Direct optical-structure correlation in atomically thin dichalcogenides and heterostructures

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ABSTRACT

Atomically thin transition metal dichalcogenides (TMDs) have distinct opto-electronic properties including enhanced luminescence and high on-off current ratios, which can be further modulated by making more complex TMD heterostructures. However, resolution limits of conventional optical methods do not allow for direct nanoscale optical-structural correlation measurements in these materials, particularly of buried interfaces in TMD heterostructures. Here we use, for the first time, electron beam induced cathodoluminescence in a scanning transmission electron microscope (CL-STEM) to measure optical properties of monolayer TMDs (WS₂, MoS₂ and WS₄Se alloy) encapsulated between layers of hBN. We observe dark areas resulting from localized (~ 100 nm) imperfect interfaces and monolayer folding, which shows that the intimate contact between layers in this application-relevant heterostructure is required for proper inter layer coupling. We also realize a suitable imaging method that minimizes electron-beam induced changes and provides measurement of intrinsic properties. To overcome the limitation of small electron interaction volume in TMD monolayer (and hence low photon yield), we find that encapsulation of TMD monolayers with hBN and subsequent annealing is important. CL-STEM offers to be a powerful method to directly measure structure-optical correspondence in lateral or vertical heterostructures and alloys.

KEYWORDS
cathodoluminescence, two-dimensional (2D) materials, transition metal dichalcogenides, interfaces, heterostructures

Transition metal dichalcogenides (TMDs) in the monolayer limit show unique optical properties including enhanced photoluminescence (PL) and spin-valley coupling [1, 2]. The fundamental optical transition is excitonic (Coulomb bound electron-hole pair), which persists at room temperatures as a consequence of large ~ 200–400 meV binding energies [3, 4]. Functionality beyond monolayers can be enhanced when using mixed (alloys) or separated (lateral or vertical heterostructures) multi-phase TMDs [5, 6]. These multi-phase materials have a wide range of applications including visible light photodetection, photovoltaics, and optical memories [7–9]. Multi-phase materials have been synthesized as well as mechanically stacked, with the interface quality and dielectric environment emerging as important characteristics to control layer coupling and opto-electronic properties [5, 10, 11].

Encapsulation between layers of a dielectric has shown to be important in measuring and controlling intrinsic opto-electronic properties of TMDs and other two-dimensional (2D) materials [12, 13]. Using this approach, enhanced opto-electronic properties such as reduced substrate doping, higher carrier mobilities enabling observation of quantum phenomena, and line-width narrowing have been observed [10, 14, 15]. Further, intrinsic coupling behavior and improvements in opto-electronic properties are observed when layers of a multi-phase van der Waals (vdW) material are in intimate contact. However, effects of the interface properties in these stacked structures have only been indirectly probed. For example, lower transistor mobility or lower inter-layer coupling have been attributed to imperfect interfaces [11, 16], but these earlier works are either non-local measurements (electrical) or they suffer from insufficient spatial resolution (optical). Thus, only limited information on effect of nanoscale inhomogeneities on opto-electronic properties has been uncovered for vdW heterostructures, with no direct optical-structure correlation.

Transmission electron microscopy (TEM) has been used extensively to investigate structure of multi-phase TMDs occurring naturally or grown by synthetic processes [12, 17]. Limited cathodoluminescence (CL) measurements using scanning electron microscopy (SEM) have provided interesting insights into luminescence of layered materials changes due to sulfur vacancies, encapsulation with dielectric layers, and coupling with other materials [18–20]. However, all of these measurements have relied on SEM, which offers limited spatial resolution compared to scanning transmission electron microscopy (STEM) due to beam broadening and larger probe sizes, and limited compositional contrast due to reliance on secondary electrons (see the Electronic Supplementary Material (ESM) and Refs. [21, 22]). We and others have previously shown that by combining CL and STEM, it is possible to directly correlate structural and optical properties with nanoscale resolution in a range of nanostructured materials [21, 23–26]. CL-STEM offers significantly higher spatial resolution—limited fundamentally by the probe size and carrier diffusion lengths—compared to other optical techniques. Thus far, CL-STEM measurements on layered...
materials have only been performed on thick few-layer samples [27, 28], but it remains unclear if the interaction of high-energy electrons in STEM with a monolayer material is sufficient to generate luminescence signal for quantitative CL analysis.

