of a

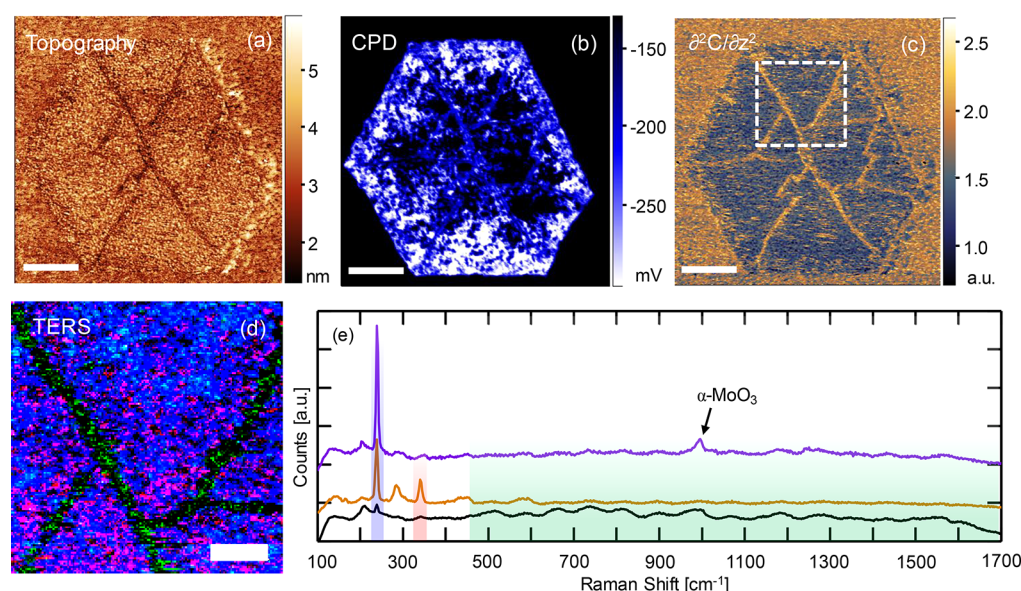


Figure 3. (a–c) Topography, contact potential difference (CPD), and d^2C/dz^2 of a polycrystalline monolayer MoSe₂ flake transferred to gold. Scale bar is 1 μm . (d) Combined TERS maps of the white box in part c. Intensity of three different features are illustrated by color: 240 cm^{-1} (blue), 340 cm^{-1} (red), and the background signal spanning 450–1750 cm^{-1} (green). The relative intensities of the peaks represented by the colors are rescaled to clearly demonstrate the presence of nanoscale domains where the less intense peaks show considerable variation. The pattern of the GBs is identical to that revealed in the topography, CPD, and capacitance images. Scale bar is 300 nm. (e) Averaged TERS spectra showing resonant response (orange), nonresonant response (purple), and from the GB regions (black, showing significantly decreased intensity of Raman signal of MoSe₂ over the GBs). The features used to make the TERS map in part d are also highlighted with their respective color. Note that the resonant spectrum shows an additional peak at 995 cm^{-1} , which we attribute to MoO₃.

similar polycrystalline MoSe₂ flake, all of which clearly show internal features that are aligned with the crystal edges. [The roughness of the underlying gold substrate is about 1 nm (see the Supporting Information section F).] In the d^2C/dz^2 maps, which show data that is proportional to the capacitance between the SPM tip and the sample (see the Supporting Information section G), we observe these features to have capacitance similar to the Au substrate, which is significantly higher than the MoSe₂ crystal, indicating that these could be regions where the MoSe₂ has been etched away along grain boundaries (GBs).

A higher-resolution TERS map was also collected, over just the white boxed area in Figure 3c (see Figure 3d). As before, we distinctly observe both resonant and nonresonant spectra (respectively, orange and purple in Figure 3e). The TERS map also reveals that the peaks corresponding to MoSe₂ (blue and red in the map) nearly vanish over the regions where the capacitance matches that of the substrate, and instead show only an increase in background signal (green). These observations support the conclusion that hot NaOH etches the polycrystalline MoSe₂ flakes along its GBs and exposes the underlying surface, but leaves monocrystalline flakes intact. By contrast, as-grown flakes allowed to age in air for 2 weeks demonstrated significantly increased topography at the GBs and edges, possibly due to oxidation (see the Supporting Information section H).

