Nano-optical Visualization of Interlayer Interactions in WSe$_2$/WS$_2$ Heterostructures

Alvaro Rodriguez, Andrey Krayev, Matěj Velický, Otakar Frank,* and Patrick Z. El-Khoury*

ACCESS

ABSTRACT: The interplay between excitons and phonons governs the optical and electronic properties of transition metal dichalcogenides (TMDs). Even though a number of linear and nonlinear optical-, electron-, and photoelectron-based approaches have been developed and/or adopted to characterize excitons and phonons in single/few-layer TMDs and their heterostructures, no existing method is capable of directly probing ultralow-frequency and interlayer phonons on the nanoscale. To this end, we developed ultralow-frequency tip-enhanced Raman spectroscopy, which allows spectrally and spatially resolved chemical and structural nanoimaging of WSe$_2$/WS$_2$ heterostructures. In this work, we apply this method to analyze phonons in nanobubbles that are sustained in these heterobilayers. Our method is capable of directly probing interlayer (de)coupling using our novel structurally sensitive nano-optical probe and the interplay between excitons and interlayer/intralayer phonons through correlation analysis of the recorded spectral images.

Single- and few-layer 2D transition metal dichalcogenide (TMD) crystals exhibit unique electronic and optical properties. Their early applications in valleytronics and field-effect transistors have motivated quests to characterize excitons and phonons in TMDs as well as TMD-featuring devices. Ultralow-frequency Raman spectroscopic measurements (\(<50\) cm$^{-1}$) that track interlayer breathing (out-of-plane) and shearing (in-plane) modes in few-layer TMDs are particularly relevant to this work. To date, the spatial resolution in these measurements is nonetheless diffraction-limited. Increasing the spatial resolution in such measurements would allow us to better understand the interplay between excitons and local nanostructural motifs that are well-known to significantly affect the properties of TMDs. This is bolstered through tip-enhanced Raman spectroscopy (TERS) and tip-enhanced photoluminescence (TEPL) measurements of TMD monolayers and heterostructures, where nanoscale structure–function relationships become possible.

Stacking different TMD monolayers leads to a host of novel properties in type II heterobilayers, including long-lived interlayer excitons and ultrafast (phonon-mediated) interfacial charge transfer. Moiré superlattices in such constructs also pave the way toward on-demand band gap/electronic structure engineering with an ultimate aim of unlocking a host of quantum phenomena that can be harnessed in modern optoelectronic devices. Another approach to tailoring the electronic states of few-layer TMDs is through localized strain. Recent studies exploited nanobubbles in monolayer WSe$_2$ and heterobilayers composed of combinations of MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$ to examine how strain affects the electronic and optical response of these systems on the nanoscale using TEPL. Here we take advantage of a similar platform to understand the interplay between interlayer phonons and excitons in a WSe$_2$/WS$_2$ heterobilayer.

Excitons in WSe$_2$/WS$_2$ heterobilayers have been previously investigated using diffraction-limited hyperspectral optical microscopy. Compared with its monolayer constituents, the bilayer sample exhibited spectral broadening and exciton resonance shifts in the visible region of the electromagnetic spectrum. Broadening was associated with faster charge separation, which was also confirmed by femtosecond pump–probe spectroscopy. The lowest exciton resonance (A) in monolayer WSe$_2$ (746 nm) shifts to 774 nm in the WSe$_2$/WS$_2$ heterobilayer, which is close to the excitation wavelength of 785 nm that we use in this work. The 774 nm band in the heterobilayer is nonetheless complex in character, particularly when the two heterolayers are closely aligned (see Figure S1). In particular, the formation of moiré superlattices is accompanied by the emergence of a host of excitonic states that preclude simple assignments of the 774 nm band on the basis of a direct comparison between monolayer and homo/heterobilayer.
spectra. Moreover, diffraction-limited measurements average over spatially varying excitonic resonances, e.g., localized excitons previously observed in TEPL mapping of defects in TMD monolayers and heterobilayers. Prior to an introduction of our distinct approach to the problem, we begin by describing our sample and its general characteristics.

