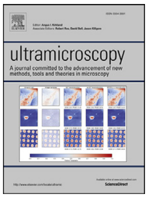
Ultramicroscopy 182 (2017) 145–155

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic



High-throughput, semi-automated quantitative STEM mass measurement of supported metal nanoparticles using a conventional TEM/STEM

Stephen D. House[a,*], Yuxiang Chen[b], Rongchao Jin[b], Judith C. Yang[a]

[a] *Department of Chemical and Petroleum Engineering, and Physics, University of Pittsburgh, Pittsburgh, PA 15261, USA*
[b] *Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA*

ARTICLE INFO

Article history:
Received 6 April 2017
Revised 30 June 2017
Accepted 2 July 2017
Available online 3 July 2017

Keywords:
Quantitative STEM
HAADF
STEM
nanoparticles
Atom counting
Mass measurement

ABSTRACT

The adaptation of quantitative STEM techniques to enable atom-counting in supported metal nanoparticles with a modern, conventional (non-aberration-corrected) TEM/STEM (a JEOL JEM2100F) without the need for any modifications or special hardware is presented. No image simulation is required, either. This technique enables the practical analysis of the size, mass, and basic shape information of statistically robust populations of hundreds to thousands of nanoparticles. The methods for performing the necessary calibrations of the microscope and images are detailed. A user-friendly semi-automated analysis program was also written to facilitate high throughput. The program optimizes the analysis parameters, applying the procedure consistently across the entire dataset, enhancing the meaningfulness of the statistics as well as the reproducibility and transferability of the results. A series of atomically precise Au nanoparticles were used to validate the technique, which was determined to be accurate within a (nearly uniform) scaling factor of around two for the given instrument, and could be brought into better agreement with a calibration standard. The magnitude of the disparity was found to significantly and unexpectedly rely on the chosen magnification and spot size, the underlying reasons for which are unclear and likely instrument-dependent. The possible sources of error from the calibration and acquisition were examined and their impact on the accuracy and precision of quantification were estimated. The scattering cross-sections measured using this technique are relatively insensitive to moderate errors in the various detector calibrations but particularly sensitive to pixel size error.

1. Introduction

The rational design of nanoparticle-based material systems, such as heterogeneous catalysts, requires an understanding of the structure-property-performance relationship, which relies on the accurate knowledge of the structure and uniformity of the synthesized materials. Transmission electron microscopy (TEM) offers the unique ability to directly characterize the structure, composition, and chemistry of materials from the micro- down to the atomic-scale with a range of imaging, diffraction, and spectroscopic techniques. This has made TEM and scanning TEM (STEM) indispensible for the study of nanostructures, including supported nanoparticles. The ability to determine the three-dimensional structure of these nanostructures is crucial since, particularly at sizes typically below a few nanometers, the physical and chemical properties are strongly impacted by even small structural differences [1–6]. In addition, correlating performance with nanoparticle structure requires a means of gauging the monodispersity of a synthesized sample. Of the most attractive techniques for characterizing nanoparticles is high-angle annular dark-field (HAADF) STEM, as the image intensity scales by a factor approaching the atomic number of the element squared (Z^2). This produces readily interpretable images where different elements are more easily distinguished–such as high-Z metallic nanoparticles on a lower-Z support, as is common in heterogeneous catalysis. Electron micrographs, however, are two-dimensional through-thickness projections of the 3D structure, introducing ambiguity into the structural analysis.

Quantitative STEM offers the ability to recover atomic-level 3D information from a single high-angle annular dark-field (HAADF) STEM image, by taking advantage of the fact that with modern detectors we are basically–or literally, in the case of direct-electron detectors–counting the number of scattered electrons. Through

---

[*] Corresponding author at: Department of Chemical and Petroleum Engineering, University of Pittsburgh, 940 Benedum Hall, 3700 O'Hara Street, Pittsburgh, PA, 15261 USA.

E-mail address: sdh46@pitt.edu (S.D. House).

http://dx.doi.org/10.1016/j.ultramic.2017.07.004
0304-3991/

careful calibration of the microscope and images, the image intensity (electron scatter) can be directly related back to the number of atoms causing that intensity (scattering the electrons).

The quantification of STEM intensities was first demonstrated by Crewe et al., who used HAADF imaging to detect single uranium atoms and determine their scattering cross-section [7]. Howie applied this technique for quantitative atom-counting through the absolute intensity of the HAADF image and the number of atoms multiplied by the electron scattering cross-section of a single atom [8], with further refinements by Treacy and coworkers [9,10]. The first practical quantitative STEM method for determining the number of atoms in supported nanoparticles was developed by Singhal et al., whose approach accounted for inhomogeneous detector response, allowing for the conversion of intensities to an absolute scale [11]. These early approaches all relied on the fact that at scattering angles of ∼100 mrad and larger–beyond the Debye–Waller cut-off for diffraction–the electron scatter is nearly entirely of the Rutherford type, avoiding significant diffraction contrast contributions [12]. The atoms can thus be treated as scattering incoherently and independently, with the total cross-section of the nanoparticle being the linear sum of the cross-sections of each atom in the particle [9,11]. Unfortunately, the old VG STEMs for which this method was developed and performed on [11,13–15] have all but disappeared.

