Uncovering topographically hidden features in 2D MoSe$_2$ with correlated potential and optical nanoprobes

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Developing characterization strategies to better understand nanoscale features in two-dimensional nanomaterials is of crucial importance, as the properties of these materials are many times driven by nanoscale and microscale chemical and structural modifications within the material. For the case of large area monolayer MoSe$_2$ flakes, kelvin probe force microscopy coupled with tip-enhanced photoluminescence was utilized to evaluate such features including internal grain boundaries, edge effects, bilayer contributions, and effects of oxidation/aging, many of which are invisible to topographical mapping. A reduction in surface potential due to $n$-type behavior was observed at the edge of the flakes as well as near grain boundaries. Potential phase mapping, which corresponds to the local dielectric constant, depicted local biexciton and trion states in optically-active regions of interest such as grain boundaries. Finally, nanoscale surface potential and photoluminescence mapping was performed at several stages of oxidation, revealing that various oxidative states can be evaluated during the aging process. Importantly, all of the characterization performed in this study was non-destructive and rapid, crucial for quality evaluation of an exciting class of two-dimensional nanomaterials.

npj 2D Materials and Applications (2020) 4:44; https://doi.org/10.1038/s41699-020-00178-w

INTRODUCTION

The unusual properties of two-dimensional (2D) materials are often generated not from a perfect crystalline lattice, but by the defects, grain boundaries, and other imperfections embedded within the structure. In 2D molybdenum diselenide (MoSe$_2$), a van der Waals semiconductor with monolayer direct bandgap of 1.5 eV$^1$, these inhomogeneities can range in size from as small as a selenium vacancy to microscale in the case of grain boundaries and locally oxidized domains$^{2-7}$. While many researchers are pushing the limits of crystal perfection, the inhomogeneities and defects have proven beneficial in the cases of quantum emission from atomic vacancies$^{8-10}$, electronic transport modification at grain boundaries$^{11,12}$, and improved catalysis in substoichiometric materials$^{13,14}$. Often, these features are only observed via low-throughput techniques such as transmission electron microscopy or scanning tunneling microscopy$^{15-19}$. To ensure implementation of 2D materials in desired applications including electronics, molecular sensors, and optoelectronics, new strategies to enable quantitative understanding of these defects using rapid, nondestructive characterization techniques will become increasingly necessary$^{17,18}$. Many techniques also vary in instrument availability, cost, and difficulty, necessitating easier methods such as kelvin probe force microscopy (KPFM) and tip enhanced photoluminescence (TEPL), as presented in this study.

Of the many subsets of nanoscale characterization methodologies available for 2D materials, scanning probe techniques routinely provide exceptional lateral resolution (~20 nm), nondestructive evaluation, and simplicity of use necessary to observe inhomogeneities in the 2D structure and chemistry. Atomic force microscopy, developed in the late 1980’s$^{19}$, is the most common of these and enables rapid evaluation of nanoscale (~0.1 nm in height) topographical features to include layer thickness, grain boundaries, and even frictional properties in 2D materials$^{20,21}$. KPFM$^{22}$, a non-contact scanning probe technique, can allow for direct measurement of surface potential and work function at a similar scale. Using this technique, the surface potential of MoSe$_2$ monolayers was shown to be highly thickness and environment-dependent, with an increase in work function with layer count due to interlayer screening effects$^{23,24}$. Further surface potential and capacitance imaging of monolayer MoSe$_2$ flakes reveal grain boundaries and edge effects, invisible to topographic mapping, exhibit a strong contribution to the localized surface potential$^{15}$.