In this work, we demonstrate quantitative CL-STEM on mechanically exfoliated monolayers of TMDs enabled by encapsulation of a single TMD layer in hBN, which we apply to study effects of interface quality on opto-electronic properties. The hBN encapsulation enhances CL yield by increasing electron beam interaction volume, and reduces electron beam induced damage [20, 29]. We first focus on tungsten disulfide (WS₂) because of its high excitonic quantum efficiency at room temperature [30]. To demonstrate generality of our approach, we then extend it to weakly luminescent molybdenum disulfide (MoS₂), which displays only ~ 1% quantum efficiency at room temperature [30], as well as a representative alloy crystal (WSe₃).

We observe strong correlation between nanoscale luminescence variations and the interface quality between layers and monolayer folding. These measurements are the first direct nanoscale optical-structural characterization of an application-relevant interface (hBN-TMD-hBN), as well as a representative monolayer alloy crystals. Finally, by measuring the effect of electron dose on the optical signal, we have laid out experimental conditions that minimize electron-beam effects to enable measurements of intrinsic properties of monolayer TMDs. These measurements show that CL-STEM is an important tool for characterizing TMDs and other atomically thin semiconductors, as well as application-relevant heterostructures.

To demonstrate feasibility of CL-STEM studies on single layer TMDs, we first started with exfoliated single layers of WS₂. Details of the experimental procedure are provided in the ESM; in short, the active material, monolayer WS₂, was first exfoliated from bulk crystals using the well-established scotch-tape method [1]. It was then sandwiched between two layers of hBN and this combined layered structure is henceforth referred to as the heterostructure. A modified dry transfer method was used to assemble the heterostructure on silicon dioxide/silicon, followed by annealing in an inert argon environment at 200 °C for ~ 8 h [16]. The thickness of each hBN layer was > 20 nm to ensure a sufficient interaction volume with the electron beam during CL measurements. The annealing process is critical to measure any CL-STEM on these samples, demonstrating the importance of a clean interface free of contaminants or trapped air. The annealing was followed by a wet transfer using polymethylmethacrylate (PMMA) on a C-flat TEM grid, followed by cleaning of polymer with acetone and isopropanol (Fig. S1 in the ESM).

White light bright field image of the heterostructure transferred to a TEM grid (Fig. 1(a)) shows contrast variations expected from thickness variations of different layers. Before stacking, thickness of each layer was first estimated using optical contrast (high reflection indicates thicker hBN and low contrast indicates thin WS₂) and confirmed using atomic force microscopy for hBN, and high PL for monolayer WS₂ (Fig. S2 in the ESM). A corresponding PL image of the heterostructure was measured using a 20× objective with green laser excitation (532 nm), and appropriate wavelength filtering to spectrally select the exciton emission (Fig. 1(b), see ESM for image acquisition details). The PL map appears mostly homogeneous, but lacks the spatial resolution to probe nanoscale features. Further, it is not possible to measure interface quality via PL spectral line-width narrowing at room temperature, since the exciton is homogeneously broadened [10, 14, 31].

To achieve direct structure–property correlation with high spatial resolution, we next simultaneously collected STEM and CL images (Fig. 1(a)). A JEOL 2100 TEM operating at an accelerating voltage of 80 kV was used to reduce knock-on damage in WS₂ [32]. STEM was operated in the dark field mode, where the contrast is a result of mass-thickness changes such that thicker (or higher atomic number) materials appear brighter. The STEM image (Fig. 1(b)) clearly shows the location of the overlapping hBN layers and the sandwiched WS₂ monolayer (Fig. S3 in the ESM for annotated STEM image). Additional smaller contrast features, discussed in detail later, are due to folds in the WS₂: monolayer or PMMA residue. CL was measured through an integrated Gatan MONOCL3+ CL system equipped with a photo-multiplier tube detector [21]. Briefly, a focused electron beam (~ 1 nm) was incident on the heterostructure, generating electron hole pairs that, due to type 1 band-gap alignment, are funneled from hBN layers into the active TMD material (inset of Fig. 2(a)). The light was sent through a spectrometer operated in the monochromatic mode to collect CL emission maps at specific wavelengths.

