

## Spatially Resolved Soft X-ray Spectroscopy in Scanning X-ray Microscopes

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Near edge X-ray absorption fine structure (NEXAFS) spectroscopy is a powerful probe of the structure and bonding of materials, especially in the soft X-ray region (50 – 2500 eV) where the high experimental energy resolution and small natural linewidths provide much better chemical sensitivity than hard X-ray spectroscopy. NEXAFS measured in soft X-ray scanning transmission X-ray microscopes (STXM) [1] is a powerful tool for materials and environmental analysis. Together STXM-NEXAFS can provide chemical speciation and quantitative mapping in 2D and 3D, with a spatial resolution better than 30 nm. In the last few years the spatial resolution has been dramatically improved from ~30 nm to less than 5 nm using ptychographic coherent diffraction imaging [2,3]. When the synchrotron source illuminating a STXM microscope is an elliptically polarizing undulator, site specific geometric and electronic anisotropy and magnetic properties can be probed and mapped. Detection of X-ray fluorescence (XRF) signal while scanning the incident photon energy provides greatly enhanced NEXAFS detection limits [4]. Results from recent studies of linear dichroism in boron nitride nanostructures [5], circular dichroism of individual magnetosomes in magnetotactic bacteria [2] and XRF-based metal speciation in an environmental biofilm [6] are used to illustrate these capabilities.

**Figure 1** presents images and linear polarization dependent B 1s spectra of a BN nanoribbon (~100 x 200 nm x 10 nm). When the shape and dichroic response of the B 1s and N 1s spectra were compared with high level VASP calculations (explicit core hole, core excited unit cell at centre of a 4x4x1 super-cell) the detailed layer stacking was deduced [5]. B 1s and N 1s spectromicroscopy of bamboo and nanotube BN structures are being used to investigate their electronic and spatial structure.

A river biofilm was exposed to 10 µg/mL Ni(II) for 5 days to examine chemical states and possible preferential absorption of the toxic Ni ions. NEXAFS stacks at the Ca, N, O, Ni, Al, Si and Fe edges were measured and analyzed to generate elemental maps and Mn, Ni and Fe speciation (**Fig. 2**). As found in earlier studies [7] the Ni was found collocated with Mn and Fe, reinforcing the conclusion that metal ion – metal ion interactions are important in determining the fate of Ni(II) in the environment. Another river biofilm sample, exposed to 1 µg/mL Ni(II) for 24 hours, was examined with both transmission and XRF detection [6]. In this case the higher XRF sensitivity allowed identification of Ni(III) as well as Ni(II) inside and outside a cyanobacterium (**Fig. 3**) [8].