Regarding the origin of the two types of Raman signatures, we note that the resonant spectra with a significantly enhanced E' peak is expected for a red excitation laser,⁴³ attributed to increased coupling of longitudinal phonons with the A and B excitons. Decreased intensity of this peak in the nonresonant spectra may suggest that the resonance conditions in these areas were suppressed due to doping variations or varied defect concentrations. This is further supported by the presence of a

new peak at 995 cm^{-1} in the nonresonant spectra in Figure 3e, which we attribute to nanoscale domains of MoO₃ that not only act as defect sites but can locally dope the MoSe₂ as well. The vibrational mode at 995 cm^{-1} is a well-known Raman peak for α -MoO₃ and corresponds to the stretching of the out-of-plane molybdenyl bond that gives α -MoO₃ its layered structure;^{36,44–46} furthermore we have observed significant TERS enhancement of this peak alone in samples of α -MoO₃ prepared by vapor phase transfer (see the Supporting Information section I). While we cannot presently determine if these oxide domains exist from growth or are a result of exposure to air or NaOH, we can conclude that nanoscale domains of MoO₃ must exist within the transferred MoSe₂ flakes.

It is worth noting that such observations require the use of subwavelength imaging spectroscopic techniques, which in the case of the gap-mode regime can provide spatial resolution in TERS maps at the level of a few nanometers over regions tens of microns across in ambient conditions. In conventional confocal Raman microscopy, where the spot size of the laser is $\sim 0.5 \mu\text{m}$, the Raman signal of the boundaries and adjacent material would be averaged over this larger spatial scale (see the Supporting Information section J). By contrast, transmission electron microscopy (TEM), while able to possibly resolve defects at the atomic level, can typically only image regions no larger than $50 \times 50 \text{ nm}$ and risk missing sparse defects. That notwithstanding, in our own TEM analysis, we do not observe any vacancies (see the Supporting Information section K), nor do we observe a previously reported⁴⁷ Se vacancy defect peak at 250 cm^{-1} in our TERS spectra, indicating that the nanoscale inhomogeneities in our samples are not related to vacancies.

Employment of subwavelength spectroscopy can also be used for tip-enhanced photoluminescence (TEPL), and Figure 4a shows emission spectra extending to the range where the

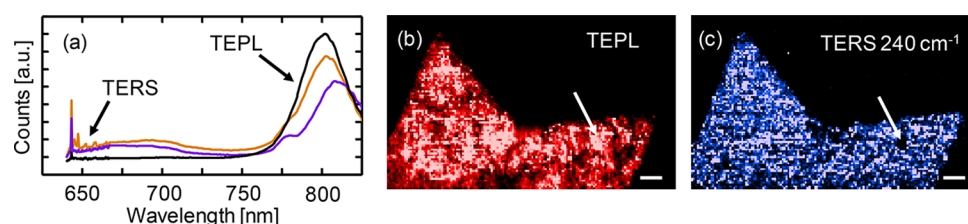


Figure 4. (a) Typical spectra showing coexistence of the TEPL and TERS (orange and purple) and a spectrum (black) from the location marked with white arrows in the maps where the TERS response was dramatically suppressed, though the PL and photocurrent signals retained significant intensity. (b, c) TEPL and TERS (240 cm^{-1} intensity) maps highlighting a region with strong TEPL and low TERS signals. Scale bar in the maps is 200 nm.

