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Identifying Nanocrystalline Domains Identified Within Oxide Aerogels Using Inverse-Fast-Fourier-Transform Techniques: Comparing Automated Mask Generation with Hand-Segmentation

Todd H. Brintlinger[1], Travis G. Novak[2], Paul A. DeSario[1], Rhonda M. Stroud[1] and Debra R. Rolison[1]

[1.] U.S. Naval Research Laboratory, Washington, DC, USA.
[2.] National Research Council Postdoctoral Associate at U.S. Naval Research Laboratory, Washington, DC, USA.

The physicochemical properties of catalytic metal nanoparticles – including chemical speciation, morphology, optical properties, and stability -- are influenced by interactions with promotional oxide supports [1-2]. Additionally, how the metal nanoparticles are sited vis-à-vis immediately adjacent oxide surfaces strongly affects chemical transport of reactants to and by-products toward and away from chemically active sites, where the oxide particles define the limiting length scale for mass and ionic transport. To characterize metal nanoparticles within the aerogel, we previously employed electron tomography, manual segmentation, and a group of nascent machine-learning classifiers [3]. In this work, we focus instead on the oxide scaffold.

To understand the distribution of nanocrystalline oxide domains within the aerogel scaffold, we first perform manual 'particle' identification within the covalently bonded network based on high-resolution transmission electron microscopy (HRTEM) images. This approach avoids such difficulties with (1) high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) where overlapping oxide domains are indistinguishable, (2) with ensemble-based techniques such as X-ray diffraction with unknown shape factors and/or fitting functions, and (3) electron-diffraction techniques with the same or similar a prioiri or unavoidably arbitrary shape factor designations/assumptions. The manually-generated inverse-fast-Fourier-transform (IFFT) method is illustrated in Fig.1, in which an HRTEM image of a Ni-based nanoparticulate shows it is situated on and within a CeO2 aerogel. A pair of manually-selected spot masks on the FFT (inset) are used to perform an IFFT (Gatan Microscopy Suite software), resulting in the green outline of the particle at the edge of the aerogel. Sample inks of metal-oxide aerogels are prepared by sonication and dropcasting on standard lacey carbon grids, which are then imaged within a JEOL JEM2200FS TEM operating at 200 kV, and acquired on a OneView camera. Here, the particle is clearly identified, both 'by eye' as well as through the IFFT, where subsequent size and/or morphology distributions, along with their spatial location, are described through counting statistics accumulated through individual particles' characteristics, as opposed to fits of ensembles [4].

To avoid inadvertent selection bias, we then compare these results with an automated inverse-fast-Fourier-transform (IFFT) based on a variety of mask sizes and Gaussian fitting using an automated algorithm which identifies circular disks within the FFT; these regions are then used to identify candidate locations for masking in which to perform IFFT operation. An automatically selected FFT spot location is shown in Fig. 2, with same operations as in Fig. 1, but in which the mask size around a central spot is defined by Gaussian fits of the radial distribution function. The main user input is in the number of rings to identify, but otherwise the algorithm selects masks, and thus particles, based on each dataset, which are rapidly visualized for user confirmation and/or comparison to manually identified regions. Using an automated analysis, several nanocrystalline domains are identified within the aerogel, in contrast with most manually-selected nanoparticulates sited at the aerogel edge. We will discuss the results of visualization of IFFT-identified nanocrystalline domains, the effect of mask size, and compare against manually-generated sizes and distributions.

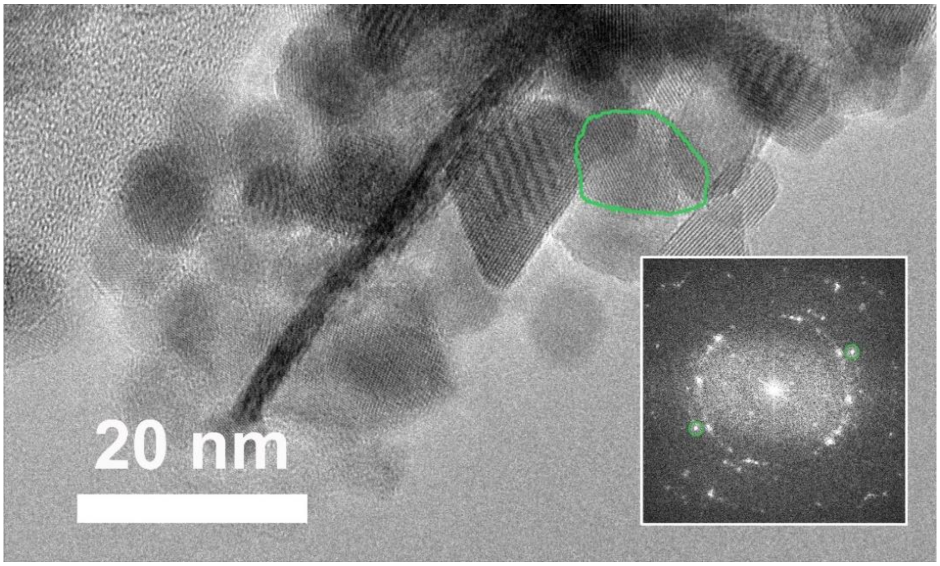

Figure 1. High-resolution transmission electron microscope (HRTEM) image of a Ni-based nanowire on and within a CeO2 aerogel framework. (Inset) Fast-Fourier-transform (FFT) of main image, with green circles identifying the mask region manually-selected to generate the inverse-FFT (IFFT) overlay of an individual nanocrystalline domain near the edge.

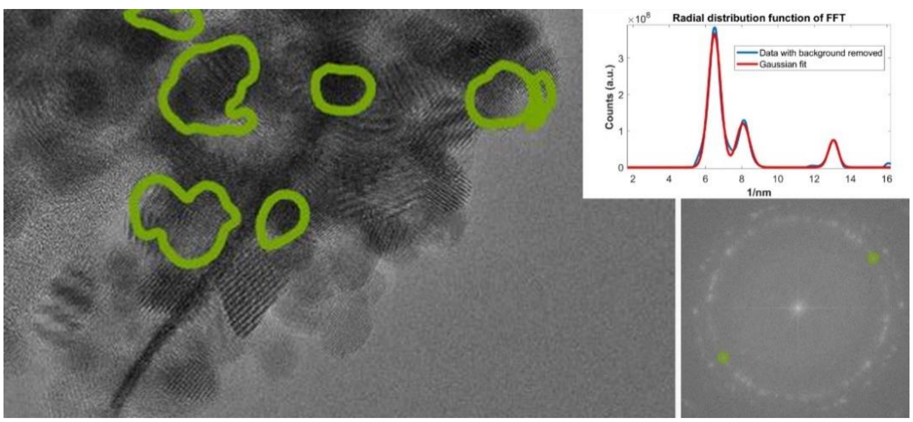

Figure 2. Automated mask selection and IFFT operation: The colored spot on the FFT mask (bottom right inset) is used to perform the IFFT operation to identify nanocrystalline domains in the main panel, and individual FFT spots are located following identification of polycrystalline rings using gaussian fitting of the radial distribution function (top right inset).

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