A representative CL spectrum is shown in the inset of Fig. 2(c) as well as Fig. S4 in the ESM, and contains response from WS₂ as well as encapsulating hBN layers. The major spectral peak in CL is still excitonic, even though the excitation is non-resonant via high energy electrons and funneled electrons from encapsulating hBN layers. To measure the WS₂ optical response, we spectrally selected the WS₂ exciton resonance (616 nm) integrated over a spectral width of ~ 3 nm. The resulting CL monochromatic image (Fig. 2(c)) shows a number of features that can be directly related to structural features in the STEM image. Specifically, a set of dark linear regions can be observed in the CL map across the monolayer, which can be directly correlated to linear folds that locally form multi-layers. Furthermore, a number of dark circular areas appear in the CL image, and we discuss these non-luminescent features in detail later.

We note that hBN layers not in direct contact with the monolayer WS₂ also display signal in the monochromatic CL image. To distinguish between these hBN and encapsulated monolayer WS₂ areas, monochromatic maps corresponding to the WS₂ exciton resonance at 616 nm as well as a non-resonant wavelength at 550 nm were taken sequentially (Figs. 2(c) and 2(d), respectively). The emission at 550 nm corresponds to a broad spectral background with contributions from partially oxidized hBN, trap states in hBN, as well as thermal radiation (centered around 400 nm) [33, 34]. On the other hand, emission at 616 nm has contributions from the same physical phenomena (which contribute to emission at 550 nm), and additionally from the comparatively narrow WS₂ exciton emission. Thus, a visual comparison of monochromatic images at 550 and 616 nm illustrates positions at which the sandwiched WS₂ monolayer ...
luminesces. To further visually isolate the WS₂ monolayer region and emphasize features due only to WS₂, in Fig. 2(e) we plot CL intensity measured at 616 nm normalized to that measured at 550 nm. To confirm the spectral response and to characterize possible spectral shifts due to inhomogeneities (strain or doping), point spectra were taken at multiple positions (inset of Fig. 2(c)). The two closely spaced positions (positions A and B) show a spectral shift ~ 10 nm, which could be related to strain or local doping; position B is supported on the TEM grid, suggesting strain-induced shift relative to position A [1, 35].

These results illustrate that emission from a single WS₂ layer can be successfully obtained using CL-STEM. We now focus on nanoscale heterogeneities in the CL images to uncover their structural and physical origin. A high magnification (50 k×) monochromatic CL image at the exciton resonance (616 nm) is shown in Fig. 3(b) along with the corresponding STEM image in Fig. 3(a). Two general types of dark features—areas with reduced or vanishing WS₂ luminescence—can be observed in Fig. 3(b) with distinct appearance and underlying cause: (1) elongated bands running from top to bottom of the figure and (2) circular regions that do not show any specific spatial arrangement. The dark bands (in CL) correspond to bright lines in the STEM image and therefore can be assigned to higher mass, i.e., few layers of WS₂ that are formed by folding of a single sheet, and consequent transition from a direct to indirect bandgap. On the other hand, dark circular areas do not show any apparent STEM contrast compared to surrounding luminescent areas, implying no thickness or compositional change. It has been shown that stacking or sandwiching of atomically thin layers can lead to formation of nanoscale “bubbles” due to localized trapped air or contaminants [36]. These are unlikely to produce

Figure 2 (a) Schematic of the CL-STEM setup. Electrons and holes are generated in thick layers of hBN by a focused electron beam, and subsequently funnel into the TMD. The electron-hole pairs recombine radiatively, and subsequent light is collected by a parabolic mirror and directed toward a CL detector. Simultaneously with the light collection via CL, STEM detector provides structural information from the same sample region. The inset illustrates the corresponding type 1 band-gap alignment. (b) STEM image of the hBN-WS₂-hBN heterostructure and (c) the corresponding monochromatic CL image obtained at WS₂ exciton resonance, 616 nm. WS₂ monolayer region is indicated by the blue dotted lines. The black dashed box in (b) is measured in Fig. 3. Inset: CL spectrum of two positions indicated by white circle (A) and yellow box (B). (d) Monochromatic CL image at 550 nm. (e) Image obtained after normalizing monochromatic data at 616 nm (exciton resonance) with data at 550 nm (broad background) to emphasize WS₂ region. Scale bar is identical for (b)–(e). All intensities are plotted on a linear scale. Maximum values in each figure were chosen to enhance contrast.

