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Understanding transition metal dichalcogenide absorption line widths in electron energy loss spectroscopy

Fuhui SHAO[1], Steffi Y. Woo[1], Nianjheng Wu[2], Andrew J. Mayne[2], Robert Schneider[3], Steffen Michaelis[3], Ashish Arora[3], Benjamin Carey[3], Johann Preuß[3], Rudolf Bratschitsch[3] and Luiz H. G. Tizei[4]

[1]Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, United States, [2]Université Paris-Saclay, Institut des Sciences Moléculaires d'Orsay, United States, [3]Institute of Physics and Center for Nanotechnology, University of Münster, Germany, [4]Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, 91405, Orsay, France, France

Two-dimensional transition metal dichalcogenides (TMDs) have attracted great excitement for potential applications in optoelectronic and valleytronic devices; however, localized states in these low dimensional materials are not completely understood. Specifically, the impact of monolayer corrugation and roughness over spatial distances of tens of nanometers scale has an impact on the optical properties and its role of absorption linewidths increase is not fully characterized. In graphene,[1] it has been observed that h-BN encapsulation reduces the monolayer roughness from 114 ± 1 to 12 ± 5 pm,[2] with a typical lateral roughness estimated to be in the tens of nanometers. A direct spatial correlation of these corrugations to their effect on the optical properties of monolayers has not yet been demonstrated.

An ideal technique to map this change is electron energy loss spectroscopy (EELS), which has been used to map excitons in TMDs monolayers [3] with a spatial resolution approaching ten nanometers. Typical exciton linewidths in ~micrometer-wide suspended monolayers are above 50 meV, both at 150 and 300 K. [3,4] This is considerably larger than purely optical measurements at similar temperatures for monolayer on substrates.[5] Encapsulated TMDs monolayers show indeed considerably sharper EELS absorption lines, of the order of 20 meV (Figure 1), with spectra comparable to extinction spectra.[6] Is the layer corrugation alone responsible for this line width increase, as these experiments indicate, or are other effects playing a role?

Here we experimentally probed the relation between the line width of the exactions absorption lines and the corrugation in freestanding WS_2 monolayers and WS_2 monolayers supported on a thin h-BN using EELS and electron diffraction in a scanning transmission electron microscope (STEM). Experiments were performed on the ChromaTEM microscope, a modified Nion HERMES 200 equipped with an electron monochromator that allows energy spreads down to below 10 meV, with samples at 150 K. The electron beam parameters were: 60 keV energy and 1mrad convergence half-angle. The EELS spectrometer dispersion was 3.3 meV/pixel EELS. To reveal the effect of corrugation on the monolayers, electron diffraction patterns were acquired with the sample tilted 470 mrad with respect to the electron beam, as demonstrated elsewhere for graphene [1,2].

As seen in Figure 1(a), the peaks identified as A, B, C, and D excitons are considerably sharper on the monolayer region which is supported by h-BN (red), while those of the freestanding are extremely broad and merging (green). These two measurements were performed on different regions of the same WS_2 monolayer, separated by a few hundred nanometers.

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Diffraction patterns obtained on these two regions (Figure 1(b-c)), with the sample tilted with respect to the incident electron direction, show a marked difference. For the freestanding monolayer, most of the diffraction spots get larger and fuzzier as a function of their magnitude (for example, those marked by green circles in Figure 1(b)). These spots with the sample orthogonal to the beam propagation direction are sharp (not shown). For the supported monolayer region, the same diffraction spots (marked by red circles in Figure 1(c)) are unchanged between the tilted and un-tilted configurations. In the diffraction pattern of the supported sample, extra diffraction spots due to the h-BN layer are seen. As the lattice parameters of h-BN and WS_2 are different, the two sets of spots are distinguishable. Finally, the diffraction spots along the sample tilt axis (two of them are marked by green squares in Figure 1 (b)) are not broadened in the freestanding layer, as observed for rough graphene [1,2].

In this contribution, we will discuss the structural differences between freestanding and h-BN supported monolayers and the possible impact on the observed optical exciton line width.