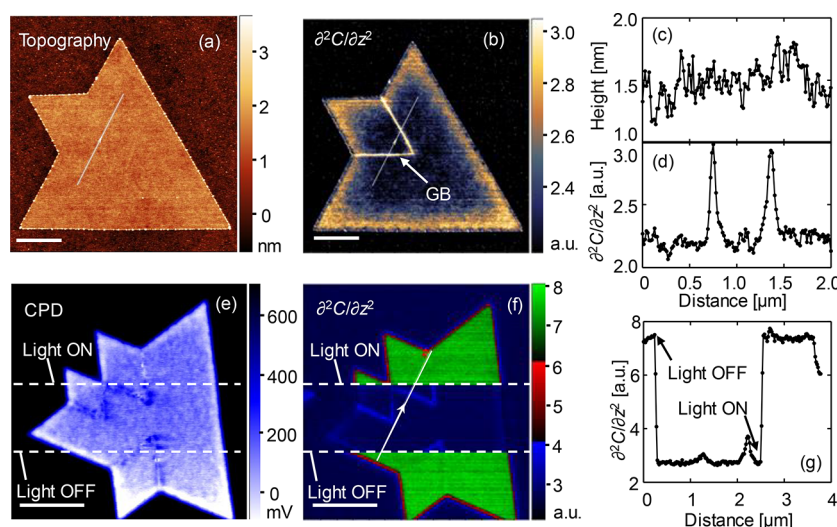


Figure 5. As-grown monolayer MoSe_2 on Si/SiO_2 . (a) Topography and (b) $\partial^2 C/\partial z^2$ maps of a flake. Scale bars are $1\text{ }\mu\text{m}$. (c, d) Topography and $\partial^2 C/\partial z^2$ cross sections along the white lines in parts a and b. Topography is completely featureless, while the GBs stand out extremely well in the capacitance image. (e, f) CPD and $\partial^2 C/\partial z^2$ of another flake on the same substrate taken in the dark and under illumination with a 638 nm laser at $75\text{ }\mu\text{W}$. In the middle of the scan the illumination was turned off which resulted in immediate drop of the capacitance signal. Scale bars are $2\text{ }\mu\text{m}$. (g) $\partial^2 C/\partial z^2$ along the line in part f, showing the greatly increased capacitance of the MoSe_2 while under illumination.

photoluminescence can be observed in addition to the Raman (TERS) signal. Strong TEPL response from MoSe_2 on gold is seen (Figure 4b), even though the flake was in good electric contact with the substrate (confirmed by significant photocurrent recorded simultaneously with these maps, see the Supporting Information section L). Contact of a 2D semiconductor with metallic⁴⁸ or even another semiconductor surface³³ can strongly quench PL emission. In our case, the TEPL signal exceeded the far-field PL by almost an order of magnitude, though the area from which the TEPL signal is collected ($<400\text{--}600\text{ nm}^2$) was almost 3 orders of magnitude smaller compared to the area from which the far-field PL signal was collected (in our case about $0.35\text{ }\mu\text{m}^2$). The strength of the emission reflects field enhancement effects that increase both the coupling of the pump laser to the sample and the rate of radiative emission.

The position of the TEPL emission feature varied from 799 to 809 nm within the map. TERS and TEPL signals coexisted across most of the imaged area, though we found several locations (about 100 nm across) in which strong TEPL and significant photocurrent were observed with very low TERS signal. Because the pixel size in these TERS/TEPL maps is $\sim 17\text{ nm}$, we can conclude that the observed preferential enhancement of TEPL and suppression of TERS was not an arbitrary event, but rather reflects specific properties of nanoscale domains.

Finally, we turn to SPM measurements on as-grown samples on SiO_2/Si to further explore the properties of GBs. Surprisingly, $\partial^2 C/\partial z^2$ imaging highlights otherwise invisible GBs, even in cases where topography of the inner parts of the polycrystalline flakes was completely featureless. In Figure 5a–d we see increased capacitance of the GBs and their somewhat counterintuitive shape protruding into the body of the MoSe_2 sample, instead of being positioned along the edge of the larger triangle. This behavior was observed in multiple flakes, even though the topography images suggest a flat, uniform surface (Figure 5a,c).

Performing SPM characterization in an instrument coupled to a Raman spectrometer has a further unique advantage in that surface potential, capacitance, conductivity, etc. can be measured in the dark and under illumination. Using this capability, we explore how capacitance and the surface potential of as-grown flakes change as a result of illumination with a 638 nm laser ($\sim 75\text{ }\mu\text{W}$, the same illumination conditions as in TERS experiments). While the GBs are only barely discernible in the CPD image, a dramatic increase of the capacitance was observed when the laser was turned on (Figure 5e–g). Turning the illumination off immediately resulted in a decrease of the capacitance signal and relatively little change in the surface potential. We also note that a slight increase of the capacitance was observed in the vicinity of the flake edges, which could be indicative of metallic edge states in 1L TMDs.⁴⁹

