

## 1. Energy Dispersive X-ray Analysis

EDS identifies elements by their characteristic X-rays, excited by energetic electrons in microscopy instruments. Moreover, the FEI Talos TEM utilizes a super-quad detector, operating in conjunction to not only capture a large solid angle but also provide spatial resolution, aided by the operation of the TEM beam in scanning tunneling mode (STM). In STEM mode, the electron beam is X-Y rastered across the sample, generating an energy-resolved X-ray map of elemental concentrations. Energy filtering of the X-rays via software permits differentiation by element. Additionally, EDS can be rendered semi-quantitative and thus potentially serve as a measure of chemisorbed oxygen concentration, analogous to XPS.

A particular advantage of EDS is its ability to analyze femtograms of material. In particular, for some of the combustion-formed soot, an insufficient amount was collected for XPS analysis of active sites. Comparative active site measurements on a particle basis would open up the possibility of studying the aging of combustion soot using thermophoretic samples while on the sampling grid. Thermophoretic samples are precise for extraction position and thus the temperature-time history of the collected soot. Additionally, the soot sample is thermally quenched by the sampling, unlike substrate deposition methods, wherein the deposited soot is exposed to flame temperature during the entire course of soot deposition. Such methods also severely distort the flow field, changing the flame structure and corresponding streamlines. Moreover, the potential to resolve active sites by EDS portends the feasibility of such measurements *in situ*, where desorption and chemisorption cycles could be run without air exposure as incurred during sample transfer between instruments.

To test for a relationship between active sites and nanostructure on such relevant soots, energy dispersive X-ray spectroscopy (EDS) was investigated for potential surface oxygen determination. Therein, combustion-formed soots were selected for their practical relevance, specifically from a diesel engine running a biodiesel blend and an ultra-low sulfur (petroleum-based) diesel fuel, ULSD. Both samples were activated by oxygen chemisorption prior to TEM and EDS imaging.

## 2. Results

Shown below in **Figs. 1 and 2** are EDS scans and an EDS elemental map. The marked region in **Fig. 1** for the B10 soot indicates the region to which the EDS scan corresponds. The general signal level (counts per second, cps) is very low for the nascent B10 soot, accounting for the noisy image. Meanwhile, **Fig. 2** shows a corresponding EDS elemental map and scan in addition to a high-angle angular dark field (HAADF) image also obtained in STEM mode for the partially oxidized (50%) B10 soot, following activated chemisorption. (The HAADF image provides a bright field TEM image as a frame of reference, outlining the particles at the same magnification as the EDS elemental map, for which selected elements are color coded.) Relative to the elemental map in **Fig. 1**, at a 5x lower magnification, the reduced scale should have increased the cps per pixel geometrically by a factor of  $\sim 25$  for the elemental map in **Fig. 2**, but this projection was not realized. Ideally, chemisorbed oxygen would appear most prominently along the particle perimeters, relative to carbon, while towards the particle center, the carbon content and counts would quickly dwarf the oxygen signal (as the chemisorbed oxygen is only a surface contribution), serving to highlight the oxygen peripheral content. Clearly, this anticipated contrast was not observed.

