Goldstein Scholar Award – Report

Sean M. Collins, University of Cambridge

This award provided essential support for a challenging and ambitious project and came at a time where it has played a transformative role in my career and opened a new research direction. The award was used to carry out experiments I would not have otherwise been able to pursue and it also provided support for the necessary time commitment to undergo intensive training with expert and world-leading staff at SuperSTEM to become an independent user of a leading ultrahigh resolution EELS microscope.

Organic optoelectronic materials are top candidates for next generation photovoltaics, electronics, and light emitting diodes. Organic semiconductor nanostructures such as those of perylene diimide (PDI) derivatives examined in this work exhibit exceptional exciton diffusion lengths, a key metric for charge transport in these materials. Yet measurements of the electronic structure and excitonic states at the length scale of any structural defects in these materials have only rarely been reported. Two derivatives of PDI were studied, both with 'nanobelt' morphology, and these were selected for comparison on the basis of different defect densities observed in bright field transmission electron microscopy. Using the Nion Hermes UltraSTEM 200MC at SuperSTEM, which can achieve <25 meV energy resolution (full width at half maximum of the zero loss peak) in electron energy loss spectroscopy (EELS), spatially resolved spectra were obtained on the PDI nanobelts at visible and ultraviolet energies.

Initially, conditions were identified to avoid beam-induced damage to the samples. The PDI samples were prone to damage at currents required to record sufficient signal on the detector, particularly for scans across the width of the belts. An alternative scanning strategy along the long axis of the belts (Figure 1) avoided damage accumulation during the scan and enabled recording spectra in the direction of significance for optical and charge transport in these materials. This scanning approach was implemented in both line profiles as well as in two-dimensional imaging modes, provided the latter was conducted in aloof and 'near-aloof' geometry with the final electron beam positions just penetrating the nanobelt. With these conditions, seven peaks could be identified between 1.5 and 3.5 eV, and the C-H stretching frequency could also be identified.

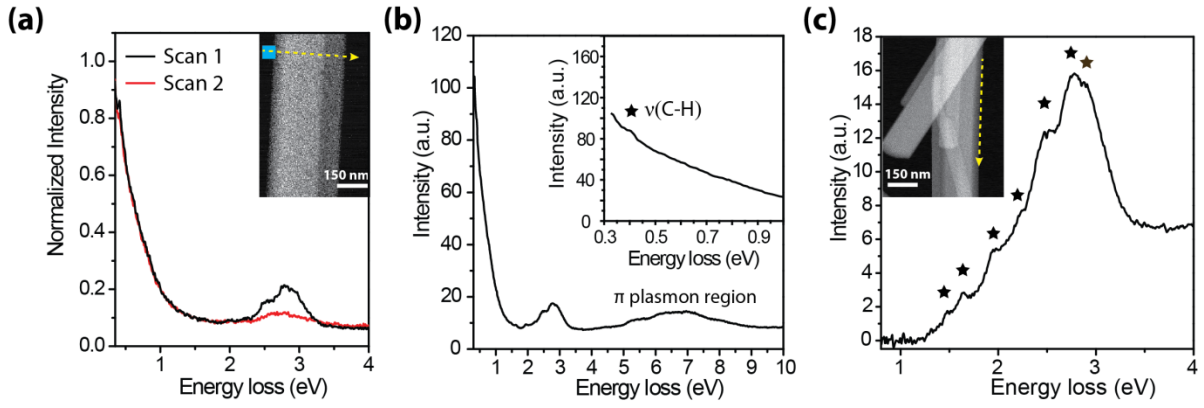

Figure 1. (a) Changes in low loss EELS observed after repeated scanning. The inset shows the total scan (dashed arrow) and the position for the spectra (square). (b)-(c) A low loss EELS sum spectrum recorded from a scan along the edge of a belt. In (c), the line scan position (inset) is shown alongside the background subtracted sum spectrum (background model: Lorentzian function with offset).