We attribute the observed increase of the $\partial^2 C/\partial z^2$ signal over the grain boundaries to significantly increased charge carrier concentration in these regions, which is in good agreement with observations from Ma et al. detailing the metallic nature of twin grain boundaries in MoSe₂ at room temperature.⁵⁰ Enhancement of the $\partial^2 C/\partial z^2$ signal in response to illumination, which increases the concentration of charge carriers, also corroborates the conclusion that variations of this signal represent the variations of the charge carrier concentration. We thus affirm that, in as-grown MoSe₂, the concentration of charge carriers is significantly increased over the (possibly metallic) GBs, as well as along the outer edges of the flakes. The latter phenomenon is to some extent the opposite compared to what was observed in WS₂ flakes where the decrease of the PL signal and corresponding increase of TERS signal in the vicinity of the edges of the as-grown flakes were attributed to the decreased concentration of charge carriers.⁵¹

CONCLUSIONS

In summary, MoSe₂ monolayers were grown in high density with crystal sizes ranging from a few μm to 100 μm . We demonstrated the importance of comprehensive SPM characterization which, in addition to commonly collected topography, included surface potential and $\partial^2 C/\partial z^2$ imaging. $\partial^2 C/\partial z^2$ images of fresh, as-grown polycrystalline monolayer flakes with near-perfect topography very clearly showed the presence of grain boundaries which were protruding toward the center of the flakes, rather than being located along the edges of the main body of the crystal. Analysis of samples aged in ambient conditions for 2 weeks showed that significant degradation occurred along these grain boundaries, with appearance of new features in the surface potential images of aged flakes.

Correlation of this advanced SPM characterization with TERS and TEPL imaging revealed a number of unexpected features in MoSe₂ monolayers transferred to gold substrates in the form of nanoscale inhomogeneity in domains as small as few tens of nanometers. Two types of TERS spectra were observed, a nonresonant spectrum with a single dominant peak at 240 cm^{-1} , and another more common, resonant type also exhibiting fairly intense peaks at 287 and 340 cm^{-1} , as well as complex overtone peaks around 460 and 550 cm^{-1} . The size of the domains with correspondingly nonresonant or resonant response was several tens of nm, which makes these domains unobservable with conventional confocal Raman microscopy. By comparing our TERS measurements of MoSe₂ to α -MoO₃, we conclude that nanoscale inclusions of MoO₃ in the MoSe₂ matrix are responsible for these differences.

Furthermore, the intensity of TERS response was greatly suppressed at GBs of crystals transferred to gold, which we attribute to complete removal of MoSe₂ over these GBs either in the process of etching the underlying SiO₂ layer in hot NaOH solution during transfer to gold, or by fast degradation of the grain boundaries in ambient conditions. This observation as well as partial oxidation of nanoscale domains in MoSe₂ imply that the transfer process of transition metal diselenides from the growth substrate with strong bases may degrade the original properties of as-grown TMD crystals. Future work along these lines should involve employing gentler transfer techniques to explore how defects of known concentrations affect the nanoscale properties of monolayer semiconductors.

Comprehensive SPM characterization of TMDs both as-grown and transferred to Au substrates, combined with nanoscale spectroscopic characterization, offers an avenue for

simple and noninvasive insights into the structure and properties of 2D semiconductors at a submicron scale. Broader use of these techniques can bridge the gap between atomic resolution imaging such as TEM and conventional optical microscopy and macroscopic characterization techniques, providing important information on both the structure and physical properties of TMDs at all relevant scales.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.7b00083.

MoSe₂ growth details, XPS spectra, SPM and TERS instrumentation, MoSe₂ transfer process, reproducibility of TERS mapping, additional grain boundary CPD and TERS data, grain boundaries of aged flakes, Raman and TERS of α -MoO₃, mapping with confocal Raman spectroscopy, TEM imaging of transferred MoSe₂, and photocurrent measurements (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: epop@stanford.edu.

