High-Throughput, Semi-Automated Quantitative STEM Atom Counting in Supported Metal Nanoparticles Using a Conventional TEM/STEM

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Transmission electron microscopy (TEM) has proven itself an invaluable tool for measuring composition, chemistry, and internal structure at the nanoscale and below. The local characterization of TEM complements ensemble techniques and informs computational modeling by providing real-world information about structural state for input. TEM micrographs, however, are inherently two-dimensional projections of the real three-dimensional object; important structural information can be lost and ambiguities introduced. Nanoparticles (NP) of different structures – which can possess dramatically different catalytic activity and effectiveness – can yield similar apparent projected sizes in micrographs [1]. The ability to distinguish between them – and, ideally, recover the 3D atomic structure – is necessary for continued improvement in catalyst design.

Quantitative scanning TEM offers a means of recovering some of this information from a single high-angle annular dark-field STEM (HAADF-STEM) micrograph, through careful calibration of the microscope and image. The first practical demonstration of atom-counting via quantitative STEM, and the method which we adapted for this work, was performed by Singhal et al. [2] based on Treacy and Rice [3]. They showed that the intensity of ultra-small nanoclusters in HAADF-STEM images acquired at sufficiently high collection angles (≥100 mrad) could be explicitly related back to the number of atoms involved in the scattering, and thus in the cluster. The old VG STEMs for which these methods were initially developed have all but disappeared. Recent developments in quantitative STEM techniques have focused on atomic-resolution reconstructions using top-of-the-line aberration-correction microscopes [4,5]. This approach is time-consuming, however, and most university facilities do not possess such expensive instruments with corresponding expensive service contracts.

For this reason, we have adapted quantitative STEM to enable its use on a conventional, non-aberration-corrected TEM/STEM – a JEOL JEM2100F – without the need for any special modifications or attachments. The approach does not require an internal calibration standard or any STEM image simulation. Forgoing atomic-resolution STEM imaging brings with it other benefits, too. The lower magnifications (2-4 MX) used in this approach means that a much larger number of nanoparticles can be present in each micrograph, such as in Figure 1a, and because there is no need for a NP to be oriented along a specific crystallographic orientation, almost every nanoparticle in an image is suitable for analysis. This greatly increases the population sizes that can be analyzed, enabling robust statistics about particle size, shape, and monodispersity to be gathered from hundreds to thousands of nanoparticles. The ability to analyze large numbers of nanoparticles also reduces the potential for selection bias. It should be noted that this approach can be paired with analysis of selected NP at atomic-resolution studies, to gain the benefit of both robust statistics and atom-level characterization.

To facilitate this process and further reduce the time required, we have developed a program for MATLAB to automatically perform the quantitative STEM analysis on batches of micrographs. For each nanoparticle, the optimal intensity integration cut-off radius is calculated via an iterative process

that determines when the scattered intensity from the NP is fully enclosed, Figure 1b. A background correction procedure accounts for local intensity variations due to underlying supports. NP size is determined via fitting with 2D rotated Gaussians, enabling size distributions and basic shape information (spherical, hemispherical, or plate-like) [6] to be gathered, as well. Figure 2 shows an example of intensity quantification applied to Au NP; the automated analysis only required ~15 minutes. [7]

References:
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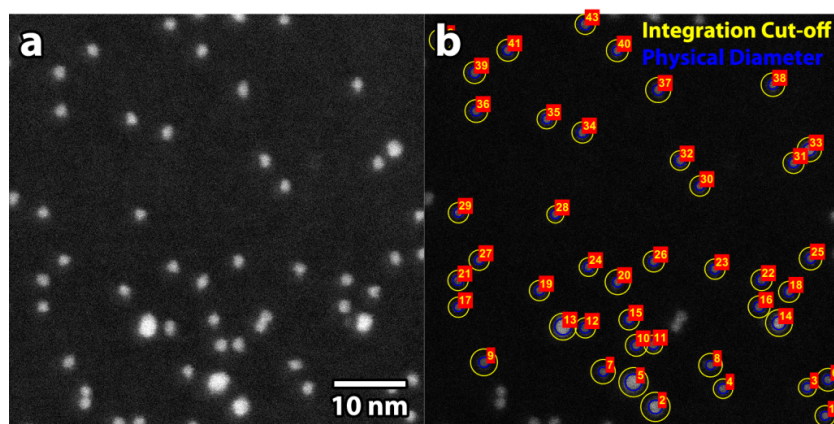
Figure 1. 4 MX HAADF-STEM micrograph of Au NP (a) before and (b) after automated NP analysis, showing the optimized integration radii (yellow) and physical sizes (blue).
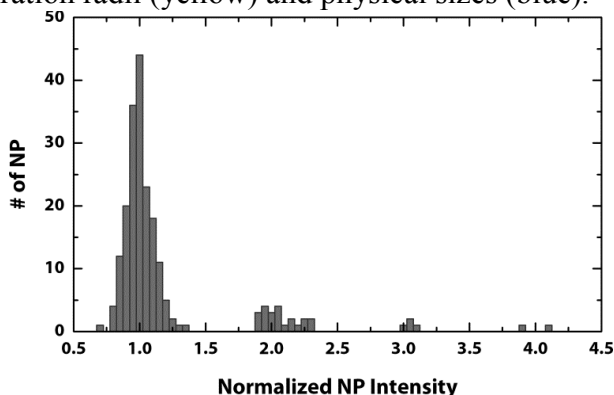

Figure 2. A histogram of 206 Au NP intensities, normalized to the average intensity of a single nanoparticle (the peak centered around 1.0). The integer spacing of the peaks in the distribution indicates that the larger particles (visible in Figure 1) were likely formed by coalescence of integer multiples of the smaller nanoparticles. The monodispersity measured by our program agrees with measurements made with ensemble techniques.