Optical analysis is fundamentally limited by the light diffraction limit (up to hundreds of nanometers for visible frequencies), which has prevented nanoscale mapping of optical signals and hence correlation of optical or excited state properties with topographic features. However, these limitations can be overcome by combining scanning probe techniques with spectroscopy. Tip-enhanced scanning probe techniques offers nanoscale-resolution imaging of optical signals, such as the Raman scattering and photoluminescence. The resolution offered is far superior as compared to diffraction-limited far field imaging due to the deep sub-wavelength confinement of light by the plasmonic mode of the metal tip. The limiting resolution is ~20 nm, mainly defined by the tip diameter$^{26}$. It has been used in the past to investigate the TEPL signal as a function of the number of layers as well as mapping of local strain, heterogeneity of emission and charged emission in transition metal dichalcogenides (TMDCs)$^{27-30}$. The techniques’ ability to resolve the nanoscale optical emission properties has enabled experimental distinction of edge and basal plane “bulk” regions, aiding in the identification of 1D to 2D quantum confinement effect in TMDCs. For example, it was recently reported that an energetically disordering nanoscale region of ~300 nm width is present at the edges and grain boundaries in CVD grown MoS$_2$, where the spectral median is blue shifted compared to basal plane “bulk” regions$^{31}$. In another
Monolayer MoSe₂ synthesis and characterization

**RESULTS AND DISCUSSION**

**Monolayer MoSe₂ synthesis and characterization**

Large area monolayer MoSe₂ flakes were synthesized directly onto a Si/SiO₂ wafer through the vaporization of MoO₃ and selenium powder at elevated temperatures, as schematically depicted in Fig. 1a and described in previous works. The resultant films were primarily monolayer with some bilayer regions and exhibited lateral flake sizes in excess of 25 µm with characteristic A₁g (241.1 cm⁻¹) and E₁₂g (287.1 cm⁻¹) peaks in the Raman spectrum (Fig. 1b). Initial Raman mapping of a microscale flake in Fig. 1c revealed apparent uniform structure at the resolution of 500 nm. Powder vaporization synthesis of 2D materials has been known to result in many features and inhomogeneities on and within the surface including bilayers and grain boundaries. These features are invisible in the initial Raman mapping but are clearly present in the topographical and KPFM maps as shown in Fig. 1d, e, respectively.

Scanning probe topography and KPFM of the monolayer flakes are not limited by the same resolution as Raman spectroscopy, but at times the data can be difficult to translate into meaningful quantitative information. The topographic mapping of the MoSe₂ flakes in Fig. 1d easily identifies bilayer triangles within the flake but is blind to chemical changes until they are very advanced to the point of structural modification of the crystal or creation of oxide complexes. Kelvin probe force microscopy mapping in Fig. 1e clearly depicts regions of varying chemical potential on the surface, with obvious deviations from the bulk flake occurring at both the edges and the bilayer regions, revealing that these techniques can successfully identify features beyond the visible diffraction limit.

KPFM measures the contact potential difference (CPD) to produce a relative work function map of the surface. It is well-known that KPFM can see changes in work function in 2D materials due to a change in layer number, grain boundaries, and chemical changes like defect densities. The phase map is less well-studied, but can generally be considered analogous to surface dielectric properties (see Supplementary Information: KPFM Operation and Theory). Unlike CPD, the phase signal is blind to surface charging, allowing resolution of finer features where charge accumulates.

Investigating nanoscale heterogeneities with KPFM

To correlate the topographical features to various chemical and dielectric states in the material, topographical mapping (Fig. 2a), KPFM (Fig. 2b, c), and phase mapping (Fig. 2d) were performed sequentially on the same flake area. Clearly, the chemical potential and dielectric properties of the edge, monolayer and bilayer regions result in a clear contrast from the rest of the flake. To further evaluate this, line scans taken from Fig. 2b internal grain boundary, and bilayer sites as well as the corresponding height profiles are shown in Fig. 2c, respectively. The edge effect is visible in Fig. 2b, but an enhanced image and line scan of an fully unoxidized flake is shown in Fig. 2e, f, respectively. The edge of the flake shows a small rise (~50 mV) in work function within a 300 nm distance from the boundary of the flake before dropping off to the substrate value of ~400 mV below the flake. We attribute this small rise in edge potential before drop-off to the molybdenum-rich MoSe₂ chemistry observed to occur due to

![Figure 1](image_url)
500 nm) is dominated by charge accumulation in the SiO$_2$ drop in potential beyond the edge of the