Our samples were prepared by mechanical exfoliation of WSe$_2$ and WS$_2$ monolayers on polydimethylsiloxane (PDMS) and their subsequent transfer onto a gold substrate using all-dry viscoelastic stamping. Moiré patterns were observed across the sample (Figure S1) in topographic images, which documents the intimate alignment between the two layers in the heterostructure. An atomic force microscopy (AFM) image of a selected area of the Au/WSe$_2$/WS$_2$ sample is shown in Figure 1. Besides nanometrically flat regions, the AFM image in Figure 1 also shows nanobubbles and wrinkles. This is consistent with the general topographic features that were recently observed in similarly prepared TMD heterobilayers and are common for van der Waals heterostructures. A simultaneously recorded AFM image and nano-Raman map along with a far-field Raman map of an isolated nanobubble are shown in Figure 2. The topographic image (Figure 2A) reveals an asymmetric morphology of the nanobubble. The same is evident in the nano-Raman map (Figure 2B), where a horseshoe-like scattering profile with a dim response toward the center of the protruded structure is observed. Our observed TERS image profile is reminiscent of TEPL maps of nanobubbles of monolayers and heterobilayers of TMDs. There, the observed patterns were faithfully reproduced using theoretical confinement potentials obtained from atomistic models based on nanobubble strain calculations and Harrison's rule. We similarly associate our observed profiles (also see Figure S2) with strain in our protruded nanostructural motifs. However, our structures are more complicated than nanobubbles composed of single layers, in part because of the contributions of multiple resonances herein arising from WS$_2$, WSe$_2$, and their combination in the heterobilayers. As we illustrate below, two-dimensional correlation analysis aids in identifying the operative local resonances through their correlations with intralayer and interlayer phonons.

The TERS spectral image of the nanobubble is analyzed in detail in Figure 3. Spectra averaged over three distinct areas (marked 1–3) in the image in Figure 3A are shown on the same plot in Figure 3D. Several observations in these spectra are important to highlight. First, with the exception of the center of the bubble (region 1), spectra taken at peripheral regions of the bubble (region 2) as well as at flat regions of the substrate (region 3) are dominated by the interlayer phonon signature at 22 cm$^{-1}$. This is evident in Figure 3D,E, where normalized spectra from regions 1–3 are shown along with the spatially averaged far-field response taken from Figure 2C. Second, the disappearance of the interlayer phonon signature is accompanied by a rise in the relative intensity of the A$_{1g}$ mode of WS$_2$ at $\sim$416 cm$^{-1}$. As discussed below, the appearance of the WS$_2$ mode is accompanied by the appearance of a local optical resonance that is distinct from its analogue in the flat regions of the substrate. Taken together, our first and second observations suggest that the two layers are decoupled toward the center of the bubble, which is marked by the disappearance of the 22 cm$^{-1}$ interlayer phonon and the 416 cm$^{-1}$ WS$_2$ A$_{1g}$ mode.

Figure 1. Representative AFM image of our WS$_2$/WSe$_2$/Au sample. Flat regions, bubbles, and a wrinkle are visible in this image and all throughout the sample used in this work.

Figure 2. Simultaneously recorded (A) AFM image and (B) 22 cm$^{-1}$ TERS intensity map of a nanobubble along with (C) a far-field Raman map of an isolated nanobubble (also at 22 cm$^{-1}$) of the same region. Experimental conditions: 785 nm laser excitation, 100 $\mu$W/µm$^2$, 50 ms time integration. The lateral step sizes used in the near-field and far-field maps were $\sim$1.7 and 5 nm, respectively.
instead, peaking in intensity exactly at the top of the bubble. Identical behavior was also observed for a different bubble (see Figure S2). The decoupling of the layers is schematically illustrated in Figure 3C. The appearance of the WS₂ signature further suggests that a localized optical resonance contributes to this optical signature. The spectroscopic features arising from WSe₂ intralayer phonons, which are resonantly enhanced at our excitation wavelength, otherwise dominate the nano-optical response away from the bubbles. This brings us to our third observation: the contribution of intralayer photoluminescence seems to be significantly dimmed, which is consistent with prior observations, wherein this effect was associated with strong interlayer coupling. Overall, the results in Figure 3 allow us to infer a spatial resolution on the order of ∼10 nm in our measurements.

