

Determining Optical Absorption Coefficients in Beam Sensitive Materials using Monochromated Electron Energy-Loss Spectroscopy

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Using electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM), it is possible to measure optoelectronic properties of materials with high spatial and spectral resolutions. In particular, low-loss spectra (energy-losses of less than 50 eV) can be used to extract the real (ϵ_1) and imaginary (ϵ_2) parts of the complex dielectric function [1] over this entire range, which encompasses ultraviolet, visible, and infrared wavelengths. Since ϵ_1 and ϵ_2 are related to the refractive index (n) and the extinction coefficient (κ), both n and κ can also be derived over this entire range with high spatial and high energy resolutions. This makes STEM-EELS a very powerful technique for probing the optoelectronic properties of materials.

However, these measurements are not straightforward in all materials. Due to the high accelerating voltages used in STEMs, the electron beam rapidly and extensively damages polymeric, organic, and biological materials, making it difficult to measure the optoelectronic properties of pure beam-sensitive materials and across interfaces of beam-sensitive materials. This is unfortunate because STEM-EELS measurements, by determination of the optoelectronic properties, could elucidate information about the local chemistry and bonding environment at such interfaces. Furthermore, as κ is directly related to the optical absorption coefficient (α), it would also be possible to extract α with high spatial resolution.

We have recently shown that it is possible to collect reliable EELS data of beam-sensitive materials utilizing a low-damage acquisition method. Additionally, we have shown that this data can be collected with high spatial resolution in addition to high energy resolution [2]. In this contribution, we take this analysis a step further and demonstrate the acquisition of the optical absorption coefficient spectra for four beam-sensitive, organic materials. These materials – poly(3-hexylthiophene) (P3HT), [6,6] phenyl-C₆₁ butyric acid methyl ester (PCBM), copper phthalocyanine (CuPc), and C₆₀ – are representative of materials commonly utilized in organic photovoltaics (OPVs). These data have been collected on two different STEMs with varying energy resolution capabilities. The absorption coefficients measured from the first, an FEI Titan³ 60-300 Image-Corrected S/TEM, are shown in Figure 1 in black, whereas the coefficients measured from the second, a Nion UltraSTEM 100 MC ‘HERMES’, are shown in green [3]. There is very good agreement between the two data sets, proving that it is possible to collect reliable spectra of α for beam-sensitive materials. This, coupled with our ability to make spatially-resolved measurements of EELS data for beam-sensitive materials systems, suggests that the optical absorption coefficient can be measured across an interface of a beam-sensitive

materials system, such as an OPV device, in an effort to investigate the optical behavior of the device near the interface [4].

References

- [1] R.F. Egerton in “Electron Energy-Loss Spectroscopy in the Electron Microscope”, (Springer, New York).
- [2] J.A. Alexander, *et al.*, *J. Mater. Chem. A* **4** (2016), p. 13636-13645.
- [3] J.A. Alexander, *et al.*, *Ultramicroscopy*, (2017), (under review).
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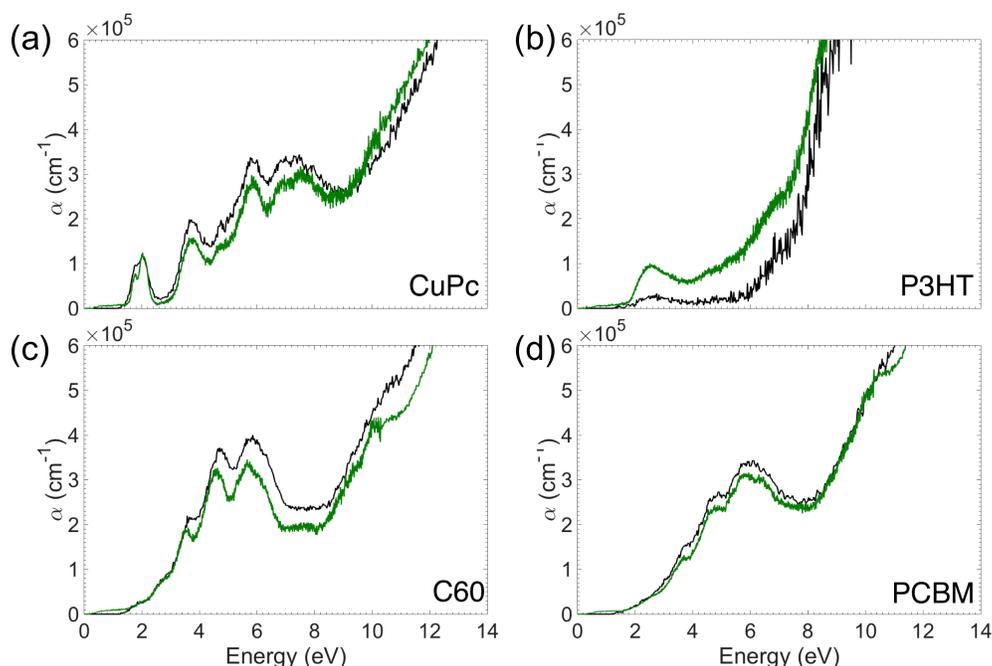


Figure 1: The optical absorption coefficient spectra determined from EELS data collected on the Nion UltraSTEM (green) and the FEI Titan³ (black) for (a) CuPc, (b) P3HT, (c) C₆₀, and (d) PCBM.