ORCID

Kirby K. H. Smithe: 0000-0003-2810-295X

Eilam Yalon: 0000-0001-7965-459X

Miguel Muñoz Rojo: 0000-0001-9237-4584

Eric Pop: 0000-0003-0436-8534

Author Contributions

○K.K.H.S. and A.V.K. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Part of this work was performed at the Stanford Nano Shared Facilities (SNSF). This work was supported in part by the Air Force Office of Scientific Research (AFOSR) Grants FA9550-14-1-0251 and FA9550-14-1-0040, by the National Science Foundation (NSF) EFRI 2-DARE Grant 1542883 and DMR-1411107, and by the Stanford Initiative for Nanoscale Materials and Processes (INMP). K.K.H.S. and C.S.B. acknowledge support from the NSF Graduate Research Fellowship under Grant No. DGE-114747, and K.K.H.S. acknowledges support from the Stanford Graduate Fellowship (SGF) program. Disclaimer: certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology.

REFERENCES

- (1) Mak, K. F.; Shan, J. Photonics and Optoelectronics of 2D Semiconductor Transition Metal Dichalcogenides. *Nat. Photonics* **2016**, *10*, 216–226.
- (2) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805.
- (3) Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C. Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271–1275.
- (4) Macneill, D.; Heikes, C.; Mak, K. F.; Anderson, Z.; Kormányos, A.; Zólyomi, V.; Park, J.; Ralph, D. C. Breaking of Valley Degeneracy

by Magnetic Field in Monolayer MoSe₂. *Phys. Rev. Lett.* **2015**, *114*, 037401.

(5) Xiao, D.; Liu, G.; Bin, Feng, W.; Xu, X.; Yao, W. Coupled Spin and Valley Physics in Monolayers of MoS₂ and Other Group-VI Dichalcogenides. *Phys. Rev. Lett.* **2012**, *108*, 196802.

(6) Zeng, H.; Dai, J.; Yao, W.; Xiao, D.; Cui, X. Valley Polarization in MoS₂ Monolayers by Optical Pumping. *Nat. Nanotechnol.* **2012**, *7*, 490–493.

(7) Mak, K. F.; He, K.; Shan, J.; Heinz, T. F. Control of Valley Polarization in Monolayer MoS₂ by Optical Helicity. *Nat. Nanotechnol.* **2012**, *7*, 494–498.

(8) Flatten, L. C.; He, Z.; Coles, D. M.; Trichet, A. A. P.; Powell, A. W.; Taylor, R. A.; Warner, J. H.; Smith, J. M. Room-Temperature Exciton-Polaritons with Two-Dimensional WS₂. *Sci. Rep.* **2016**, *6*, 33134.

(9) Ugeda, M. M.; Bradley, A. J.; Shi, S.-F.; da Jornada, F. H.; Zhang, Y.; Qiu, D. Y.; Ruan, W.; Mo, S.-K.; Hussain, Z.; Shen, Z.-X.; Wang, F.; Louie, S. G.; Crommie, M. F. Giant Bandgap Renormalization and Excitonic Effects in a Monolayer Transition Metal Dichalcogenide Semiconductor. *Nat. Mater.* **2014**, *13*, 1091–1095.

(10) Mak, K. F.; He, K.; Lee, C.; Lee, G. H.; Hone, J.; Heinz, T. F.; Shan, J. Tightly Bound Trions in Monolayer MoS₂. *Nat. Mater.* **2013**, *12*, 207–211.

(11) Palummo, M.; Bernardi, M.; Grossman, J. C. Exciton Radiative Lifetimes in Two-Dimensional Transition Metal Dichalcogenides. *Nano Lett.* **2015**, *15*, 2794–2800.

(12) Arora, A.; Nogajewski, K.; Molas, M. R.; Koperski, M.; Potemski, M. Exciton Band Structure in Layered MoSe₂: From a Monolayer to the Bulk Limit. *Nanoscale* **2015**, *7*, 20769–20775.

(13) Chang, Y.; Zhang, O. W.; Zhu, O. Y.; Han, Y.; Pu, J.; Chang, J.; Hsu, W. Monolayer MoSe₂ Grown by Chemical Vapor Deposition for Fast Photodetection. *ACS Nano* **2014**, *8*, 8582–8590.