In Figure 4, we further analyze the recorded TERS map using 2D correlation analysis. The goal is to understand the correlations between the different phenomena that are captured in our recorded image cube without interpretation bias that could potentially interfere in multipeak fitting procedures. The correlation map is shown in Figure 4A, whereas correlation slices taken at different resonances are shown in Figure 4B. The cross-sectional cuts may be used to infer the correlations between the different sharp peaks we observe that arise from interlayer (22 cm⁻¹) and intralayer (>100 cm⁻¹) phonons and, more importantly, the correlations between the phonons and the broad photoluminescence signatures that track excitonic states in our heterobilayer. The 22 cm⁻¹ correlation slice shown in Figure 4B (black spectrum) reveals a positive correlation between the interlayer phonon and a background centered at ∼780 nm assigned to the WSe₂ exciton. The central wavelength of the background is consistent with previously reported WS₂/WSe₂ reflectance spectra that exhibited a broad resonance at 774 nm. The redshifted resonance we capture in our case is attributed to the effect of the Au substrate here, in contrast to sapphire in the previous work. The 22 cm⁻¹ slice also shows (i) a weak correlation between the interlayer phonon and WSe₂ intralayer phonons (at ∼250 cm⁻¹) and (ii) a negative correlation between the interlayer phonon and the A₁g mode of WS₂. The fact that the interlayer phonon is correlated with the ∼780 nm resonance and noncorrelated with the WSe₂ phonons emphasizes the complex nature of the transition that we excited using our driving laser, as discussed elsewhere.
mentioned in our introductory remarks. The negative correlation of the 22 cm$^{-1}$ interlayer phonon with the A$_{1g}$ intralayer phonon of WS$_2$ emphasizes the picture painted by the analysis of the TERS images above: the center of the nanobubble enhanced/dimmed WS$_2$/interlayer phonon signatures. In the same vein, the cross-correlation slice taken at the WS$_2$ resonance maximum (416 cm$^{-1}$) reveals a negative correlation with the 22 cm$^{-1}$ interlayer phonon as well as the $\sim$780 nm exciton of WSe$_2$. Interestingly, the A$_{1g}$ mode of WS$_2$ is strongly correlated to a broad peak centered at $\sim$810 nm that seems to arise from a localized indirect WS$_2$ exciton.\textsuperscript{33,34} Although a definite assignment of the underlying background to a localized WS$_2$ exciton is difficult, the observed (i) correlation between the broad band and the WS$_2$ intralayer phonon, (ii) disappearance of the interlayer phonon indicating that the two layers are decoupled toward the center of the protrusion, and (iii) proximity of the inferred exciton resonance to an indirect transition in WS$_2$ bilayers all support our tentative assignment.

In conclusion, this work describes a novel approach based on ultralow-frequency tip-enhanced Raman spectroscopy that is capable of tracking phonons on the nanoscale. In the model system used herein to describe our new capability, this approach may be used to directly track interlayer (de)coupling in a TMD bilayer. Further analysis of the recorded hyperspectral Raman nanoimages allowed us also to track the interplay between excitons and phonons (both intralayer and interlayer) on the nanoscale. In nanobubble structures, we found that local resonances that vary on the nanometer scale govern the recorded TERS images. We also observed the decoupling of the two layers, as marked by the disappearance of the ultralow-frequency interlayer phonon TERS signature. Beyond the scope of this work, our approach should be generally capable of correlating nanostructural motifs with electronic and optical properties in both model systems and state-of-the-art solid-state devices.

**METHODS**

Samples were prepared using a previously described procedure.\textsuperscript{25} Briefly, we used mechanical exfoliation of bulk crystals (HQ graphene). The WS$_2$ and WSe$_2$ monolayers were separately exfoliated on PDMS stamps and consecutively transferred onto 50 nm sputtered Au-coated SiO$_2$/Si substrates using a dry-transfer technique. Figure S1 shows topographic AFM and photoluminescence spectra from the samples used in this study.