![Fig. 1](image1.png) compared to the potential map. The relatively slow excluds this region, but has relatively low contrast (Supplementary Fig. 1) compared to the potential map. The relatively slow drop in potential beyond the edge of the flake (on the order of 500 nm) is dominated by charge accumulation in the SiO$_2$ substrate. A significant drop in potential (~50 mV) was observed at the grain boundary, which is invisible in the topographic map but very apparent in surface phase map (Fig. 2b). This is a very favorable feature of utilizing KPFM to evaluate 2D materials in that chemical changes and features in the film are easily observable, in this case even when structurally they would otherwise be indistinguishable. Additionally, bilayers interrogated with KPFM showed a rise in surface potential of nearly 100 mV. It was determined, and will be discussed later, that the majority of this top-most plane on bilayer flakes was oxidized at the point of taking this measurement, which affects the relative grain boundary and bilayer potentials as the flakes age and resulting in an increase in surface potential when oxidized.

Due to their atomically-thin structure, the electronic and optical properties of single layer TMDCs can be significantly influenced by elements of the surrounding environment such as chemical dopants, fixed charges and nature of the dielectric medium.

As discussed above, the KPFM phase characterization reflects the dielectric property of materials and it therefore impacts optical properties of the layers. Hence, to further correlate KPFM to optical properties, specifically luminescent properties, we perform TEPL measurements on the MoSe$_2$ flakes.

Correlation of nanoscale features using tip-enhanced photoluminescence

We first focus on a region composed of monolayer MoSe$_2$ and also bilayer parts as shown in the topographical map in Fig. 3a. With increased aging of the flake, a natural hump emerges near the internal grain-boundary where it was invisible initially in topography. This can be attributed to physisorption or chemisorption of foreign molecules due to the chemically active nature of the surface at this grain boundary. Corresponding KPFM phase mapping of the grain boundary shows a lower phase value than basal plane, similar to the result at Fig. 2b. Corresponding spatial variation of TEPL peak position is shown in Fig. 3c. Overall, the PL peak positions throughout the flakes are redshifted compared to the peak positions of previously reported PL emission of MoSe$_2$ at ~800 nm, which is attributed to oxygen adsorption on the flakes. It has been widely reported that oxygen easily adsorbs to chalcogen vacancy sites in TMDCs and acts as a $p$-dopant. This results in an increase in the number of positively charged excitons (trions) rather than neutral excitons and hence the PL is red-shifted. Taking this into account, we speculate that the as-prepared sample has stoichiometric composition variation throughout the flakes. This presumed composition variation is likely composed of differences in selenium vacancy concentration, and hence the variance in the extent of subsequent oxygen chemisorption on the surface. Due to the varying degrees of oxidation, the surface in Fig. 3c shows four different regions of varying emission spectra denoted as Region 1–4, corresponding to a grain boundary, highly oxidized basal plane, basal plane and edge. Each region emits a peak PL at 818.2 nm (Region 1), 820.0 nm (Region 2), 817.3 nm (Region 3), and 814.0 nm (Region 4) on average.

KPFM phase and TEPL maps were compared to elucidate more quantitative information regarding the microstructure and chemistry in this study. Although each region is not clearly distinguished in topography (Fig. 3a), KPFM phase changes with time and the corresponding TEPL peak position map (Fig. 3c) resembles the phase map. The KPFM phase can be directly correlated to the static dielectric constant of the sample medium. Therefore, upon comparing Fig. 3b, c, it is evident that the static dielectric constant varies even in a topographically homogeneous single flake from the chemisorption of oxygen and has a critical role in the resultant luminescent properties. More specifically, at Region 2, a dimmer KPFM phase region appears at the center and the peak position for the corresponding wavelength is far red-shifted compared to the other region. This result can be attributed to oxygen chemisorption on to MoSe$_2$ flake and alteration of the dielectric environment on...
the flake. In agreement with a previous study reporting shifts in the
PL peak position with different surrounding dielectric media due to
reduced dielectric screening,\textsuperscript{45} the corresponding binding energy
becomes stronger and its PL peak position is red-shifted. The
dimmer KPFM phase region is therefore characterized by a
comparatively smaller dielectric constant and that local variation
of KPFM phase suggests partial oxidation or chemisorption. More
details of oxidation evolution are discussed further below.

