Composition and Atomic Arrangement of Binary-Element Atom Columns through Analytical Transmission Electron Microscopy

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Three-dimensional structure determination of materials at atomic-scale is fundamental in understanding structure - synthesis - property relationships, and therefore critical in designing novel materials. Recent progress in quantitative HAADF-STEM imaging[1,2] and EDX spectroscopy[3] has made absolute counting of the number of atoms for single-element materials possible. However, the complexity increases dramatically when two elements co-exist in an atomic column due to dynamical diffraction (channeling) of the probe along the atomic columns. Atom columns having the same number of each atom type but in a different arrangement can show different intensities of the respective HAADF or EDX signals. As a result, atom columns may show intensities indistinguishable within the experimental error, but have different number of atoms or different atom configurations.

Here, we report efforts to tackle the challenges in two-element column quantification by investigating the structure and chemistry change of a PtMo/C catalyst nanoparticle, around 2 nm in diameter and a maximum thickness of 6 atoms, under electron-beam exposure. When two elements co-exist in an atomic column, quantitative STEM by comparison to a library of simulated intensities requires a sizeable library size of $\sum_{i=1}^{n} 2^i$, where *n* is the possible maximum number of atoms within a column. Thin samples (small *n*), reduce the size of the library and produce less intensity overlap from different configurations. However, small catalyst particles and other thin samples are subject to radiation-induced modification of the structure. Careful selection of accelerating voltage, dose, dose rate, and detector brightness and contrast setting not only controls the speed of radiation modification, but also optimizes the signal-to-noise ratio of the final time-series images.

We have applied a hybrid statistics- and simulation-based method[4] together with prior knowledge from EDX measurement averaged over many nanoparticles to construct a 3-D structure model of one PtMo particle. Figure 1(a) shows one frame of a HAADF STEM time-series recorded along the [110] axis in a probe-aberration-corrected FEI Titan at 300 kV with dose per image of $6.8*10^5$ e/A^2. A histogram of the scattering cross sections from all the images, integrated over Gaussian functions fitted to the atom columns in the HAADF image, is shown in Figure 1(b), fit to a Gaussian mixture model.[4] Figure 1(c) is the Integrated Classification Likelihood criterion (ICL)[4] applied to determine that 32 components are needed to represent the whole time-series of images. The model-determined components are later assigned back to each individual column, as illustrated in Figure 1(d) for the frame shown in (a). Considering the prior-knowledge of population composition from EDX data, we can correlate each component to between 1 and 3 configurations with known Pt to Mo ratio giving same information about, *e.g.,* elemental segregation. Figure 1(e) shows the top-view of one of the final reconstructed model of the particle shown in (a).

More details and the possibility to extend to thick samples will be further discussed.

References:

1 S. van Aert *et al.*, Procedure to Count Atoms with Trustworthy Single-Atom Sensitivity, Phys. Rev. B, 2013, 87(6), 064107.

2 M. Yu *et al.*, Integrated Computational and Experimental Structure Refinement for Nanoparticles, ACS Nano 2016, 10, 4031-4038.

3 Z. Chen *et al.*, Energy Dispersive X-Ray Analysis on an Absolute Scale in Scanning Transmission Electron Microscopy, Ultramicroscopy 2015, 157, 21-26.

4 A. De Wael *et al.*, Hybrid Statistics-Simulations Based Method for Atom-Counting from ADF STEM images, Ultramicroscopy 2017, 177, 69-77.

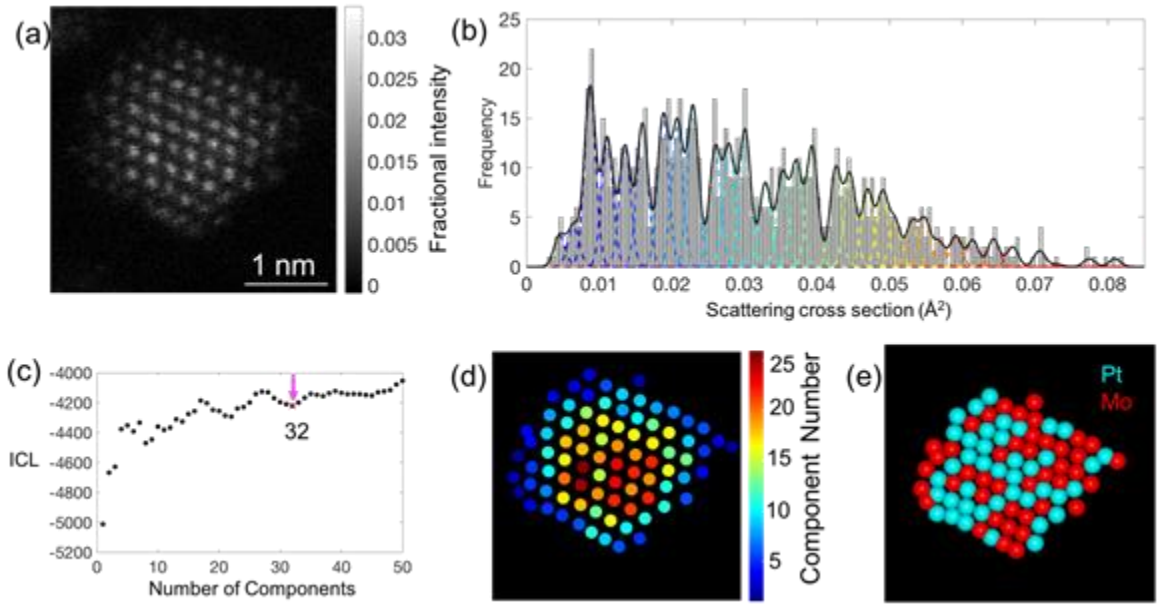

Figure 1: (a) One frame of the HAADF STEM image series of a PtMo/C nanoparticle with intensity expressed as a fraction of the incident beam intensity; (b) set of scattering cross sections from all images in the time series. The solid black curve shows the estimated Gaussian mixture model, whereas the colored curves indicate the individual components; (c) ICL criterion plot with the number of total components for the whole time-series arrow labeled, details about the axes can be found in ref. 4; (d) column components of the image in (a); (e) top-view of the 3-D reconstructed model of the image in (a).