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Identifying Spatial Relationships in Metal-nanoparticle/Insulating-aerogel Catalytic Systems with Electron Tomography: Manual Segmentation vs. Machine-learning Classifiers

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Catalytic systems based on the incorporation of metal nanoparticles into insulating aerogels show great promise in optimizing multiple chemical reactions, including CO oxidation [1], contaminant remediation [2], and water splitting [3]. The method of incorporation of the metal particles within the aerogel host has important implications in the mechanism driving these various chemical pathways. Synthetic techniques to control the three-dimensional orientation of metals in insulating hosts are essential for understanding how catalytic reactions are affected by morphologically complicated yet chemically simple systems.

In addition to the traditional method of deposition precipitation to support metal nanoparticles on the aerogel support, we have also developed a route for directly integrating metal nanoparticles, usually gold, into titania aerogels [4], this novel integration is shown in high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field imaging with scanning transmission electron microscopy (HAADF-STEM) in Fig. 1. This technique allows us to vary the metal nanoparticle size. By carefully matching the nominal size of the host with the more chemically active metal nanoparticles, we observe increased catalytic performance; moreover, the specific location of the metal relative to the insulating aerogel also has an effect on catalysis. To understand this relationship, we apply electron tomography to build 3-dimensional models of our systems. We use a high-tilt holder (Fischione 2030) in a transmission electron microscope (JEOL JEM2200FS) operating at 200 kV in order to acquire series of HRTEM images at different tilts of metal/aerogel particles. The particles are prepared by sonication in isopropyl alcohol and drop cast onto lacey-carbon grids specifically designed for tomography. Tilt series are acquired with predictive software (serialEM) [5] and a high-speed CMOS electron camera (Gatan OneView) using 300 nm defocus and 2° increments over a ± 72° range. Tomograms are assembled from these tilt series using a back-projection algorithm (the etomo portion of the IMOD package) [6]. With these systems, while HAADF-STEM resolves the gold nanoparticles quite well, bright-field TEM provides good intensity contrast between titania, gold, and vacuum without significant errors resulting from other contrast mechanisms (diffraction, strain, etc.).

Following tomographic reconstruction, segmentation is a critical step in comparing various metal/aerogel types. Initial work involved the careful manual segmentation of individual tomograms with various thresholding and filtering algorithms [7], but this strategy is prone to selection bias and implicit identification criteria. To enable more objective sample-to-sample comparison, we have implemented multiple machine learning classifiers (Adaboost, Random Forest, & Extra Trees) with varying sets of parameters that have been trained on manually segmented tomograms of different Au/TiO_2 samples. We compare the results of using different trained classifiers to segment previously unanalyzed tomograms, as well as validate both manual and trained classifiers using HAADF-STEM. We also discuss the impact of this machine-learning approach on the eventual interpretation this data and how it describes the behavior of metal/aerogel systems, as well the bias-variance tradeoff as regards these materials.

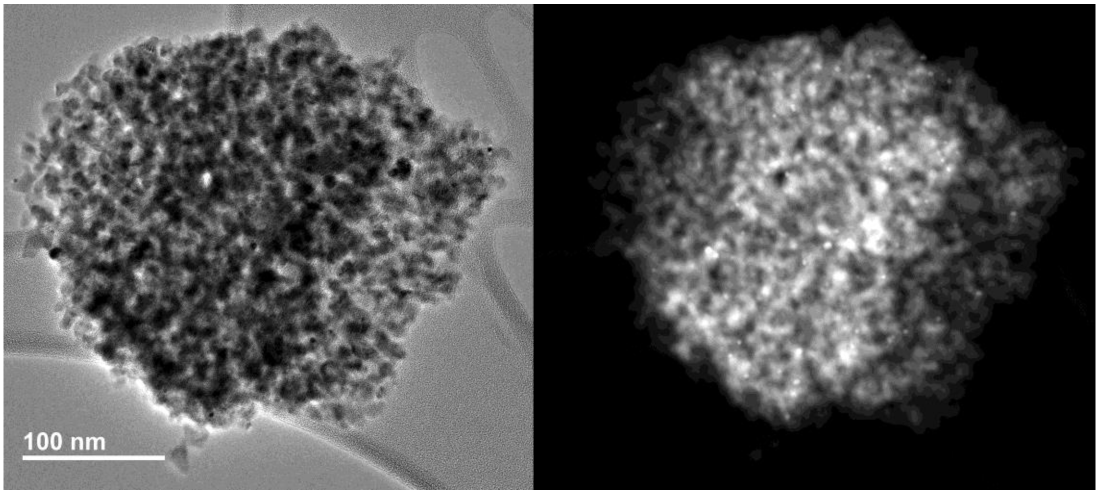

Figure 1. Gold nanoparticles in titania aerogel seen with transmission electron microscopy (left) and high-angle annular dark-field imaging with scanning transmission electron microscopy (right)

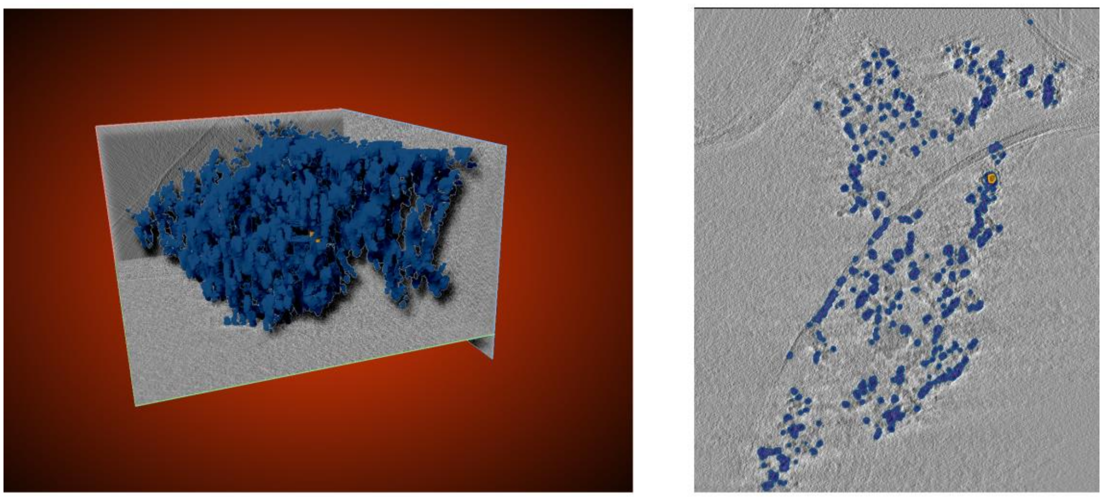

Figure 2. Reconstructed tomogram in 3d depiction on left with original data (greyscale) and manually segmented regions of titania (blue) and gold (orange). Single 2d slice of the same tomogram is shown on right with same color scheme as 3d. Tomogram is 811 x 967 x 500 voxels with 0.37 nm/pix.

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