Figure 3c further suggests that our observed PL emission is
even more redshifted than that of trion (813 nm) and neutral
exciton (800 nm, 1.55 eV) PL normally observed\textsuperscript{55}, leading to the
consideration of the potential occurrence of higher order excited
states in addition to the trion. Prior reports suggest that biexciton
formation in bilayer MoSe\textsubscript{2} occurs even at room temperature and
further confirmed that biexcitons are formed by the combination
of a trion and an excess free carrier (i.e. an electron or a hole)\textsuperscript{51}. A
key requirement for stable biexciton formation is high exciton
density as well as a binding energy greater than the room
temperature thermal energy. One main difference in previously
published results describe biexcitonic emission in both monolayer
as well as bilayer MoSe\textsubscript{2}. We attribute this result to tip-mode
enhancement of PL which causes plasmonic enhancement at
vicinity of the tip apex due to the Purcell effect\textsuperscript{52}. Since interaction
with the tip creates excess carriers in an extremely localized region
due to the small tip radius (~20 nm), exciton density in the region
is dramatically higher as opposed to far-field excitation at same
total power, hence the formation of stable biexcitons at room
temperature. The stable biexciton formation in our case is
supported by the prior report about resonant excitation of
CsPbBr\textsubscript{3} perovskite nanoplate inside the Ag nanowire-Ag film
plasmonic nanogaps\textsuperscript{56,57}, which reported that the necessary exciton
occupancy for excitation was significantly reduced by ~10\textsuperscript{6} times
from the plasmonic gap. We rule out the possibility of detrimental
influence of the Purcell effect on MoSe\textsubscript{2} since plasmonic
resonators are well known for large and reproducible enhance-
ment of spontaneous emission\textsuperscript{52,54-56}. For example, recent reports
on time varying series of tip-enhanced photoluminescence of
WSe\textsubscript{2} by repeated engaging and disengaging the tip has proven
Purcell enhancement of PL unambiguously. The same work also
showed that WSe\textsubscript{2} monolayer is stable under frequent exposure to
high-electric field induced by Purcell effect\textsuperscript{52}. Further, biexciton
emission due to such high intensity laser has thus far only been
observed in the far-field\textsuperscript{51,57}. The biexciton emission in our case
from a near field signal is indicative of a cumulative effect of
Purcell enhancement and oxygen induced doping. Considering
this, we evaluated the trion/biexciton contribution of the TEPL
spectrum. Figure 3d demonstrates energy states of the ground
exciton (A\textsubscript{1s}), trion (A\textsubscript{XX}−/+) and biexciton (A\textsubscript{XX}) energy band.
Since the biexciton originates from a trion, its energy state is lower
than that of the trion and separated by its binding energy\textsuperscript{51}. Based
on the energy level, the PL spectrum can be deconvoluted into A\textsubscript{XX}−/+
(red) and A\textsubscript{XX} (green) peaks, as shown in Fig. 3e and supporting
information (Supplementary Fig. 2). Note that the neutral exciton
signal (800 nm) is negligible in comparison to A\textsubscript{XX}−/+ and A\textsubscript{XX}
contribution as we assumed before. Figure 3f, g displays the PL
intensity from A\textsubscript{XX}−/+ and A\textsubscript{XX}, respectively, where A\textsubscript{XX}−/+
emission is uniform over the entire flake while the PL intensity from A\textsubscript{XX}
is particularly high in Region 2. This suggests that the A\textsubscript{XX} are readily
formed at the oxidized region because of low dielectric screening
(dimmer KPFM phase), which contributes to enhancement of the
binding energy. This observed trend is in agreement with previous
reports about large binding energy of biexciton at nanomaterials
such as two dimensional PbI\textsubscript{4} under small dielectric medium\textsuperscript{58}.