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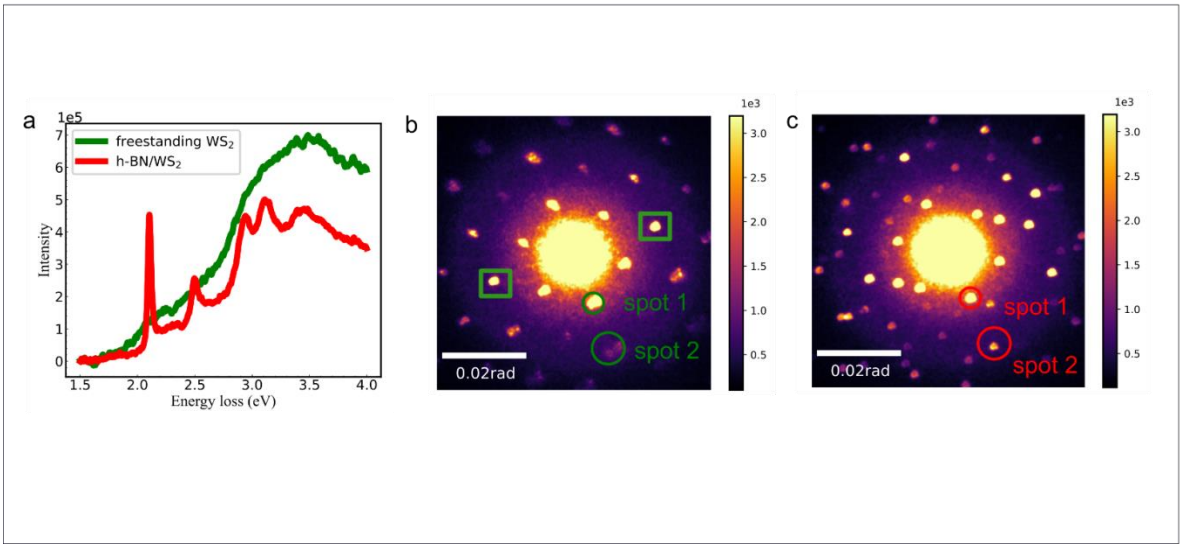

Figure 1. (a) Monolayer WS2 EELS absorption spectrum of a freestanding (green) and a h-BN support (red) region of the same spectrum. (b) and (c) Diffraction patterns of the two different zones where the spectra in (a) were measured with the sample tilted to 470 mrad with respect to the electron beam propagation direction. The circles in (b-c) mark spots which get broader as a function of the reciprocal space vector magnitude. The spots marked by squares are positions close to the rotation axis of the sample and are not considerably broadened.

References

[1] Meyer, J. C., Geim, A. K., Katsnelson, M. I., Novoselov, K. S., Booth, T. J., & Roth, S. (2007). The structure of suspended graphene sheets. *Nature*, 446(7131), 60–63.

https://doi.org/10.1017/S1431927621004426 Published online by Cambridge University Press

[2] Thomsen, J. D., Gunst, T., Gregersen, S. S., Gammelgaard, L., Jessen, B. S., et al. (2000). Suppression of intrinsic roughness in encapsulated graphene. *Physical Review B*, 96(1), 014101.
[3] Tizei, L. H. G., Lin, Y.-C., Mukai, M., Sawada, H., Lu, A.-Y., et al. (2015). Exciton Mapping at Subwavelength Scales in Two-Dimensional Materials. *Physical Review Letters*, 114(10), ,107601.
[4] Gogoi, P. K., Lin, Y.-C., Senga, R., Komsa, H.-P., Wong, S. L., et al. (2019). Layer Rotation-Angle-Dependent Excitonic Absorption in Van der Waals Heterostructures Revealed by Electron Energy Loss Spectroscopy. *ACS Nano.* 13 (8), 9541-9550.
[5] Arora, A., Wessling, N. K., Deilmann, T., Reichenauer, T., Steeger, P., et al. (2020). Dark trions govern the temperature-dependent optical absorption and emission of doped atomically thin semiconductors. *Physical Review B*, 101(24), 241413.
[6] Bonnet, N., Lee, H. Y., Shao F., Steffi Y. Woo, Blazit, J. D., et al. (2021). Nanoscale modification of WS_2 trion emission by its local electromagnetic environment. ArXiv:2102.06140.

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