(14) Zhang, Y.; Chang, T.-R.; Zhou, B.; Cui, Y.-T.; Yan, H.; Liu, Z.; Schmitt, F.; Lee, J.; Moore, R.; Chen, Y.; Lin, H.; Jeng, H.-T.; Mo, S.-K.; Hussain, Z.; Bansil, A.; Shen, Z.-X. Direct Observation of the Transition from Indirect to Direct Bandgap in Atomically Thin Epitaxial MoSe₂. *Nat. Nanotechnol.* **2014**, *9*, 111–115.

(15) Shaw, J. C.; Zhou, H.; Chen, Y.; Weiss, N. O.; Liu, Y.; Huang, Y.; Duan, X. Chemical Vapor Deposition Growth of Monolayer MoSe₂ Nanosheets. *Nano Res.* **2014**, *7*, 511–517.

(16) Lu, X.; Utama, M. I. B.; Lin, J.; Gong, X.; Zhang, J.; Zhao, Y.; Pantelides, S. T.; Wang, J.; Dong, Z.; Liu, Z.; Zhou, W.; Xiong, Q. Large-Area Synthesis of Monolayer and Few-Layer MoSe₂ Films on SiO₂ Substrates. *Nano Lett.* **2014**, *14*, 2419–2425.

(17) Xia, J.; Huang, X.; Liu, L.-Z.; Wang, M.; Wang, L.; Huang, B.; Zhu, D.-D.; Li, J.-J.; Gu, C.-Z.; Meng, X.-M. CVD Synthesis of Large-Area, Highly Crystalline MoSe₂ Atomic Layers on Diverse Substrates and Application to Photodetectors. *Nanoscale* **2014**, *6*, 8949–8955.

(18) Wang, X.; Gong, Y.; Shi, G.; Chow, W. L.; Keyshar, K.; Ye, G.; Vajtai, R.; Lou, J.; Liu, Z.; Ringe, E.; Tay, B. K.; Ajayan, P. M. Chemical Vapor Deposition Growth of Crystalline Monolayer MoSe₂. *ACS Nano* **2014**, *8*, 5125–5131.

(19) Pradhan, N. R.; Rhodes, D.; Xin, Y.; Memaran, S.; Bhaskaran, L.; Siddiq, M.; Hill, S.; Ajayan, P. M.; Balicas, L. Ambipolar Molybdenum Diselenide Field-Effect Transistors: Field-Effect and Hall Mobilities. *ACS Nano* **2014**, *8*, 7923–7929.

(20) Larentis, S.; Fallahzad, B.; Tutuc, E. Field-Effect Transistors and Intrinsic Mobility in Ultra-Thin MoSe₂ Layers. *Appl. Phys. Lett.* **2012**, *101*, 223104.

(21) Verma, P. Tip-Enhanced Raman Spectroscopy: Technique and Recent Advances. *Chem. Rev.* **2017**, *117*, 6447–6466.

(22) Saunin, S. A.; Krayev, A. V.; Zhizhimontov, V. V.; Gavriluk, V. V.; Grigorov, L. N.; Belyaev, A. V.; Evplov, D. A. Systems and Methods for Non-Destructive Surface Chemical Analysis of Samples. U.S. Patent 9,568,495 B2, 2017.

(23) Su, W.; Roy, D. Visualizing Graphene Edges Using Tip-Enhanced Raman Spectroscopy. *J. Vac. Sci. Technol., B: Nanotechnol. Microelectron.: Mater., Process., Meas., Phenom.* **2013**, *31*, 041808.

(24) Beams, R.; Cançado, L. G.; Jorio, A.; Vamivakas, A. N.; Novotny, L. Tip-Enhanced Raman Mapping of Local Strain in Graphene. *Nanotechnology* **2015**, *26*, 175702.

(25) Stadler, J.; Schmid, T.; Zenobi, R. Nanoscale Chemical Imaging of Single-Layer Graphene. *ACS Nano* **2011**, *5*, 8442–8448.

(26) Su, W.; Kumar, N.; Mignuzzi, S.; Crain, J.; Roy, D. Nanoscale Mapping of Excitonic Processes in Single-Layer MoS₂ Using Tip-Enhanced Photoluminescence Microscopy. *Nanoscale* **2016**, *8*, 10564–10569.

