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Imaging and analysis of low atomic number materials in the STEM

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Advanced (scanning) transmission electron microscopes, (S)TEMs, can resolve individual atoms and measure atomic displacements with near picometer precision. The ability to probe in the STEM chemistry, bonding and electronic properties of materials using monochromated electron energy-loss spectroscopy (EELS) is providing important insights in inorganic functional and structural materials. Large area silicon drift detectors (SDD), or combinations of SDDs, are being utilized in X-ray energy dispersive spectroscopy (XEDS) in the STEM to obtain compositional maps with remarkable signal to noise for quantitative analysis of composition with high spatial resolution.

However, applying these methods to materials that are entirely or predominantly made up of low atomic number elements presents some significant challenges. In the study of organic and biological materials electron beam damage is always a major consideration. In organic-inorganic composites, or interfaces, in addition to differential damage rates, the challenges of samples preparation may cause significant thickness variations. Materials comprised of low Z elements can be more susceptible to electronic charging effects in some cases, and in many cases these materials are sensitive to the environment requiring specialized samples holders or transfer systems.

In our previous work on organic materials, or in hybrid organic and inorganic materials, low-contrast between phases, and electron beam sensitivity presented considerable challenges. [1] It is essential to understand the "electron budget" for each experiment; in other words, the electron dose that will lead to changes in the parameter being measured. In many cases, the budget makes use of core-loss excitations prohibitive, in part due to current detector limitation, and consequently, valence EELS (VEELS) was explored as an alternative method. While VEELS does not give direct information on composition or bonding, the low-loss spectra can be used to extract the real (ε_1) and imaginary (ε_2) parts of the complex dielectric function. 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. In Figure 1 is shown mono-STEM-EELS data from a range of beam sensitive materials relevant to organic photovoltaics to illustrate the power of this approach. The materials include organic materials commonly used in OPVs, such as C_{60}, copper phthalocyanine (CuPc), [6,6] phenyl C_{61} butyric acid methyl ester (PCBM), and poly(3-hexylthiophene) (P3HT). [1,2]

Vanadium tetracyanoethylene ($V[TCNE]_x$) is a promising magnetic material that is an alternative to soft ferrite materials, such as yttrium iron garnet (YIG), for planar microwave devices. [3] In this second example, STEM-EELS is being explored as a method to probe the structure and electronic properties of $V[TCNE]_x$ ($x{\sim}2$), an organic-based ferromagnetic semiconductor with room temperature magnetic ordering and a bandgap of 0.5 eV. In addition to the challenges of being a mixture of low Z and high Z elements and being susceptible to beam damage, this material is also air sensitive. As illustrated in Figure 2, we have developed a method to prepare a specimen and transfer into the STEM will minimal

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air exposure. Both core loss and valence loss EELS are providing new insights into the properties of this exciting material.

In the final topic I will discuss how recent improvements in detector technology combined with monochromation are showing promising signs that we may be able to revisit the use of core loss spectroscopy in low Z systems. [4] In particular, we are exploring the improved sensitivity of EELS systems retrofitted with a Gatan K2 direct electron detector for core loss spectroscopy in polymers and polymer composites to determine if it may be possible to achieve spatial resolved mapping of organic functional groups in polymers, composites and biomaterials applications. [5]

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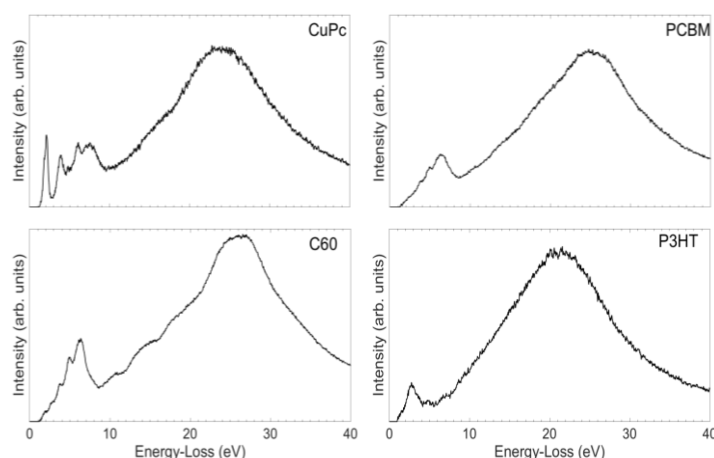

Figure 1. VEELS results for CuPc, PCBM, C_{60} and P3HT.

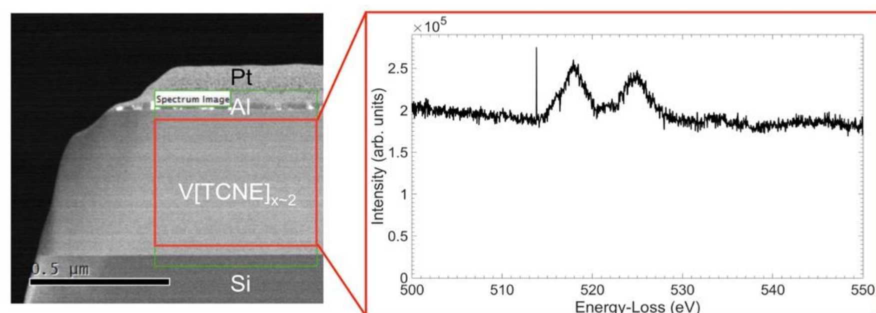

Figure 2. STEM-HAADF image and EELS spectrum of V(TCNE)x from a FIB prepared cross-section showing the V $L_{2,3}$-edge and minimal presence of intensity at the oxygen K-edge.