

Zooming in on the electronic properties of van der Waals Heterostructures

Work Description

Discoveries in materials science have gone hand-in-hand with advances in light-based microscopies and spectroscopies. Imaging experiments at synchrotron light sources have now reached a spatial resolution on the nanometer length scale, which is leading to new insights on the interplay of structure, chemical composition and function in advanced materials [1]. Nanoscale spatial resolution has also been realized in photoemission experiments employing synchrotron light to photoexcite electrons that carry information on the complete quantum mechanical energy landscape of the studied material. Such techniques play a key role for uncovering the electronic properties of emerging quantum materials, including two-dimensional (2D) van der Waals heterostructures [2].

I have contributed to the development of a new angle-resolved photoemission spectroscopy method that incorporates nanoscale spatial resolution (nanoARPES). The experimental concept is outlined in Fig. 1(a): High-brilliance synchrotron light is focused to a nanoscale spot-size on a sample using precision piezo-controlled X-ray optics (a zone-plate) and sample stages inside an ultra-high vacuum (UHV) environment. This leads to photoemission of electrons due to the photoelectric effect. An electron analyzer measures the kinetic energy and momentum of the photoelectrons emitted from a nanoscale area. By scanning the beam over the sample a real space map of the photoemission intensity as a function of energy and momentum is achieved.

Here, I will discuss experiments carried out at the Microscopic And Electronic STRucture Observatory (MAE-STRO) at the Advanced Light Source (ALS), Berkeley Lab. I used nanoARPES to investigate the electronic properties of a 2D heterostructure built from single-layer (SL) tungsten disulfide (WS_2) on hexagonal boron nitride (hBN) supported on titania (TiO_2) [3, 4]. The 2D transition metal dichalcogenides (TMDs) such as WS_2 are direct gap semiconductors with strong Coulomb interactions that result in tightly bound quasiparticles known as excitons and trions when the materials are excited by light [5]. Using a 2D insulator such as hBN in a heterostructure with WS_2 reduces the interlayer interactions and screening to such an extent that these interesting quasiparticles can be excited in the nanoARPES experiments [6].

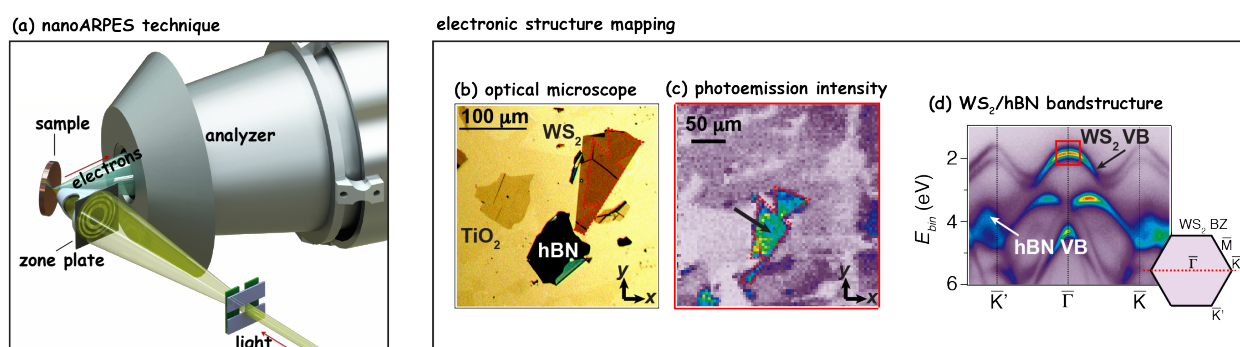


Figure 1: (a) Operating principle of a nanoARPES experiment. (b) Optical micrograph and (c) real space map of photoemission intensity from the same region of a WS_2/hBN heterostructure on TiO_2 (see red dashed outlines in both images, which mark the same feature). (d) Bandstructure of WS_2/hBN from the middle of the flake as marked by an arrow in (c). The ARPES intensity was obtained along the WS_2 high symmetry direction marked by a red dashed line on the Brillouin zone (BZ). The intensity map in (c) has been extracted from the (E, k) -region marked by a red box in (d).

Figure 1(b) presents an optical microscope image of the sample, which was made by scotch tape exfoliation of hBN on TiO₂ followed by a polymer-assisted transfer of SL WS₂ on top of both materials [3]. Pieces of SL WS₂ straddling both TiO₂ and hBN are visible in the optical micrograph upon close inspection. The nanoARPES photoemission intensity map in Fig. 1(c) provides much stronger contrasts, as the intensity is composed from the region of k -space that contains the SL WS₂ valence band (VB) maximum. This is shown via the dispersion plot in Fig. 1(d) where the red box demarcates the (E, k) -region mapped in Fig. 1(c). Such four-dimensional (4D) datasets with the (E, k, x, y) -dependent intensity permit a straightforward separation of electronic bandstructures from the distinct material combinations in the heterostructure.

At the edge of a mechanically transferred 2D flake it is possible to create one-dimensional (1D) nanoscrolls by folding the edge of the parent 2D crystal, as sketched for WS₂ on hBN in Fig. 2(a). Detailed nanoARPES scans (step-size of 75 nm) near the edges of our heterostructures indeed reveal the presence of parallel sets of 1D WS₂ nanoscrolls as shown in the photoemission intensity map in Fig. 2(b). This measurement currently holds the record for the smallest object ever imaged and measured with ARPES. It shows that the quantum mechanical electronic structure of the 1D nanoscroll is vastly different from that of the 2D crystals it originates from as seen via the comparison of the bandstructures in Figs. 2(c)-(d). The fundamental electronic band gap of the system is observed to be dramatically different in 1D due to an additional splitting of the electronic states at the $\bar{\Gamma}$ -point, which will lead to distinct optical and electrical properties at the 1D edge of the 2D crystal.

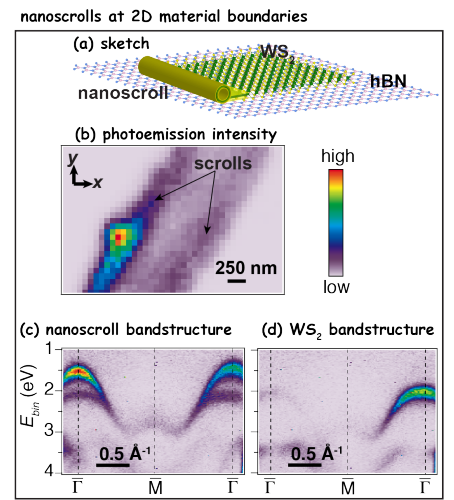


Figure 2: (a) Sketch of a nanoscroll in a WS₂/hBN heterostructure. (b) Real space map of ARPES intensity from a region with two parallel nanoscrolls. (c) Bandstructure from a nanoscroll and (d) from a central WS₂ region.

Finally, I will discuss the results of changing the charge carrier concentration in SL WS₂ by potassium deposition. The extra electrons from the potassium leads to the population of the conduction band (CB) minimum of WS₂, revealing the direct band gap. By increasing the doping the spin-orbit splitting between the two top-most valence bands increases dramatically from 430 meV to 660 meV, causing a substantial renormalization of the band gap energy. I will present our interpretation of the effects, which involves a three-particle many-body interaction between the "photohole" and the excited electron-hole pairs in the occupied CB states near the Fermi level [6]. Such a hole-hole-electron interaction is consistent with the formation of trions which have been observed in photoluminescence experiments [5] but not previously in ARPES.

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