

## Screening of Individual Nanostructures with STEM-EELS and EFTEM Spectral Imaging

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Nanotechnology promises to bring about the “next industrial revolution,” and is expected to play a major role in the 21<sup>st</sup> century economy. The fulfillment of this promise will rely upon the discovery of new classes of materials and structures that could not exist but for the methods of self-assembly that are native to the nanoscale. Combinatorial methods, commonly used for the discovery of new drugs, provide a mechanism for testing thousands of distinct variations in the “recipe” used for synthesizing a particular class of nanostructures in a single experiment. However, there is currently no efficient screening tool for sampling the chemical makeup of these variations to identify novel structures. Such screening would be designed to distinguish between those variations that correlate with a change in synthesis conditions and those naturally occurring at a single condition, as well as to identify the “interesting outlier” that may exhibit desired behavior although synthesized by chance. In this paper, we explore electron energy-loss spectroscopy (EELS) spectral imaging, performed in both conventional transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) modes, as a screening tool for individual nanostructures.

An application of STEM-EELS spectral imaging to catalytically grown carbon nanofibers is shown in Fig. 1. “Forests” with billions of such nanofibers are grown from annealed 3d transition metal catalyst films on silicon wafers, as shown in Fig. 1a [1,2]. The secondary electron image shows fibers with a range of diameters capped with a conically shaped catalyst particle. A STEM high-angle annular dark field (HAADF) and STEM-EELS spectral image are shown in Figs. 1b and 1c, respectively. The data were acquired with a Philips CM200FEG operated at 200 kV and equipped with a Gatan Imaging Filter (GIF) and an EMiSPEC Vision integrated acquisition system. The microscope was operated in HR-STEM mode with  $\sim 1$  nA current in a  $\sim 1.5$  nm probe. The 64x64 spectral image was acquired with drift correction performed at the end of each row of pixels, a sampling of 2 nm per pixel, a 1 s dwell time, and a dispersion of 1 eV per pixel, capturing a spectral range of  $\sim 100$  eV  $< E < \sim 1100$  eV. Elemental maps were extracted for C-K, N-K, O-K, Fe-L, and Co-L with 25 eV windows for background extrapolation and 70 eV windows for signal integration. The RGB composite image shown in Fig. 1c reveals an unexpected feature: a silicon nitride particle at the base of the catalyst particle interfacing to the relatively hollow core of the fiber. However, the number of pixels is limited for sampling nanoscale features and the  $\sim 1$  h acquisition time is too long for efficient screening. Newer model spectrometers such as Enfina offer much shorter dwell times, and thus possible improvements in pixel density and acquisition time, although at expense of signal.

An application of energy-filtered TEM (EFTEM) spectral imaging is shown in Fig. 2. The specimen is comprised of a bimodal nanoscale distribution of NiO particles in a Ni<sub>2</sub>TiO<sub>4</sub> matrix that self-assembles during high-temperature ( $> \sim 1700$  K) equilibration and quenching of oxide mixtures of NiO-15 wt% TiO<sub>2</sub> [3]. The 256x256 spectral image was acquired with a Philips CM300FEG operated at 300 kV and equipped with a Gatan Imaging Filter (GIF), with  $\sim 1$  nA total current, 2 nm pixel size, and a 1 s exposure per image. A series of 24 images were acquired with  $8$  eV  $\leq E \leq 100$  eV, a 4 eV increment, and a 5 eV energy window. Data analysis was performed with the AXSIA spectral image analysis program in PCA image mode with statistical normalization in both spectral and image dimensions [4]. The acquisition time of 30s for the full spectral image (90s including set-up and data storage) is well suited for screening of multiple structures or for 3D chemical imaging [5]. The bright-field image (2a) shows that there is little diffraction contrast. The spectral image (2b) clearly shows the NiO particles (blue) in the Ni<sub>2</sub>TiO<sub>4</sub> matrix (green). However, for  $t / \lambda > 0.5$  (green-red transition in 2c), a separate spectral component (red) is identified in the spectral image

(b), because of multiple scattering. The removal of multiple scattering effects to extract the single scattering function for thicker specimens will be discussed [6,7].