Likewise, near the flake edge (Region 4) and the grain boundary
(Region 1), the exciton has higher binding energy because the
dielectric constant is relatively lower than that of the symmetric,
defect free basal plane (Region 2, 3 in Fig. 3b). Interestingly, we
found the PL intensity at the edge and grain boundary are much
stronger than that at the basal plane. The large variations in PL of
edges vs basal plane regions have been made previously in both
CVD grown and exfoliated flakes, and many explanations have been
pointed out for this including presence of oxidation of the edge
site\textsuperscript{51,52,57} to local disorder to potential confinement of excitations
near the edge. However, these results are not sufficient to explain
this solely by oxidation or due to the structural and electronic
property difference between basal plane and the edge. As indicated
in Fig. 3b, the KPFM phase gradient is present from the basal plane
to the edge or the grain boundary. We believe the dielectric
gradient can be a driving force to funnel the exciton in the vicinity
of these line defects because the low dielectric medium offers
stronger oscillation bond in the electron-hole pair and more stable
exciton formation\textsuperscript{52}. It is supported by the fact that the line cut of

Fig. 3 Correlation of KPFM to TEPL in monolayer MoSe\textsubscript{2} flakes. a Topography b KPFM phase, and c near-field PL wavelength mapping of monolayer MoSe\textsubscript{2}, d Energy diagram of exciton, trion, and biexciton state, e representative deconvoluted averaged PL Spectrum of Region 1, f Near field PL mapping of A\textsubscript{XX}−/+ (~1.520 eV) and g A\textsubscript{XX} (~1.490 eV), and h Areal PL contribution of trion and biexciton at Region 1–4. All scale bars are equivalent to 3 µm.

Published in partnership with FCT NOVA with the support of E-MRS

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combining AX recombination rate of the trion and biexciton (10^{15} \text{ cm}^{-2} \text{s}^{-1}) on MoS\text{2} exceeds that of exciton under high generation rate on the edge while it does not on the basal plane. Note that the intensity of the basal plane is stronger than the edge. Correspondingly, AXX recombination rate (10^{16} \text{ cm}^{-2} \text{s}^{-1}) is high intensity of the laser excitation. In addition, electrostatic p-doping facilitates a high recombination rate (10^{15} \text{ cm}^{-2} \text{s}^{-1}) at even lower generation rates (10^{16} \text{ cm}^{-2} \text{s}^{-1}). Moreover, the dielectric gradient driven exciton funneling effect can further enhance the trion and biexcitonic emission rather than neutral exciton at the edge and the grain boundary due to the lower dielectric constant at the edge and grain boundary. The biexciton intensity is unusually high at the grain boundary (Region 1) while low at the edge. This can be further explained by the funneling effect as discussed above.

The graph in Fig. 3h reveals the PL intensity of both the AX and AXX at Region 1–4. The main contribution of the PL arises from A_{\Gamma-\Gamma}. Since A_{\Gamma-\Gamma} is a charged exciton, stronger A_{\Gamma-\Gamma} emission reflects higher concentration, with oxygen chemisorption affecting the basal plane more strongly than the edge. Correspondingly, A_{\Sigma} emission tracks the spatial variation of the A_{\Gamma-\Gamma} emission at the edge while it does not on the basal plane. Note that the intensity of A_{\Sigma} is smaller than that of A_{\Gamma-\Gamma} because the A_{\Sigma} is formed by combining A_{\Gamma-\Gamma} and an excess carrier. One distinguishing feature of the edge and grain boundary is that the biexciton intensity is unusually high at the grain boundary (Region 1) while low at the edge. This can be further explained by the funneling effect as discussed above.