Nano-optical characterization was performed using a custom LabRam-Nano AFM-Raman system (HORIBA Scientific) equipped with a 785 nm laser and a 300 lines mm$^{-1}$ grating. To resolve ultralow-frequency Raman signatures, three consecutive Bragg notch filters (OptiGrate) with total laser line suppression of OD 11 were used in the collection path. For TERS mapping, the laser power at the sample was kept at $\sim$350 $\mu$W, and the signals were time-integrated for 50 ms with a lateral step size of $\sim$2 nm. We used OMNI-TERS-SNC-Au probes from Applied Nanostructures Inc. for these measurements. To extract Raman peak intensities, linear background was subtracted from the relevant part of the spectra within the range of $\pm$20 cm$^{-1}$ from the expected peak frequency, and the peak was fitted with a Lorentzian line shape.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.2c01250.

AFM and PL measurements of the heterobilayers described in the main text and AFM, nano-optical, and correlation analysis of a second nanobubble (PDF)

Transparent Peer Review report available (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

Otakar Frank – J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, 182 23 Prague, Czech Republic; orcid.org/0000-0002-9661-6250; Email: otakar.frank@jh-inst.cas.cz

Patrick Z. El-Khoury – Physical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington
Single-Layer MoS2 Transistors.  

490  

Effect in MoS2 Transistors.  

REFERENCES  

The authors declare no competing financial interest. The data that support the findings of this study are available from the corresponding authors upon reasonable request.  

ACKNOWLEDGMENTS  

A.R. and M.V. acknowledge the support of the Czech Science Foundation (Project 20-11802). P.Z.E. acknowledges support from the Laboratory Directed Research and Development Program through the support of the Czech Science Foundation (Project 20-04408S). O.F. acknowledges the support of the Czech Science Foundation (Project 20-08633X). P.Z.E. acknowledges support from the Laboratory Directed Research and Development Program through the Chemical Dynamics Initiative at Pacific Northwest National Laboratory.  

REFERENCES  

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

(2) 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.  

(3) Mak, K. F.; McGill, K. L.; Park, J.; McEuen, P. L. The Valley Hall Effect in MoS2 Transistors. Science 2014, 344, 1489–1492.  

(4) Zhang, Y. J.; Oka, T.; Suzuki, R.; Ye, J. T.; Iwasa, Y. Electrically Switchable Chiral Light-Emitting Transistor. Science 2014, 344, 725–728.  

(5) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-Layer MoS2 Transistors. Nat. Nanotechnol. 2011, 6, 147–150.  

(6) Miao, J.; Liu, X.; Jo, K.; He, K.; Saxena, R.; Song, B.; Zhang, H.; He, J.; Han, M.-G.; Hu, W.; et al. Gate-Tunable Semiconductor Heterojunctions from 2D/3D van der Waals Interfaces. Nano Lett. 2020, 20, 2907–2915.  

(7) Jo, K.; Kumar, P.; Orr, J.; Anantharaman, S. B.; Miao, J. S.; Motala, M. J.; Bandypadhyay, A.; Kisslinger, K.; Muratore, C.; Shenoy, V. B.; et al. Direct Optoelectronic Imaging of 2D Semiconductor-3D Metal Buried Interfaces. ACS Nano 2021, 15, 5618–5630.  

(8) Moore, D.; Jo, K.; Nguyen, C.; Lou, J.; Muratore, C.; Jariwala, D.; Glavin, N. R. Uncovering topographically hidden features in 2D MoSe2 with correlated potential and optical nanoprobe. npj 2D Mater. Appl. 2020, 4, No. 44.  

(9) Zhang, X.; Qiao, X.-F.; Shi, W.; Wu, J.-B.; Jiang, D.-S.; Tan, P.-H. Phonon and Raman Scattering of Two-Dimensional Transition Metal Dichalcogenides from Monolayer, Multilayer to Bulk Material. Chem. Soc. Rev. 2015, 44, 2757–2785.  