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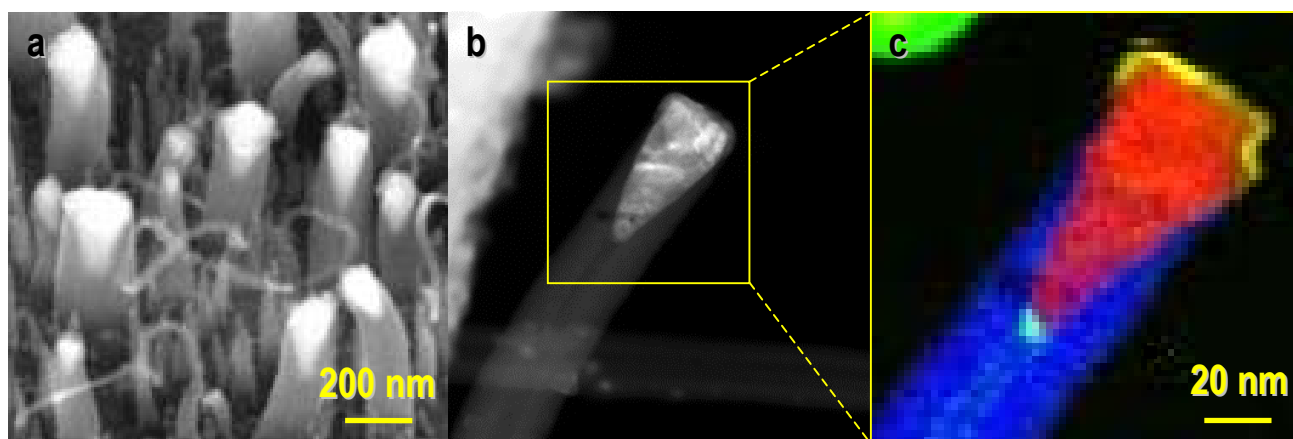


FIG. 1. Images of carbon nanofibers grown by plasma-enhanced CVD: (a) SEM secondary electron image; (b) STEM-HAADF image; (c) STEM-EELS spectral image. For the nanofiber shown in (c), a silicon nitride particle (cyan) sits at the growth interface between the iron-cobalt catalyst particle (red) and the carbon nanofiber (blue); the catalyst particle is capped with an oxide scale (yellow).

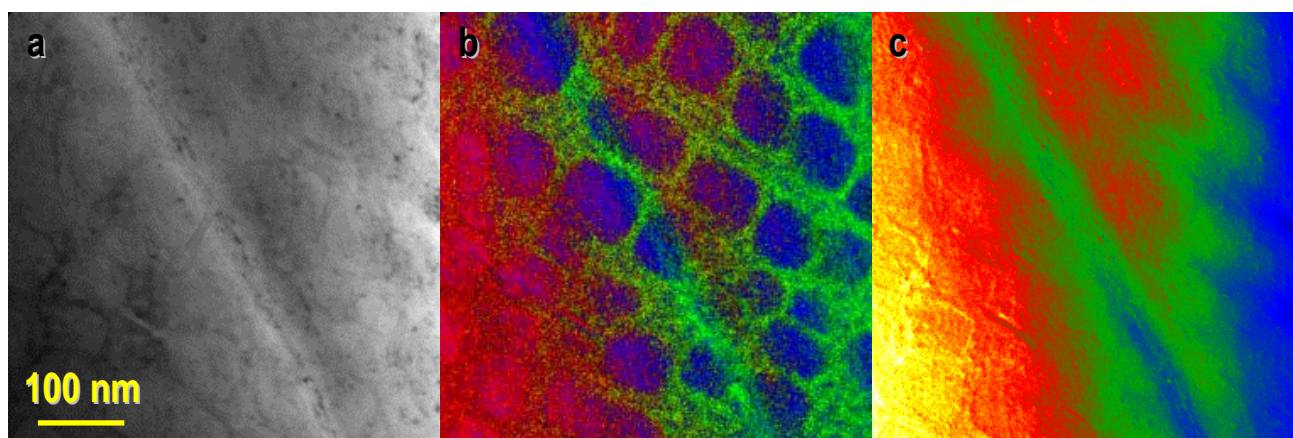


FIG. 2. EFTEM images of NiO/Ni<sub>2</sub>TiO<sub>4</sub> two-phase microstructure: (a) BF image; (b) EFTEM spectral image; (c)  $t/\lambda$  map. The spectral image shows NiO particles (blue) in a Ni<sub>2</sub>TiO<sub>4</sub> matrix (green). Regions of the specimen with  $t/\lambda > 0.5$  (green-red transition in c) are identified as spectrally distinct (red areas in b) using linear multivariate analysis methods because multiple scattering shifts intensity within the spectrum.