Tracking oxidation and aging

Oxidation was first observed on flakes that were a few months old and subjected to prolonged exposure to a combination of glovebox storage and ambient air. The spot region of oxidation on the top and left image of the flake in Fig. 3a reveals an approximately 30 mV reduction in surface potentials relative to the adjacent unoxidized basal plane. Over the course of the 6 months, the regions on two different flakes were observed to grow in both KPFM and TPEL, until they filled nearly the entire flakes (Fig. 4a–c). Since oxidation p-dopes the MoS\text{2} flake, KPFM potential is lowered as the workfunction of MoS\text{2} increases. It is further verified from the PL peak position mapping, showing that the lower potential region emits PL at lower energy peak position. Interestingly, the oxidation does not start at the grain boundary but at the basal plane. Previous reports state that the grain boundary and edge of the flake is vulnerable to oxidation, because the untempered molybdenum edges are more chemically active than the basal plane\textsuperscript{[47]}. This result is in contrast to the previous reports and this phenomenon was repeatedly observed on multiple flakes (Fig. 3c and 4a). As the flake oxidized, the potential value changes throughout the flake, resulting in a decrease in potential by 48 mV as indicated in Fig. 4b. Additionally, it was clear that the oxidation influenced the bilayer region differently than the monolayer regions. Interestingly, bilayers atop the oxidized region showed a potential higher even than the basal plane, whereas bilayers on the basal plane showed a much lower potential consistent with literature values in pristine TMD flakes\textsuperscript{[23,61,62]}. This is hypothesized to be due to potentially different oxidative states within the material such as chemisorption of oxygen to the bilayer rather than physisorption. It was reported that chemisorption of oxygen influences MoS\text{2} to be n-doped while physisorption induces p-doping, which was supported by first-principle calculation stating that oxygen chemisorption results in conduction band minimum shift downward with respect to fermi level\textsuperscript{[35]}. On the other hand, physisorption is favorable at monolayer region, leading to p-doping and consequently lower potential. The bilayer potential is significantly changed after oxidation (\Delta V = +100 \text{ mV}) while that of monolayer (\Delta V = -40 \text{ mV}) is relatively small. We attribute this to chalcogen p-orbital perturbation due to the adsorption of oxygen. The band structure of MoS\text{2} is composed of \Gamma(Q) states in the band dominated by p-orbital of Se and K valley states dominated by d-orbital of Mo. The monolayer band structure is mostly determined by K states composed of the d-orbitals of Mo. In the case of bilayer MoS\text{2}, the \Gamma(Q) states are shifted due to the interlayer coupling, while the K states are almost constant\textsuperscript{[36]}. Since the adsorbates directly contact to the chalcogen layer and couples with p-orbitals, bilayer MoS\text{2} exhibits a large change in CPD after...
oxidation compared to the monolayer. Note that the time-
dependent CPD change is unlikely to be related to substitution
of Se site by oxygen since forming SeO$_2$ is thermodynamically
unfavorable in the basal plane. Hence the CPD changes result
from vacancies formed during material synthesis, and the bilayer
is eventually further distinguished from monolayer in the case of
oxidized flakes as indicated in Fig. 4b. This localized oxidative and
chemical state within the MoSe$_2$ flakes reinforces the necessity to
further develop nanoscale characterization techniques for these
unique and exciting class of nanomaterials.

Characterization of large area monolayer MoSe$_2$ flakes by surface
potential mapping, phase mapping, and tip-enhanced photolumi-
nescence evaluation reveal many nanoscale features invisible to
topographical mapping, and provide insight into local chemical and
excitonic states within the material. Observed increase in surface
potential approaching 300 nm from the edge of the flake reveal n-
type doping due to substoichiometric film growth. Internal grain
boundaries with no visible height increase are clearly observed in
KPFM from chemical modifications and drive a local surface
potential decrease of nearly 50 mV. Correlated KPFM phase
mapping and TEPL track the local dielectric properties to both
biexciton and trion states, critical to optimizing and understanding
future optical applications. Finally, by performing both surface
potential evaluation and optical nanoprobes, tracking of oxidation
over time can allow for understanding the influence of environ-
mental conditions on these important features. As these nanoscale
to microscale defects, grain boundaries, and surface states will drive
much of the observed properties of 2D materials, the non-
destructive characterization provided herein provides for another
tool for scientists and engineers looking towards applications of this
exciting class of nanomaterials.