Advancements in aberration-corrected STEM spurred a renewed interest in quantitative STEM nearly a decade later, with most of the development focusing on atomic-resolution quantitative STEM. For this, there are three primary approaches for performing the quantification: by using a mass calibration standard [16–18], statistical analysis (Integrated Classification Likelihood, ICL) [18–21], or direct comparison against image simulation [22–29]. The first uses either samples of a known thickness/size or a single isolated atom for scaling the values of the other intensities in the image. In the second, a collection of image intensities of the atomic columns is statistically analyzed to determine the most likely decomposition into numbers of atoms. The groundwork for the third option was laid by LeBeau and Stemmer, who reported a method for spatially mapping the ADF detector response and converting image intensities into units of fractional beam current [22]. This allows the images to be directly matched against a library of simulated images of varying thickness and/or composition to determine the corresponding number of atoms in each atomic column of the particle. Once the number of atoms in each atomic column is known–from either of the three approaches–3D structures can be estimated using *a priori* knowledge about the crystal structure and either discrete tomography [19], image simulation [28], or various energy minimization–based computational modeling methods [27,29].

These studies demonstrate the impressive potential of quantitative STEM to directly determine the positions–and in some cases elemental identity–of each atom in a nanostructure. The ability to extract this information from only a single image (or two, for certain methods) makes quantitative STEM an attractive alternative to electron tomography for beam-sensitive specimens due to the long exposure times required by the latter. Quantitative STEM also achieves a higher resolution than conventional tomography. The atomic-resolution quantitative STEM approaches, however, do share a few drawbacks. The most obvious is the need for an aberration-corrected STEM, which is a capital investment beyond the budgets of most facilities. The acquisition and analysis processes are time-consuming, which greatly limits the number of particles in a sample that be analyzed in this manner, bringing into question how representative the results are of the whole sample population. Finally, these methods require specialized expertise in either STEM image simulation or ICL calculations to perform, putting it out of reach of a "standard" user.

In this work we present an alternative and complementary quantitative STEM approach to address these issues by adapting and updating the methodology proposed by Singhal et al. [11] for use on a modern conventional (non-aberration-corrected) TEM/STEM, a JEOL JEM2100F, a fairly ubiquitous instrument. This method allows for size, mass, and basic shape information to be rapidly gathered from statistically robust nanoparticle populations, making it well-suited for applications such as rapid screening of samples. All the necessary calibrations were carried out–including improvements to the detector efficiency mapping approach–without the need for any modifications or special attachments to the microscope. The technique was validated using a series of atomically precise gold nanoparticles, and the sources of error–and their impact–were cataloged. We also introduce a user-friendly, semi-automated program written to facilitate the application of this quantitative STEM analysis method. The program enables high-throughput analysis, making the quantitative analysis of hundreds to thousands of nanoparticles a matter of minutes rather than days. The automated optimization and consistent application of the procedures reduces the chance for human measurement error or bias, and greatly improves the reproducibility and transferability of results. In addition to extending quantitative STEM ability to a wider range of facilities, the ability to practically analyze large numbers of nanoparticles renders it an excellent technique for pairing with smaller-population, atomic-resolution approaches.

2. Experimental methods

2.1. Sample preparation

Two different sizes of thiolate-protected gold nanoclusters–$Au_{25}(PET)_{18}$ [30] and $Au_{144}(PET)_{60}$ [31] (where PET = 2-phenylethylthiolate)–were synthesized according to our previously reported size-focusing methodology. This method generally consists of two main steps. In step I, a polydispersed nanocluster crude product, i.e., $Au_x(SR)_y$ with proper size distribution was first prepared. In step II, the polydispersed crude product obtained from step I was converted into a single-sized nanocluster through etching with excess thiol at elevated temperatures. By carefully tuning the initial size distribution and rational selection of the different thiolate ligands, the aforementioned gold nanoclusters have been obtained with molecular purity in the present study. The detailed synthetic procedures of the gold nanoclusters can be found in the Supporting Information.

Specimens for STEM observation were produced by pipetting 6 µL of dilute solutions of a given nanoparticle sample in dichloromethane onto ultrathin carbon-coated 400 mesh Cu TEM grids (Ted Pella). After drying, requiring only a second or two, the samples were stored under roughing vacuum to outgas (at least 18 h) until taken to the microscope for imaging. No appreciable changes in particle size and shape were observed over the course of STEM examination, indicating sufficient stability to the electron beam for the imaging conditions used.

2.2. Instrumentation

The electron microscopy for this study was performed on a conventional JEOL JEM2100F TEM/STEM operated at 200 kV and equipped with a Schottky field-emission gun (FEG) and an analytical polepiece. Imaging was performed using the built-in JEOL annular dark-field (ADF) and bright-field (BF) STEM detectors and a Gatan SC200D Orius CCD camera. The convergence semiangle of the probe was 13.8 mrad, yielding a ∼2 Å probe size. A 10 µm (#4) condenser aperture was inserted for detector mapping, while a 40 µm (#3) aperture was used for specimen imaging. The inner and outer collection semiangles of the ADF detector were