### References:

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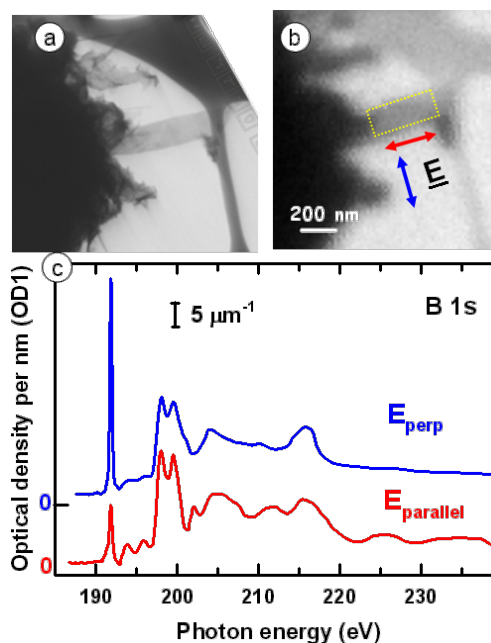
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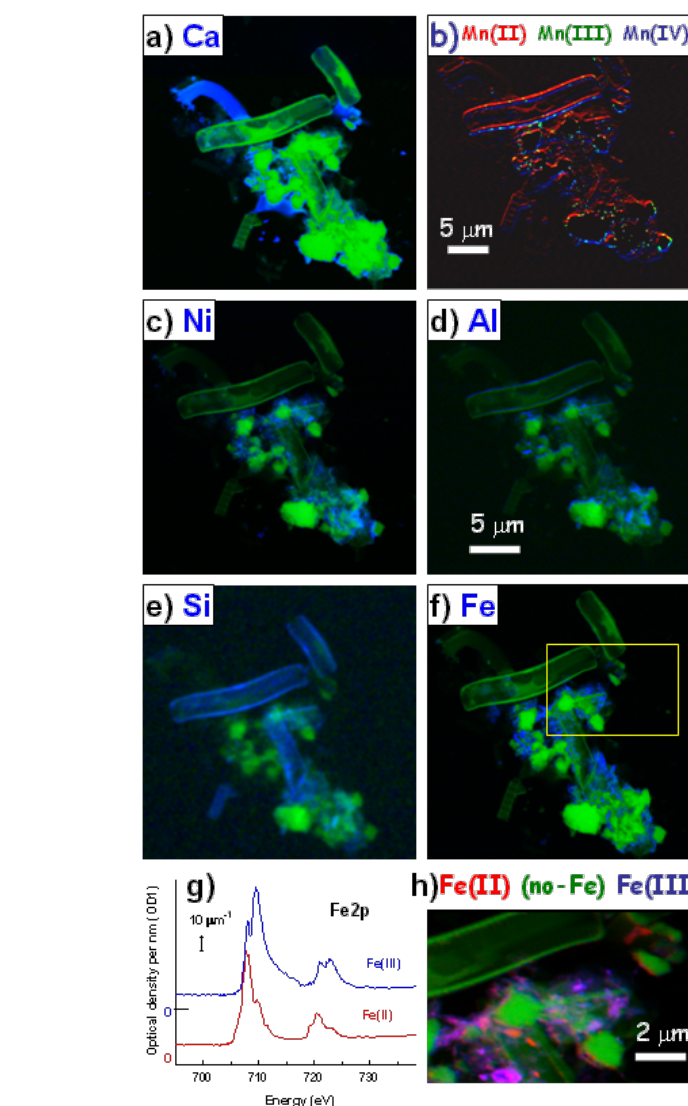
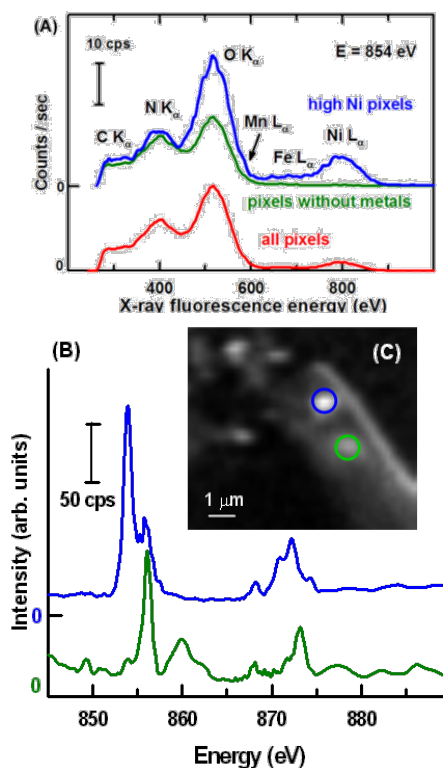
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**Figure 1.** (a) Transmission electron microscope (TEM) image in same region as (b) STXM transmission image at 191.9 eV of a BN nanoribbon (yellow box). (c) B 1s NEXAFS spectra of the nanoribbon with  $E_{\perp}$  and  $E_{\parallel}$ .



**Figure 2.** (a-f) Elemental maps of the indicated elements (blue) from peak – pre-edge signals, combined with pre-edge images (green) from a river biofilm exposed to 10  $\mu\text{g}/\text{mL}$  Ni(II) for 5 days. (g) Fe L NEXAFS of Fe(II) and Fe(III) used to fit the Fe L stack of the biofilm. (h) Fe speciation maps of yellow box area in (f).

**Figure 3.** (A) XRF spectrum measured with primary energy of 854 eV from several areas of a river biofilm exposed to 1  $\mu\text{g}/\text{mL}$  Ni(II) for 1 day. (B) Ni L NEXAFS spectra of the spots circled with blue and green in (C) average XRF yield image (60 energies from 845 to 890 eV).