(10) Liang, L.; Zhang, J.; Sumpter, B. G.; Tan, Q.-H.; Tan, P.-H.; Muenier, V. Low-Frequency Shear and Layer-Breathing Modes in Raman Scattering of Two-Dimensional Materials. ACS Nano 2017, 11, 11777–11802.  

(11) Gabel, M.; El-Khoury, P. Z.; Gu, Y. Imaging Charged Exciton Localization in van der Waals WS2/MoSe2 Heterobilayers. J. Phys. Chem. Lett. 2021, 12, 10589–10594.  

(12) Albagami, A.; Ambardar, S.; Hrim, H.; Sahoo, P. K.; Emirov, Y.; Gutierrez, H. R.; Voronine, D. V. Tip-Enhanced Photoluminescence of Freestanding Lateral Heterobubbles. ACS Appl. Mater. Interfaces 2022, 14, 11006–11015.  

(13) Garrity, O.; Rodriguez, A.; Mueller, N. S.; Frank, O.; Kusch, P. Probing the Local Dielectric Function of WS2 on an Au Substrate by Near Field Optical Microscopy Operating in the Visible Spectral Range. Appl. Surf. Sci. 2022, 574, 151672.  

(14) Garg, S.; Fix, J. P.; Kravay, A. V.; Flanery, C.; Col Grove, M.; Sulkane, A. R.; Wang, M.; Liu, G.-Y.; Borys, N. J.; Kung, P. Nanoscale Raman Characterization of a 2D Semiconductor Lateral Heterostructure Interface. ACS Nano 2022, 16, 340–350.  

(15) Kravay, A.; Chen, P.; Terrones, H.; Duan, X.; Zhang, Z.; Duan, X. Importance of Multiple Excitation Wavelengths for TERS Characterization of TMDCs and Their Vertical Heterostructures. J. Phys. Chem. C 2022, 126, 5218–5223.  

(16) Zheng, Q.; Saidi, W. A.; Xie, Y.; Lan, Z.; Prezhdo, O. V.; Petek, H.; Zhao, J. Phonon-Assisted Ultrafast Charge Transfer at van der Waals Heterostructure Interface. Nano Lett. 2017, 17, 6435–6442.  

(17) Jin, C.; Regan, E. C.; Yan, A.; Iqbal Bakti Utama, M.; Wang, D.; Zhao, S.; Qin, Y.; Yang, S.; Zheng, Z.; Shi, S.; et al. Observation of Moiré Excitons in WS2/WS2 Heterostructure Superlattices. Nature 2019, 567, 76–80.  

(18) Kang, J.; Tongay, S.; Zhou, J.; Li, J.; Wu, J. Band Offsets and Heterostructures of Two-Dimensional Semiconductors. Appl. Phys. Lett. 2013, 102, 012111.  

(19) Zhu, X.; Monahan, N. R.; Gong, Z.; Zhu, H.; Williams, K. W.; Nelson, C. A. Charge Transfer Excitons at van der Waals Interfaces. J. Am. Chem. Soc. 2015, 137, 8313–8320.  

(20) Huang, S.; Ling, X.; Liang, L.; Kong, J.; Terrones, H.; Meunier, Y.; Dresselhaus, M. S. Probing the Interlayer Coupling of Twisted Bilayer MoS2 Using Photoluminescence Spectroscopy. Nano Lett. 2014, 14, 5500–5508.  

(21) Liu, K.; Zhang, L.; Cao, T.; Jin, C.; Qiu, D.; Zhou, Q.; Zetli, A.; Yang, P.; Louie, S. G.; Wang, F. Evolution of Interlayer Coupling in Twisted Molybdenum Disilicide Bilayers. Nat. Commun. 2014, 5, 4966.  

(22) Zhao, W.; Regan, E. C.; Wang, D.; Jin, C.; Hsieh, S.; Wang, Z.; Wang, J.; Wang, Z.; Yumigeta, K.; Blei, M.; et al. Dynamic Tuning of Moiré Excitons in a WSe2/WS2 Heterostructure via Mechanical Deformation. Nano Lett. 2021, 21, 8910–8916.  