(27) Bao, W.; Borys, N. J.; Ko, C.; Suh, J.; Fan, W.; Thron, A.; Zhang, Y.; Buyanin, A.; Zhang, J.; Cabrini, S.; Ashby, P. D.; Weber-Bargioni, A.; Tongay, S.; Aloni, S.; Ogletree, D. F.; Wu, J.; Salmeron, M. B.; Schuck, P. J. Visualizing Nanoscale Excitonic Relaxation Properties of Disordered Edges and Grain Boundaries in Monolayer Molybdenum Disulfide. *Nat. Commun.* **2015**, *6*, 7993.

(28) Park, K. D.; Khatib, O.; Kravtsov, V.; Clark, G.; Xu, X.; Raschke, M. B. Hybrid Tip-Enhanced Nanospectroscopy and Nanoimaging of Monolayer WSe₂ with Local Strain Control. *Nano Lett.* **2016**, *16*, 2621–2627.

(29) Zhang, Y.; Voronine, D. V.; Qiu, S.; Sinyukov, A. M.; Hamilton, M.; Liege, Z.; Sokolov, A. V.; Zhang, Z.; Scully, M. O. Improving Resolution in Quantum Subnanometre-Gap Tip-Enhanced Raman Nanoimaging. *Sci. Rep.* **2016**, *6*, 25788.

(30) Voronine, D. V.; Lu, G.; Zhu, D.; Krayev, A. Tip-Enhanced Raman Scattering of MoS₂. *IEEE J. Sel. Top. Quantum Electron.* **2017**, *23*, 138.

(31) Rahaman, M.; Rodriguez, R. D.; Plechinger, G.; Moras, S.; Schüller, C.; Korn, T.; Zahn, D. R. T. Highly Localized Strain in a MoS₂/Au Heterostructure Revealed by Tip-Enhanced Raman Spectroscopy. *Nano Lett.* **2017**, *17*, 6027–6033.

(32) Kastl, C.; Chen, C. T.; Kuykendall, T.; Shevitski, B.; Darlington, T. P.; Borys, N. J.; Krayev, A.; Schuck, P. J.; Aloni, S.; Schwartzberg, A. M. The Important Role of Water in Growth of Monolayer Transition Metal Dichalcogenides. *2D Mater.* **2017**, *4*, 021024.

(33) Ling, X.; Lee, Y.-H.; Lin, Y.; Fang, W.; Yu, L.; Dresselhaus, M. S.; Kong, J. Role of the Seeding Promoter in MoS₂ Growth by Chemical Vapor Deposition. *Nano Lett.* **2014**, *14*, 464–472.

(34) Smithe, K. K. H.; English, C. D.; Suryavanshi, S. V.; Pop, E. Intrinsic Electrical Transport and Performance Projections of Synthetic Monolayer MoS₂ Devices. *2D Mater.* **2017**, *4*, 011009.

(35) Tran, M. D.; Kim, J. H.; Lee, Y. H. Tailoring Photoluminescence of Monolayer Transition Metal Dichalcogenides. *Curr. Appl. Phys.* **2016**, *16*, 1159–1174.

(36) Julien, C.; Khelfa, A.; Hussain, O.; Nazri, G. Synthesis and Characterization of Flash-Evaporated MoO₃ Thin Films. *J. Cryst. Growth* **1995**, *156*, 235–244.

(37) Li, Y.; Chernikov, A.; Zhang, X.; Rigosi, A.; Hill, H. M.; Van Der Zande, A. M.; Chenet, D. A.; Shih, E. M.; Hone, J.; Heinz, T. F. Measurement of the Optical Dielectric Function of Monolayer Transition-Metal Dichalcogenides: MoS₂, MoSe₂, WS₂, and WSe₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *90*, 205422.

(38) Amani, M.; Chin, M. L.; Mazzoni, A. L.; Burke, R. A.; Najmaei, S.; Ajayan, P. M.; Lou, J.; Dubey, M. Growth-Substrate Induced Performance Degradation in Chemically Synthesized Monolayer MoS₂ Field Effect Transistors. *Appl. Phys. Lett.* **2014**, *104*, 203506.

(39) Chen, C.; Hayazawa, N.; Kawata, S. A 1.7 nm Resolution Chemical Analysis of Carbon Nanotubes by Tip-Enhanced Raman Imaging in the Ambient. *Nat. Commun.* **2014**, *5*, 3312.

