Intensity calibration and atomic imaging of size-selected Au and Pd clusters in aberration-corrected HAADF-STEM

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Abstract. We report an experimental calibration of the exponent $\alpha$, which relates intensity ($I$) and atomic number ($Z$) in HAADF-STEM imaging. The method employs size-selected Au$_{923}$ and Pd$_{923}$ clusters in an aberration-corrected 200 kV microscope. We find $\alpha = 1.46 \pm 0.18$ for an inner collection angle of 62 mrad. The value of $\alpha$ is needed in the quantitative compositional analysis of, e.g., bimetallic nanostructures. The atomic structures of the two examples of size-selected magic-number clusters are also reported.

1. Introduction

High Angle Annular Dark Field (HAADF) imaging [1-4] in the aberration-corrected Scanning Transmission Electron Microscope (STEM) has established itself as a powerful method to obtain structural and chemical information with atomic resolution [5-8]. An appealing feature of the technique is that the measured image intensity ($I$) follows a simple relationship with specimen thickness ($t$) and atomic number ($Z$), $I \sim tZ^\alpha$, in the limit of sufficiently thin samples. The exponent $\alpha$ would be 2 for pure Rutherford scattering, although this value is reduced by the electronic screening of the nuclear charge [9]. In practice, the exponent $\alpha$ obtained in the STEM will vary with the experimental parameters employed (mainly the inner collection angle). An exact value of $\alpha$ is required for quantitative HAADF imaging, e.g. the determination of chemical composition in bimetallic clusters. A precise experimentally calibration of $\alpha$ is however not trivial, due to the difficulties of accurately measuring the sample thickness inside the microscope. For example, a difference of 25% is found when convergent beam electron diffraction and low-loss electron energy spectra are used to measure the film thickness for an SrTiO$_3$ sample [10]. In this study, we report an experimental calibration of the exponent $\alpha$ based on statistical HAADF intensity analysis of size-selected Au and Pd nanoclusters, specifically Au$_{923}$ and Pd$_{923}$ clusters that were generated in a cluster beam source with a mass-selection accuracy of 5%. The atomic imaging and structural comparison of these two examples of magic number clusters is also presented, with an aim to provide a reference for understanding some morphology/structure-relevant catalytic phenomena of nanoclusters.

2. Experimental method

Size-selected Au$_{923}$ and Pd$_{923}$ clusters were prepared in a magnetron-sputtering, gas-condensation cluster-beam source coupled to a lateral time-of-flight mass filter (M/\Delta M=20 nominally) [11-13]. An
impact energy (500 eV per cluster) in the “soft-landing” regime (<1 eV per atom) was used when depositing the clusters onto amorphous carbon films supported by Cu TEM grids. STEM imaging was performed in a 200 kV JEM2100F STEM (JEOL) with a spherical aberration corrector (CEOS). The signal was collected by a high-angle annular dark-field detector with inner and outer collection angles of 62 and 164 mrad at a probe convergence angle of 19 mrad.

3. Results and discussion

HAADF-STEM imaging of the Au_{923} and Pd_{923} clusters was performed under the same experimental conditions to allow for direct intensity comparison. Figure 1 presents examples of HAADF images of the two kinds of clusters. The intensity difference between the two clusters can be clearly seen and is attributed to their widely different atomic numbers (Au, 79; Pd, 47).

![Typical HAADF-STEM images of (a) Au_{923} and (b) Pd_{923} clusters on amorphous carbon films acquired under the same imaging conditions (see text). The same greyscale settings (brightness/contrast) were also used in both cases to allow direct visual comparison of the relative intensities.](image)

The quantitative integrated intensity analysis for the two kinds of cluster is performed using “as – recorded” HAADF images. The integrated intensity from a circular annulus around the cluster is taken as the background intensity. The annulus has the same normalized area as the projected cluster area. After the background subtraction, the intensity measurement of the two cluster ensembles is obtained, figure 2. It can be seen that the peak intensity values of the two clusters are well separated. The calculated mean intensities and corresponding standard deviations are 2.42 ± 0.13 for the Au_{923} and 1.10 ± 0.09 for the Pd_{923} clusters, in arbitrary unit. Since the two reference clusters contain the same number of atoms, and identical experimental conditions were used for recording HAADF images, the exponent \( \alpha \) is then simply derived from an intensity comparison using the relationship \( I_{\text{Au}}/I_{\text{Pd}} = (Z_{\text{Au}}/Z_{\text{Pd}})^\alpha \). By this method, we obtained the value \( \alpha = 1.46 \pm 0.18 \).