(23) Darlington, T. P.; Carmesian, C.; Florian, M.; Yanev, E.; Ajayi, O.; Ardelean, J.; Rhodes, D. A.; Ghiotto, A.; Krayev, A.; Flanery, C.; Colgrove, M.; et al. Imaging Strain-Localized Excitons in Nanoscale Bubbles of Monolayer WSe2 at Room Temperature. Nat. Nanotechnol. 2020, 15, 854–860.  

(24) Darlington, T. P.; Kravay, A.; Venkatesh, V.; Saxena, R.; Kysar, J. W.; Borys, N. J.; Jariwala, D.; Schuck, P. J. Facile and Quantitative Estimation of Strain in Nanobubbles with Arbitrary Symmetry in 2D Semiconductors Verified using Hyperspectral Nano-Optical Imaging. J. Chem. Phys. 2020, 153, 024702.  

(25) Rodriguez, A.; Kalbė, M.; Frank, O. Strong Localization Effects in the Photoluminescence of Transition Metal Dichalcogenide Heterobilayers. 2D Mater. 2021, 8, 025028.  

(26) Wang, K.; Huang, B.; Tian, M.; Ceballos, F.; Lin, M.-W.; Mahjouri-Samani, M.; Boulesbaa, A.; Puretzky, A. A.; Rouleau, C. M.; Yoon, M.; et al. Interlayer Coupling in Twisted WSe2/WS2 Bilayer Heterostructures Revealed by Optical Spectroscopy. ACS Nano 2020, 10, 6612–6622.  

(27) Shi, J.; Li, Y.; Zhang, Z.; Feng, W.; Wang, Q.; Ren, S.; Zhang, J.; Du, W.; Wu, X.; Su, X.; et al. Twisted-Angle-Dependent Optical Behaviors of Intralayer Excitons and Triions in WS2/WSe2 Heterostructure. ACS Photonics 2019, 6, 3082–3091.  

(28) Castellanos-Gomez, A.; Buscema, M.; Molenar, R.; Singh, V.; Janssen, L.; van der Zant, H. S. J.; Steele, G. A. Deterministic Transfer
of Two-Dimensional Materials by All-Dry Viscoelastic Stamping. 2D Mater. 2014, 1, 011002.

(29) Khestanova, E.; Guinea, F.; Fumagalli, L.; Geim, A. K.; Grigorieva, I. V. Universal shape and pressure inside bubbles appearing in van der Waals heterostructures. Nat. Commun. 2016, 7, 12587.

(30) Lui, C. H.; Ye, Z.; Ji, C.; Chiu, K.-C.; Chou, C.-T.; Andersen, T. I.; Means-Shively, C.; Anderson, H.; Wu, J.-M.; Kidd, T.; et al. Observation of Interlayer Phonon Modes in van der Waals Heterostructures. Phys. Rev. B 2015, 91, 165403.

(31) Noda, I.; Ozaki, Y. Two-Dimensional Correlation Spectroscopy: Applications in Vibrational and Optical Spectroscopy. John Wiley & Sons, 2004; p 310.

(32) El-Khoury, P. Z.; Hess, W. P. Vibronic Raman Scattering at the Quantum Limit of Plasmons. Nano Lett. 2014, 14, 4114–4118.

(33) Zeng, H.; Liu, G.-B.; Dai, J.; Yan, Y.; Zhu, B.; He, R.; Xie, L.; Xu, S.; Chen, X.; Yao, W.; et al. Optical Signature of Symmetry Variations and Spin-Valley Coupling in Atomically Thin Tungsten Dichalcogenides. Sci. Rep. 2013, 3, 1608.

(34) Cao, L.; Zhong, J.; Yu, J.; Zeng, C.; Ding, J.; Cong, C.; Yue, X.; Liu, Z.; Liu, Y. Valley-Polarized Local Excitons in WSe2/WS2 Vertical Heterostructures. Opt. Express 2020, 28, 22135–22143.