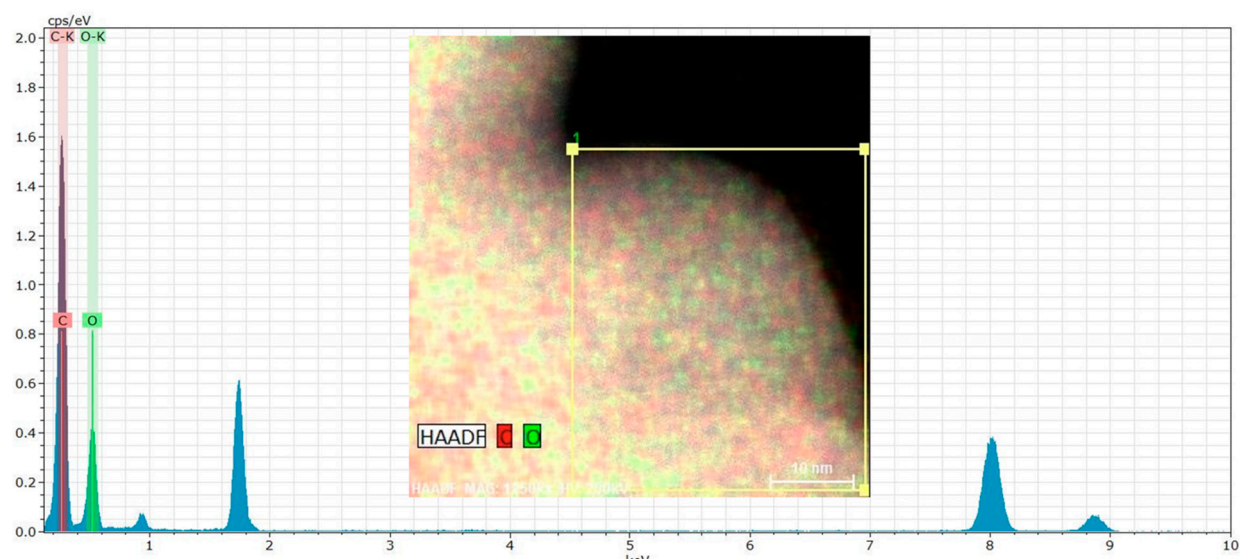


Figure S1. EDS scan, elemental map and HAADF image for the nascent B10 soot.

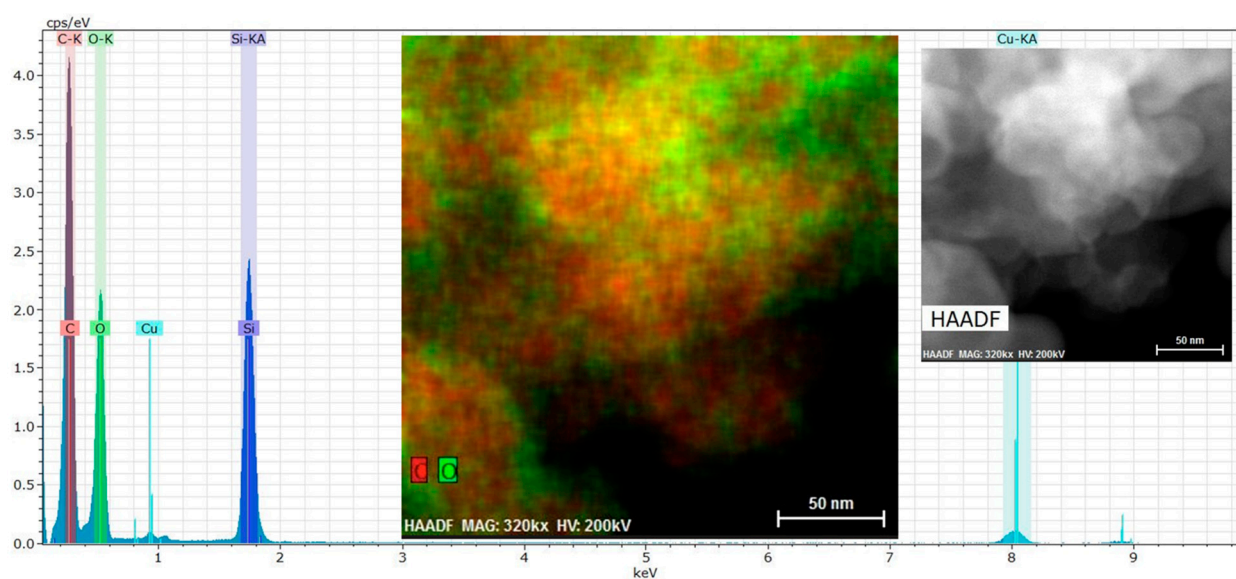


Figure S2. EDS scan, elemental map and HAADF image for the partially oxidized (50%) B10 soot.

### 3.0. Implications for Active Sites and Nanostructure Relationships

While preliminary, these samples demonstrate the limitations of EDS and TEM imaging to connect active sites to nanostructures and do not bode well for potential in situ observations by this approach.