The Role of Simulation of Valence Electron Energy Loss Spectroscopy (EELS) for Understanding Electronic Structure and Optical Properties of Materials

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Recent years have seen an increase in the interest and application of the low-loss region (<~50 eV) of electron energy-loss spectroscopy (EELS). The spectral detail in this region is associated with excitations of the valence electrons and includes interband transitions and collective excitations. As a consequence, this valence EELS displays a rich and complex array of spectral features. Each phase in the material will have distinct valence EELS signature and, in the first instance, a simple fingerprinting approach can be used for phase identification and mapping as illustrated in Figure 1.

In addition, surface plasmons are observed at metal-dielectric interfaces and the mapping of surface plasmons has been one of the main applications of valence EELS in recent years. For example, surface plasmons can also be observed in Figure 1 and their location and energy is modified by the corrosion product. The simulation of plasmon excitations using electrodynamics simulations [1], to understand and identify plasmon modes has been a key aspect of the development of this approach. For example Ag nanotriangles display a diverse range of edge and surface modes [2].

Figure 2 shows an example showing the rich spectral detail available in EELS. In general, however, the analysis of the fine structure with the valence EELS has not been extensively applied. The difficulty lies in the interpretation of the complex array of spectral details. Calculations of the valence EELS can be performed using density functional theory (DFT). In the independent particle approximation (IPA) the electron and hole generated are assumed to not influence the other electron states and to not interact with one another. That is, quasiparticle and excitonic effects are ignored. This approach has been successfully applied to predict the overall spectral shape of a number of materials, especially metals [3] and it does reasonably well for the example of Na_xWO_3 in Figure 2. However, for many materials, particularly semiconductors and insulators but also some metals, the spectral details are not well reproduced. Bandgaps, when present, are always underestimated and in the worst cases the calculations completely fail to predict the spectral shape. One such example is KBr as shown in Figure 3.

The valence EELS is directly connected to optical response functions (e. g. the complex dielectric function) and there are a number of sophisticated computer codes already available to calculate these, where quasiparticle corrections can be introduced with the GW approximation and excitonic effects with the Bethe-Salpeter equation (BSE) [4]. In some cases the inclusion of local field effects (LFE) and exploration of the momentum dependence is also important. In some cases these computationally expensive approaches can be avoided by instead by using alternative exchange-correlation potentials. An example of these higher order corrections to KBr is shown in Figure 4. However, such calculations are computationally demanding, already requiring many hours of parallel processing time and will require over 1TB of RAM for further improvement. The large energy range required for EELS data puts unique demands the computational processing required and careful selection of the appropriate level of calculation required needs to be made. This presentation will review such requirements.