Once these conditions were identified, measurements were carried out on both PDI derivatives. To correlate monochromated low-loss EELS measurements with defects, a scanning transmission micrograph was obtained immediately after EELS spectrum imaging using a bright field detector. The diffraction contrast enabled visualization of defects (dark lines, Figure 2). The spectrum images were analyzed using independent component analysis which identified spatial features at the defect positions without. These differences could also be identified by inspection of selected area spectra from the defect and bulk regions, highlighting changes in the valence EELS intensities (Figure 2(b)). These experiments will be complemented by ongoing work using scanning electron diffraction experiments to identify the crystallography of the characteristic line defects in PDI and, ultimately, to model the atomic and electronic structure associated.

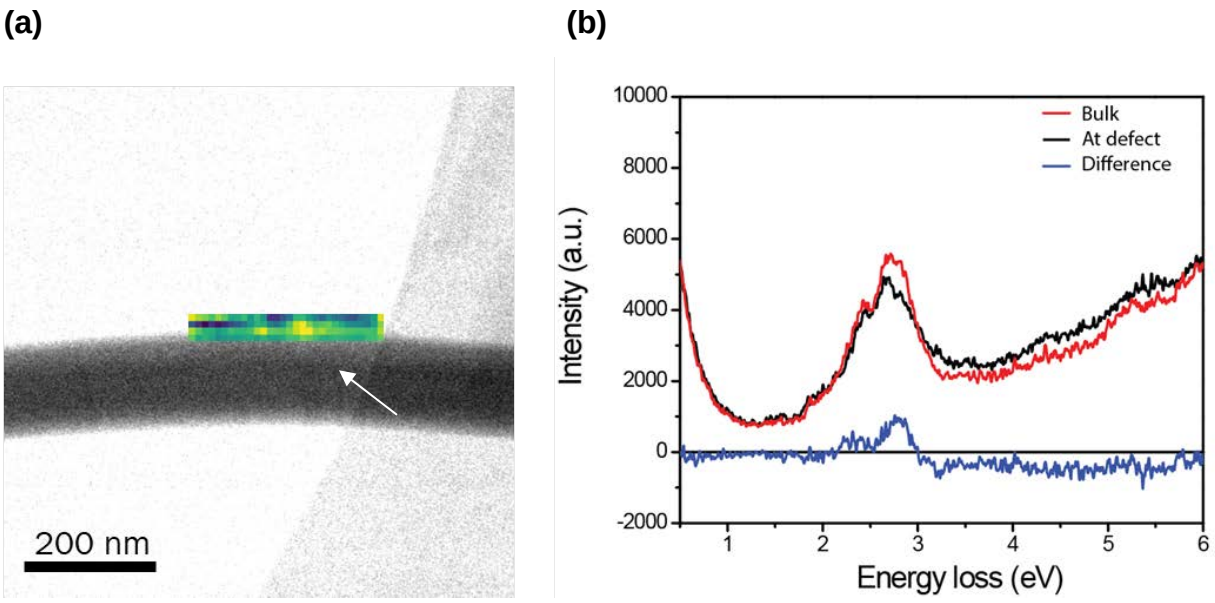

Figure 2. (a) Bright field STEM image and overlaid independent component analysis map associated with the line defects (arrow marks one of two identified in this field of view). (b) EEL spectra from the bulk and at a defect from an additional scan. The difference is plotted to highlight changes in the valence EELS at the defect.

In conjunction with this experimental work, the award was used to support training in the operation of the Nion Hermes UltraSTEM for ultrahigh resolution EELS. One-on-one training sessions with Dr. Demie Kepaptsoglou included training on sample loading, tuning of the monochromator, and alignment of the probe corrector. Over the course of an approximately three week visit, I was able to operate the microscope independently to acquire EELS at visible and UV energies as well as for vibrational spectroscopy at mid-infrared energies (<15 meV energy resolution).

The unique access to these capabilities and training made possible through the award have given me the opportunity to undertake research on a challenging materials system, and the success around these first experiments now motivates me to launch an expanded research program on organic semiconductors through cutting edge electron microscopy in my future career.