Figure 3 (a) STEM image and (b) corresponding monochromatic CL image at exciton resonance (616 nm) at 50 k× magnification. Scale bars in both cases are 1 μm. The exact measurement area is indicated in Fig. 2(b) with a black dashed box. Localized bright spots in STEM correspond to positions of earlier point spectra measurements, resulting in carbon contamination. (c) Monochromatic CL image from another encapsulated hBN-WS₂-hBN heterostructure (Sample-B) at high magnification (100 k×). Spatial resolution is measured by taking a line intensity profile along the white dashed line crossing a dark spot (attributed to an air bubble). Line profile (solid white line) of CL intensity indicates spatial resolution of ~ 100 nm. Maximum values in each figure were chosen to enhance contrast.
a significant STEM contrast, but we suggest are significant enough to reduce interlayer coupling between hBN and WS₂ and dramatically reduce CL intensity. Our results show that CL-STEM acts as a high-resolution diagnostics tool that provides information about these inhomogeneities and their role on interlayer coupling, even in the absence of any structural signature in STEM.

We next comment on the spatial resolution of CL-STEM in assessing the interlayer coupling. The high spatial resolution of the measurement is exemplified by a CL image (Fig. 3(c)) obtained at even higher magnification of 100 k× from another encapsulated hBN-WS₂-hBN heterostructure (Sample-B). To characterize the spatial resolution, we take a line intensity profile along a dark feature (attributed to air bubble), and measure a full width half maximum of ~100 nm along the dark feature. We note that the spatial resolution is likely limited by signal to noise ratio of our detection system as well as lack of smaller features in this monolayer sample [25]. Factors contributing to signal to noise ratio are background signals from CL (stray electrons hitting TEM grid, mirrors etc.), detector thermal noise and dark counts. Further increase in the signal could be achieved by using thicker layers of hBN, but this may cause degradation of the spatial resolution due to lateral diffusion of carriers within hBN before funneling into WS₂. Hence, an optimum thickness of hBN may be required, coupled with high efficiency detection. Alternatively, other encapsulating materials including higher quality hBN, plasmonic materials and scintillating sources could be explored to enhance light emission [37, 38]. After optimizing for hBN thickness and interface quality, evaluating other encapsulating materials, as well as improving detectors, measurements of atomic structure and single point defects could be explored.

In the ESM, we also discuss spatial resolution differences between CL-SEM and CL-STEM. We find that CL-STEM offers higher spatial resolution, and direct structure-optical correspondence. We note that understanding of the CL resolution also enabled us to distinguish between (multi)layer folding and termination edges, from which we show that folding has longer-range effects on the interlayer coupling (see Fig. S5 in the ESM).

After establishing CL-STEM as a method to directly visualize interlayer coupling in WS₂ as a model system, we now extend the technique to other 2D materials, specifically monolayer MoS₂ and an alloy monolayer WS₂-Se₁.₂. Remarkably, using our approach we could measure significant CL even for a low quantum efficiency material MoS₂. Like in the case of WS₂, CL maps of hBN-sandwiched monolayer MoS₂ shows heterogeneous features (Fig. 4(a)). Dark features in CL images can be directly correlated to bright features in STEM (Fig. 4(b)), which are most likely related to more significant interlayer contamination. Monolayer WS₂Se alloy crystals show qualitatively similar heterogeneities in CL-STEM. The STEM image (Fig. 4(d)) shows increased intensity at areas which are dark in the corresponding CL image (Fig. 4(c)). These areas are again attributed to larger contamination. We also measured point spectra at different positions in the alloy crystal, and do not observe any significant spectral shifts (not shown here). Thus, these alloy crystals are not observed to have gross compositional fluctuations at the resolution of our measurement. Together, these results show that CL-STEM measurements enable evaluation of the interface quality in a range of TMDs, and are thus general in nature.