Obviously, the experimental value of the exponent \( \alpha \) is much smaller than the value for true Rutherford scattering (\( \alpha = 2 \)). We found similar behavior in our uncorrected HAADF-STEM relative intensity measurements of Au_{923} and Pd_{923} clusters [14]. We identified the inner collection angle of the detector as chief culprit – a value of \( \alpha \) as large as \( \sim 1.8 \) was obtained when the inner collection angle was increased to 103 mrad. Measurements of \( \alpha \) as a function of scattering angle in the new aberration-corrected instrument are in progress. In general, we find that very large collection angles are problematic for the quantitative measurements, especially for thin samples, due to poor signal to noise ratios (SNR). The significant contribution from the background noise will undermine the measurement precision. Thus, collection angles such as the one used in the present experiment, where the value of \( \alpha \) may be far from 2, are perhaps best suited to quantitative analysis [15]. In consequence, an accurate calibration of the value of \( \alpha \) will be critical for some kinds of compositional analysis.
One question that might arise is – what is the effect of diffraction contrast on the value of \( \alpha \) obtained? Since the measurement depends on the integrated cluster intensities this is a fair question. However, considering that in this study the exponent \( \alpha \) is calibrated by using the statistical HAADF intensities, which are obtained by averaging over a large number of clusters that locate on the amorphous carbon films with random orientation, the effect of orientation and thus diffraction contrast should be minimal. This is also reflected in the previous experimental calibration of mass-intensity relationship for \( \text{Au} \) clusters [5], which demonstrated a linear relationship between the integrated HAADF intensity from the clusters and the number of constituent atoms up to at least 1000, indicating that the influence of the diffraction contrast is trivial for the small clusters.

It is believed that the catalytic activity (and selectivity) of nanoparticles depends on their size and geometric structure [16-17]. Thus, while the atomic structure of the size-selected \( \text{Au} \) and \( \text{Pd} \) clusters is not our focus here, we show in figure 3 examples of the measured high-resolution STEM images of these particles. The \( \text{Au}_{923} \) and \( \text{Pd}_{923} \) clusters have significantly different internal structures, even though they have the same nuclearity (size). In general, the \( \text{Au}_{923} \) clusters show more ordered atomic arrangements than \( \text{Pd}_{923} \). Three typical structures are observed for \( \text{Au}_{923} \) – decahedron, FCC polyhedron and icosahedron, while \( \text{Au} \) adatoms on the cluster facets are also observed. The Marks-like decahedron and FCC polyhedron are the dominant structural forms, and are illustrated in figure 3(a)-(c). By contrast, \( \text{Pd}_{923} \) often show more disordered structures; an example image and corresponding FFT transform are shown in figure 3(d). In some cases, icosahedral-type motifs can be observed, as illustrated in figure 3(e)-(f). The cluster presents rather like a fivefold-axis orientated icosahedron according to the ring features observed, but it is difficult to match the data precisely with a STEM simulation obtained using a standard icosahedral atomic model.

4. Conclusion
We have calibrated the exponent \( \alpha \) in the formula \( I \sim Z^\alpha \), applicable to HAADF imaging in the (aberration-corrected) STEM, using size-selected \( \text{Au}_{923} \) and \( \text{Pd}_{923} \) clusters. We find \( \alpha = 1.46 \pm 0.18 \). This value is far from that defined by ideal Rutherford scattering (\( \alpha=2 \)), which is highly relevant to compositional analysis. The atomic structures of the \( \text{Au}_{923} \) clusters show more ordered atomic arrangements than the \( \text{Pd}_{923} \) clusters.
Figure 3. Representative HAADF-STEM images (5 × 5 nm) of (a)-(b) Au$_{923}$ clusters and (d)-(e) Pd$_{923}$ clusters deposited on amorphous carbon films. The inset in (d) is an FFT power spectrum. (c) and (f) are 3D colour plots of (b) and (e), respectively. The surface Au or Pd adatoms marked by arrows show the relationship between the orientations of the corresponding 2D and 3D images. The circle in (e) marks a ring feature observed in the icosahedra-like Pd$_{923}$ cluster.

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