References:
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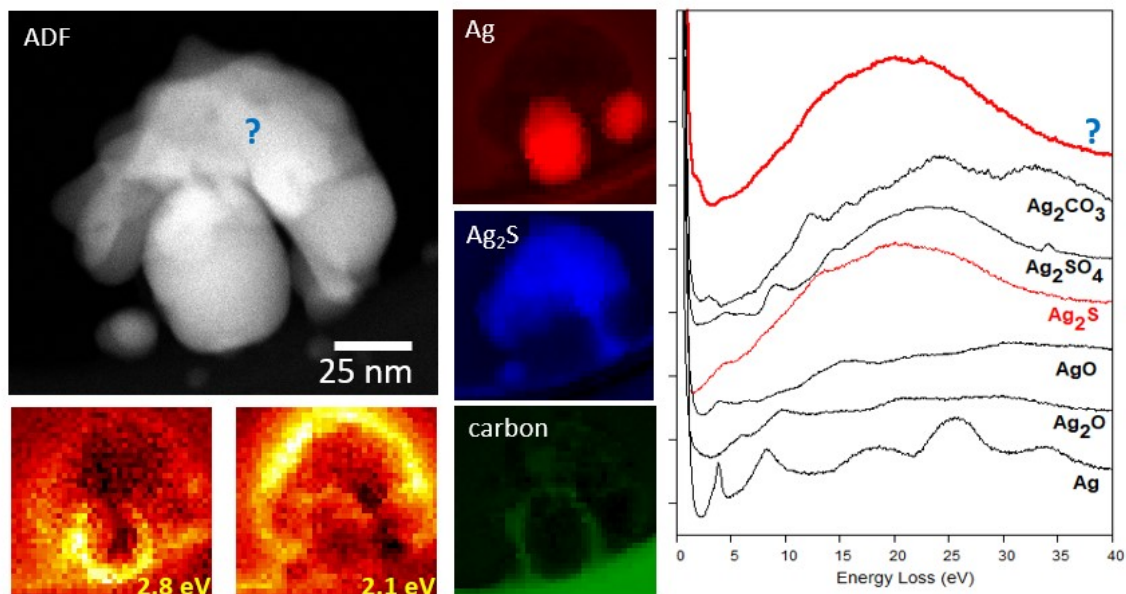
Figure 1. A corroded silver nanoparticle. Comparison with reference spectra allows the identification of Ag_2S as the corrosion product. Multiple linear least squares fitting to reference spectra permits mapping of the different phases present. Typical surface plasmons of an Ag sphere are observed at 2.8 eV, but the the corrosion product introduces a resonance at 2.1 eV at the edge of the corrosion product instead.
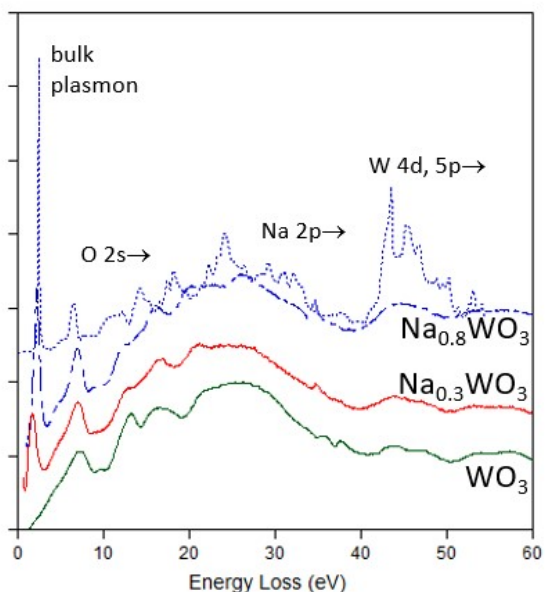
Figure 2. Valence EELS spectra for Na_xWO_3 showing complex spectra and subtle changes. The IPA calculations for $Na_{0.8}WO_3$ show reasonable agreement with experiment.
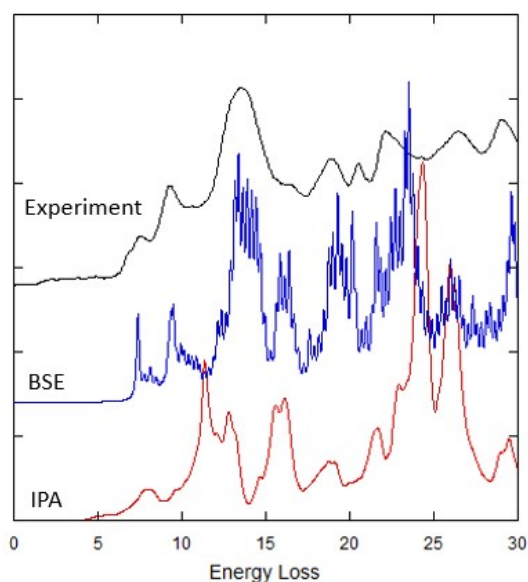
Figure 3. Experimental valence EELS for KBr compared to IPA and BSE calculations. The IPA fails to predict the spectral details and the BSE still requires optimization.