Unveiling nanoscale optical and structural properties of TMD monolayers using combined electron spectroscopies

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Transition metal dichalcogenide (TMD) semiconductors with the form MX₂ (M a transition metal, W or Mo, and X a chalcogen atom, S, Se or Te) with the 2H phase have an indirect bandgap when in bulk, and a direct bandgap when exfoliated down to a monolayer, leading to bright photoluminescence (PL) [1]. These monolayers display attractive properties, such as stable quantum emission [2] or valley-polarization of excitonic transitions [3]. The optical response of these monolayer is determined by excitons, trions, and defected-related transition lines [4].

A major challenge to understanding and optimizing these monolayers, their heterostructures, and possible future devices is the characterization of their optical properties down to the nanometer scale and the correlation of these to their structure and chemistry. Correlated TEM and optical experiments can lead to some understanding of the influence of chemical or structural modifications on optical properties. However, a direct correlation at the nanoscale would be more straightforward. Electron spectroscopy techniques allow for the measurement of optical quantities at high spatial resolution: emission from cathodoluminescence (CL), a nanoscale counterpart of PL [5] and absorption from low-loss electron energy loss spectroscopy (EELS) [6].

In this contribution, the relation between optical, chemical, and structural properties of a h-BN encapsulated monolayer of WS₂, with a spatial resolution down to the tens of nanometer scale is discussed. In particular, we have observed spatial variations of the emission of the A exciton (Xₐ) [7], the charged A exciton (trion: Xₐ⁻), and the lower energy localized excitons (L). These spatial variations are linked to chemical changes at the surface of the WS₂ monolayers, leading to changes in the Xₐ to X emission intensity ratio.

The experiments were performed in a modified NION Hermes 200 equipped with a monochromator and a Mönch CL system from Attolight [8] (Fig. 1c). CL measurements were done at 60 keV, with an electron beam with a 10 mrad convergence semi-angle, and the sample kept at 150 K using a liquid-nitrogen cooled sample holder. Low-loss EELS was measured with an electron beam with a 10-20 meV energy width and the collection semi-angle of the spectrometer was set to 25 mrad. Core-loss EELS and diffraction experiments were done in a NION UltraSTEM 200, at 100 keV, with an electron beam of 30 mrad convergence semi-angle for chemical mapping, and the sample was kept at room temperature.

Fig. 1a represents a scheme of the excitations leading to light emission upon electron-beam excitation of WS₂: Xₐ, X₁, and L (described before). The h-BN encapsulation of the monolayer is crucial to obtain sufficient cathodoluminescence signals [9]. The sample design allows for atomically-resolved imaging, even with the encapsulation (inset of Fig. 1a). In absorption, several excitons (Xₐ, X₈ and X₇) are seen (Fig. 1b). Only the Xₐ is optically active, leading to light emission (a CL spectrum is shown on the inset of Fig. 1b). The energy difference between the absorption and emission of Xₐ, called Stokes shift (SS), can be locally measured with combined EELS and CL (Fig. 1c). The variations in SS can give insights on the origin of Xₐ energy shifts [10].

Fig. 2 shows an example of the nanometer-scale variations of the Xₐ and the X observed in the h-BN encapsulated WS₂, as well as the localized, lower energy, L emission lines. The emission (Fig. 2b, c, d) can be directly compared
to the high angle annular dark field (HAADF) image (Fig. 2a). One sees that the $X^-$ emission maxima are related to regions of reduced intensity in the HAADF images. This HAADF intensity reduction is present in several places of the sample, and displays a similar behavior: the $X_A$ emission is mostly homogeneous across the field of view, and tends to show a dip in intensity where the $X^-$ and/or L emissions are brighter. The $X^-$ emission is localized on the darker spots visible in HAADF, while the L lines are very localized in space, but do not match directly the intensity changes observed in the HAADF image.

Hence, from the correlation between nanoscale CL and HAADF imaging, one can already question the origin of the emission variation: L and $X^-$ are not present at the same locations, which points towards possibly different production mechanisms. To understand the nature of the intensity changes seen in HAADF we have used core-loss EELS elemental mapping on the regions of higher intensity. They are rich in C, O and Si [11], which are probably contaminants from the sample preparation. The HAADF intensity variation matches well the chemical map of these contaminants, indicating that the $X^-$ localization is probably linked to the absence of the residues, which changes the local dielectric environment. The modification of the local dielectric environment can increase the local density of free electrons, favoring the formation of $X^-$ rather than excitons.

In conclusion, the CL/EELS characterization of WS$_2$ encapsulated monolayer together with high-resolution imaging and chemical mapping have shown localization effects of the negatively-charged exciton, $X^-$, that were caused by dielectric environment changes. These variations are not correlated to strain. The observation of localized light emitters paves the way for additional experiments, coupled to light intensity-interferometry, to determine the microscopic structure behind quantum emitters in TMD monolayer [5, 11, 12].

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**Figure 1.** Fig. 1: Scheme of the experiment: (a) Scheme of the WS$_2$ monolayer (W atoms in grey, S atoms in yellow) encapsulated in h-BN (purple). The different types of optical transitions observed in the experiments, $X_A$, $X^-$ and L, when the heterostructure is excited by the electron beam are also sketched. The inset shows an atomically-
resolved HAADF image of an edge in the encapsulated WS2 monolayer (the scale bar is 2 nm). (b) Typical EELS spectrum (orange curve) with the peaks labeled associated to different excitonic transitions excitons (XA, XB, XC). A typical CL emission is shown on the inset (purple curve), where both XA and X- are visible. The energy difference between the absorption (EELS) and emission (CL) of XA is the Stokes shift (SS). (c) Scheme of the STEM microscope used for the experiment. The monochromator allows for high energy resolution low-loss EELS absorption measurements. Light emitted from the sample upon electron excitations (CL) is collected by a parabolic mirror (NA= 0.5) and directed to an optical spectrometer. On the same setup diffraction patterns and images at different collection angles can also be measured in parallel to spectroscopic information. The measurements were performed with the sample kept at 150K using a liquid nitrogen cooled sample holder.

Figure 2. Fig. 2: CL measurements on a heterogeneous area of the WS2 encapsulated monolayer: (a) HAADF image of the area where the CL spectral information was acquired. The brighter areas contain C, O, and Si, which are probably present due to residues from sample preparation. (b-d) Intensity maps for the X-, XA and L transitions, respectively. The maps were integrated in around the main transitions energies: 2.012 eV for XA, 2.043 eV for X-, and 1.997 eV for L. A spatial correlation is observed between intensity maxima of X- map (b) and intensity minima in the HAADF image (a).
References