Finally, to investigate the possible role of the electron beam on CL—and to ascertain that CL inhomogeneities discussed above are not caused by possible structural damage by electron beam—we characterized evolution of the CL signal as a function of the electron beam exposure. When electron beam is focused on a specific position, e.g. to obtain point CL spectra, we observed reduction of ~50% in CL intensity when comparing subsequent point spectra acquired for 70 s (1st and 2nd scan in Fig. 5(a)), and reduction by 5%–10% in subsequent scans (compare 7th scan with 2nd scan). At the accelerating voltages used in the experiment (80 keV), direct knock-on damage is reduced, but not completely prevented [39]. The sulfur vacancy damage threshold for encapsulated samples is expected to be higher compared to a bare monolayer as the encapsulation provides a protective barrier [29], and prevents escape of the removed sulfur into the vacuum [40]. The self-limiting electron beam induced damage is suggested to be a result of direct knock-on at a small area, whereas the luminescence is expected to result from a larger area due to lateral diffusion of carriers in surrounding hBN layers. Although damage can occur in surrounding hBN layers [41], it is expected to be limited due to their thickness.

In contrast to the point spectra, monochromatic mapping requires significantly shorter acquisition time of 1.4 ms/pixel with the same current density (50 k× lower dose), for which no observable change in the intensity or in the spatial extent of the luminescence was observed (Sample-B, Figs. 5(b) and 5(c) and the Fig. S6 in the ESM). Therefore, we conclude that the CL inhomogeneities measured in regions in which no significant e-beam dwelling was applied (Figs. 2–4) are intrinsic to the heterostructure, and not electron-beam induced artifacts. Thus, measuring monochromatic images offers a suitable way to characterize nanoscale areas without causing damage.

In conclusion, we have utilized CL-STEM to measure nanoscale heterogeneities in monolayer TMDs (WS₂, MoS₂, WS₂Se) encapsulated in dielectric layers (hBN). We directly measured the effect of an imperfect interface—resulting from contaminants and layer folding—on the luminescence, resulting in the first direct nanoscale optical-structural characterization of the interface.

**Figure 4** (a) Monochromatic CL image (at exciton resonance, 646 nm) and (b) corresponding STEM image of a sandwiched MoS₂ monolayer. (c) Monochromatic CL image (at exciton resonance, 720 nm nm) and (d) corresponding STEM image of a sandwiched WS₂Se monolayer. Dark CL regions for both samples are indicated by dashed lines. Maximum values in each figure were chosen to enhance contrast.
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**Electronic Supplementary Material:** Supplementary material (CL-STEM experimental conditions, discussion on electron-beam monochromatic images, effect of encapsulation and annealing on CL, differences between CL-SEM and CL-STEM. The files are available free of charge) is available in the online version of this manuscript at this article at https://doi.org/10.1007/s12274-019-2601-7.

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**Figure 5** (a) Sequential (1st, 2nd, and 7th) point spectra of WS2 each acquired for 70 s, illustrating beam-induced reduction of CL intensity. Comparison of monochromatic images for (b) first and (c) subsequent data collection on encapsulated WS2 sample-B. Maximum values in each figure were chosen to enhance contrast.

As these nanoscale inhomogeneities are a general feature of single phase and multi-phase heterostructures, it is important to understand their role for enabling higher quality optoelectronic devices. Further, we observed that even excitation by high energy electrons (80 kV) in a TEM primarily results in ground state exciton CL, allowing direct comparison with PL measurements, but with higher spatial resolution. We quantified the effect of electron beam irradiation on the CL magnitude, and demonstrated a suitable imaging condition with reduced damage to the sample. These first CL-STEM measurements on monolayer TMDs should pave the way forward for further direct nanoscale structure-optical measurements in application relevant multi-phase materials. By enhancing signal to noise by using thicker hBN and improved detectors, direct defect mapping may be possible in future measurements.
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