METHODS

Monolayer MoSe$_2$ synthesis

Chemical vapor deposition of MoSe$_2$ films were performed in a Thermo
Scientific Lindberg Blue Mini Mite tube furnace. All reagents were obtained
from Millipore Sigma. MoO$_3$ precursor is placed in a ceramic boat with a
cleaned Si/SiO$_2$ substrate suspended face down above MoO$_3$ located
at the center of furnace, where maximum temperature reaches 750 °C. A second
ceramic boat containing Se powder is located upstream where maximum
temperature reaches 500 °C. After 1 min of purging, the furnace is heated
to 750 °C from room temperature in 20 min and kept at the reaction
temperature for 5 min. The furnace is cooled unassisted to room
temperature resulting in triange films of MoSe$_2$. Throughout the entire
process, N$_2$ is continuously streamed into the furnace at a rate of 150 sccm.
During the reaction time, a mixture of H$_2$ and Ar (10% H$_2$) is streamed into
the furnace at a rate of 20 sccm and shut off once cooling begins.

KPFM characterization

KPFM measurements were performed with a Bruker Dimension Icon using
PFONE-AL probe tips. The tips were calibrated against an Al/Al standard.
Data was normalized to the basal plane of the flake. To quantify the
potential, the potential of select areas corresponding to features of interest
was exported to OriginPro and fit to a Gaussian curve. The peak of this fit
was then selected as a data point for that feature. KPFM measurement
conditions were adjusted for each sample based on roughness and adhesion
considerations. The lift height was between 25 and 35 nm. To compensate
for charging in the flake, KPFM potential maps were normalized to the basal
plane and line scans of relevant features were performed. For more
information on KPFM characterization, see Supplementary Methods.

Tip-enhanced photoluminescence (TEPL) characterization

TEPL characterizations were performed in LabRam-Nano AFM-Raman
systems (Horiba Scientific). A 633 nm laser was focused on Au-coated AFM
tip (Omini TERS Probe) and the signal was collected by 100 g/mm grating.
The spectra were averaged over the selected region covering at least
100 x 100 pixels with each pixel size of 80 x 80 nm$^2$.

DATA AVAILABILITY

All data generated or analyzed during this study are available upon request to the
responding authors. The data that support the findings of this study are available from
the corresponding author upon reasonable request.

Received: 15 June 2020; Accepted: 10 November 2020
Published online: 09 December 2020

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**ACKNOWLEDGEMENTS**

N.G. acknowledges support of Air Force Office of Scientific Research grant FA9550-19YCOROSO. D.J. and K.J. acknowledge primary support for this work by the Air Force Office of Scientific Research (AFOSR) FA9550-21-1-0035 and FA9550-20-1-0474 and partial support from U.S. Army Research Office under contract number W911NF-19-1-0109. D.J. also acknowledges partial support from National Science Foundation (DMR-1905883) and from Penn Engineering Start-up funds. The near-field work was carried out at the Singh Center for Nanotechnology at the University of Pennsylvania which is supported by the National Science Foundation (NSF) National Nanotechnology Coordinated Infrastructure Network Grant NNCI-1542513. J.L. and N.G. acknowledge support from the Welch foundation grant C-1716 and NSF EUCR Center for Atomically Thin Multifunctional Coatings (ATOMIC) under award NIP-1539999.

**AUTHOR CONTRIBUTIONS**

All authors contributed to this study. D.M. and K.J. contributed equally to the manuscript, with D.M. performing the KPFM analysis and K.J. the PL mapping. C.N. and J.L. synthesized and characterized the MoS$_2$ flakes. C.M. contributed intellectually and D.J. and N.G. were the thought leaders in the study.

**COMPETING INTERESTS**

The authors declare no competing interests.

**ADDITIONAL INFORMATION**

**Supplementary information** is available for this paper at [https://doi.org/10.1038/s41699-020-0177-w](https://doi.org/10.1038/s41699-020-0177-w).

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