Measuring hybridisation in Van der Waals heterostructures using momentum-resolved EELS

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Background

Van der Waals heterostructures have become omnipresent in materials research today as they offer sheer endless opportunities to tune properties by stacking [1]. In a Lego-like fashion, researchers combine a range of two-dimensional (2D) materials to create ever-more complex structures. However, regarding the properties of stacked 2D materials, the question arises: do we make something new or do we have a simple sum of its parts? We are still often lacking a means to study these complex stacked materials. One particular challenge that is frequently faced is that the phenomena under investigation might lie in an energy-momentum space that is impossible to access using optical methods.

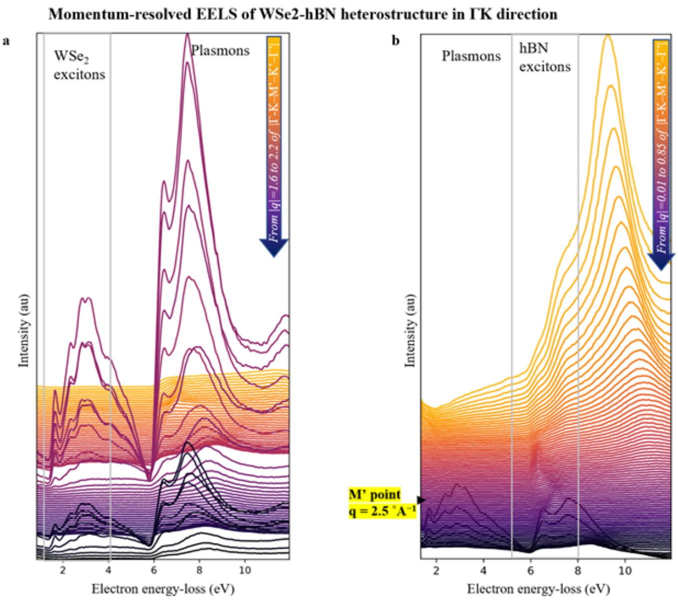
Methods

Here, we show that using modern electron microscopy (EM), the energy-momentum space that becomes available can cover several Brillouin zones (BZ) in the momentum direction and several electron-volts in the energy direction. EM therefore represents an excellent opportunity to study stacked heterostructures. We combine the resolving power of the Nion HERMES instrument with the detection capabilities of a direct detector camera (Dectris ELA) to map phenomena across the BZ. Using this approach, the behaviour of phonons, excitons and plasmons can be mapped across the entire BZ. Results were compared to time-dependent density functional theory (TD DFT). To demonstrate this technique, we present the findings from a heterostructure commonly used in nanoscience research today. Hexagonal boron nitride (hBN) is the most common encapsulant for nanoelectronics and nanodevice fabrication as it is thought to not affect the properties of the TMDCs, due to its insulating character. It is known to even enhance the excitonic intensities and to decrease the excitonic bandwidth of TMDCs [2].

Results and Conclusions

Momentum-resolved EELS (q-EELS) was employed to obtain ωq maps of hBN, WSe2 and a hBN – WSe2 heterostructure along the high symmetry directions ΓM and ΓK of the crystal structure and the results are presented here.[3] Figure 1, a shows q-EELS as acquired of the hBN – WSe2 heterostructure. The spectra are shown for steps in q= 0.0106 x |Γ-K-M’-Γ’| to cover the |q| distance from 1.6 to 2.2 of |Γ-K-M’-Γ|. This partially shows the detection challenge at hand. There is a significant difference in intensities at q=0 at Γ and Γ’ of excitonic and plasmonic peaks compared to the finite q intensities between the Γ points. Figure 1, b shows the peak evolution between the Γ points. This time the spectra of the same data set are shown for steps in q= 0.0106 x |Γ-K-M’-Γ| for |q| from 0.01 to 0.85 of |Γ-K-M’-Γ|. Both, excitons and plasmons and their hybridisation were studied using this approach. When comparing the energy-momentum dispersion of the main plasmon peaks, clear signs of hybridisation in the hBN – WSe2 heterostructure were observed when compared to the individual components of the heterostructure. The π-π* and the π- σ plasmon peaks were found to shift to energies that matched neither WSe2 nor hBN. Aside from the plasmon peaks, hybridisation in excitons was also investigated. hBN represents a particular challenge due to the presence of excitons that have a highly directional q dependence and lie at high q and high in energy. The presence of the fine structure at the M point as shown in Figure,b is originating from the hBN itself and is also found in hBN alone. The peak at the M point is thought to originate from vertical e-h transitions between the k points belonging to the ML line in the band structure.[4] This fine structure is absent in the ΓM direction. These findings are in excellent agreement with BSE calculations [4] as well as non-resonant inelastic x-ray scattering data from a synchrotron facility [5]. It shows that EM combined with modern direct detector technology can at least rival the results from x-ray facilities with the added benefit that the EM brings improved spatial resolution. Our results regarding the plasmon hybridisation also show that great care has to be taken when predicting properties of Van der Waals heterostructures.

Graphic:



Keywords:

momentum-resolved-EELS, excitons, plasmons, TMDC, hBN

Reference:

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