(40) Picardi, G.; Chaigneau, M.; Ossikovski, R.; Licitra, C.; Delapierre, G. Tip Enhanced Raman Spectroscopy on Azobenzene Thiol Self-Assembled Monolayers on Au(111). *J. Raman Spectrosc.* **2009**, *40*, 1407–1412.

(41) Deckert-Gaudig, T.; Deckert, V. Tip-Enhanced Raman Scattering Studies of Histidine on Novel Silver Substrates. *J. Raman Spectrosc.* **2009**, *40*, 1446–1451.

(42) Deckert-Gaudig, T.; Bailo, E.; Deckert, V. Tip-Enhanced Raman Scattering (TERS) of Oxidised Glutathione on an Ultraflat Gold Nanoplate. *Phys. Chem. Chem. Phys.* **2009**, *11*, 7360–7362.

- (43) Soubelet, P.; Bruchhausen, A. E.; Fainstein, A.; Nogajewski, K.; Faugeras, C. Resonance Effects in the Raman Scattering of Mono- and Few Layers MoSe₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, *93*, 155407.
- (44) Koike, K.; Wada, R.; Yagi, S.; Harada, Y.; Sasa, S.; Yano, M. Characteristics of MoO₃ Films Grown by Molecular Beam Epitaxy. *Jpn. J. Appl. Phys.* **2014**, *53*, 05FJ02.
- (45) Sivakumar, R.; Sanjeeviraja, C.; Jayachandran, M.; Gopalakrishnan, R.; Sarangi, S. N.; Paramanik, D.; Som, T. MeV N⁺-Ion Irradiation Effects on α -MoO₃ Thin Films. *J. Appl. Phys.* **2007**, *101*, 034913.
- (46) Illyaskutty, N.; Sreedhar, S.; Sanal Kumar, G.; Kohler, H.; Schwotzer, M.; Natzeck, C.; Pillai, V. P. M. Alteration of Architecture of MoO₃ Nanostructures on Arbitrary Substrates: Growth Kinetics, Spectroscopic and Gas Sensing Properties. *Nanoscale* **2014**, *6*, 13882–13894.
- (47) Mahjouri-Samani, M.; Liang, L.; Oyedele, A.; Kim, Y. S.; Tian, M.; Cross, N.; Wang, K.; Lin, M. W.; Boulesbaa, A.; Rouleau, C. M.; Puzos, A. A.; Xiao, K.; Yoon, M.; Eres, G.; Dusch, G.; Sumpter, B. G.; Geohegan, D. B. Tailoring Vacancies Far beyond Intrinsic Levels Changes the Carrier Type and Optical Response in Monolayer MoSe_{2-x} Crystals. *Nano Lett.* **2016**, *16*, 5213–5220.
- (48) Bhanu, U.; Islam, M. R.; Tetard, L.; Khondaker, S. I. Photoluminescence Quenching in Gold - MoS₂ Hybrid Nanoflakes. *Sci. Rep.* **2015**, *4*, 05575.
- (49) Zhang, C.; Johnson, A.; Hsu, C.-L.; Li, L.-J.; Shih, C.-K. Direct Imaging of Band Profile in Single Layer MoS₂ on Graphite: Quasiparticle Energy Gap, Metallic Edge States, and Edge Band Bending. *Nano Lett.* **2014**, *14*, 2443–2447.
- (50) Ma, Y.; Kolekar, S.; Coy Diaz, H.; Aproz, J.; Miccoli, I.; Tegenkamp, C.; Batzill, M. Metallic Twin Grain Boundaries Embedded in MoSe₂ Monolayers Grown by Molecular Beam Epitaxy. *ACS Nano* **2017**, *11*, 5130–5139.
- (51) Yu, Y.; Hu, S.; Su, L.; Huang, L.; Liu, Y.; Jin, Z.; Alexander, A.; Geohegan, D. B.; Kim, K. W.; Zhang, Y.; Cao, L. Equally Efficient Interlayer Exciton Relaxation and Improved Absorption in Epitaxial and Non-Epitaxial MoS₂/WS₂ Heterostructures. *Nano Lett.* **2015**, *15*, 486–491.