

Counting the Atoms in Supported, Monolayer-Protected Gold Clusters

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Thiolate-protected Au_N nanoparticles (containing N gold atoms) have attracted much attention due to their unique electronic, optical, and catalytic properties,¹ as well as the recent revolutionary discovery of the binding motif of the Au atoms and protecting ligands.² However, accurate mass determination for particles composed of only a few tens of atoms can be challenging. For example, compounds which were first assigned as Au₃₈(SC₂Ph)₂₄ clusters, based on laser desorption-ionization time-of-flight (LDI-TOF) mass spectrometry, thermogravimetric analysis (TGA), and UV–visible spectra, etc.,^{3a,b} were recently reassigned as Au₂₅(SC₂Ph)₁₈ clusters via more sensitive high-resolution electrospray ionization mass spectrometry (ESI-MS).^{3c} Similarly, Au₂₅(SR)₁₈ clusters^{3d} were also initially assigned as Au₂₈(SR)₁₆ clusters,^{3e,f} although in this case ESI-MS was used as the original characterization tool. Moreover, the above techniques look at the ensemble of all the clusters in solution and thus any residual polydispersity or aggregation⁴ can skew the results. In this paper, we present the mass determination of supported, hexanethiolate monolayer-protected, nominally Au₃₈ (MP-Au₃₈) nanoclusters via quantitative high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM), using size-selected Au clusters as mass standards.⁵ We exploit a calibration of the exponent *n* in the Z^{*n*} (*Z*, atomic number) dependent HAADF intensity vs the camera length (acceptance angle)⁶ to account for the contribution of the both metal atoms and ligands to the intensity. Assuming 24 hexanethiolate ligands,^{7a} we find that the MP-Au₃₈ monomers contain 38 ± 2 Au atoms.

Hexanethiolate protected Au₃₈ clusters were prepared using the optimized Brust–Schiffrin two-phase method as previously reported.^{7b} The prepared cluster solution was then dried under nitrogen for storage and transfer. Toluene was used to disperse the clusters, and a small drop of the resulting MP-Au₃₈ solution was drop-cast onto one-half of each of a set of Cu TEM grids covered with an amorphous carbon film. Size-selected Au_N clusters were deposited onto the other half of the same TEM grids. The Au_N clusters, with *N* = 25, 38, and 55, were produced in a magnetron sputtering, gas aggregation cluster source and mass selected (*M*/*ΔM* = 20) by a lateral time-of-flight mass filter.⁸ The quantitative HAADF-STEM investigation was performed in a field-emission scanning transmission electron microscope, a 200 kV FEI Tecnai F20, with a high-angle annular dark-field detector (Fischione Model 3000).

Figure 1a shows a representative HAADF-STEM image of MP-Au₃₈ clusters. It can be seen clearly that the observed clusters display a rather wide size distribution, possibly due to cluster aggregation on the TEM grid during drying.⁹ We performed a statistical analysis of the integrated HAADF intensities of more than 100 particles with diameters of 1.1 to 2 nm, as shown in Figure 1b. This shows

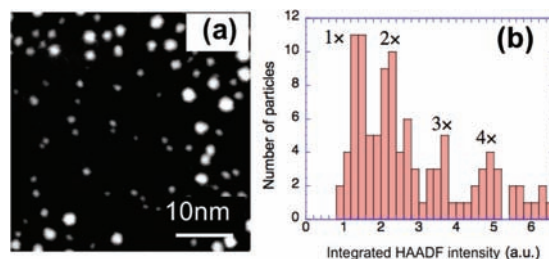


Figure 1. (a) Typical morphology of MP-Au₃₈ clusters obtained by HAADF-STEM. (b) Histogram of integrated HAADF intensity for 105 particles with smaller diameters.

that the intensity distribution is consistent with discrete multiples of the intensity of the smallest clusters (monomers). We therefore conclude that the large aggregates are mainly formed as a result of the coalescence of the monomers, in line with previous studies of monolayer-protected Au₁₃ clusters.¹⁰

To determine how many Au atoms the monomers (the first peak in the intensity distribution) contain, size-selected Au₃₈, Au₂₅, and Au₅₅ clusters are each used as a mass balance in quantitative HAADF-STEM. Depositing both kinds of clusters on the same TEM grid, as shown in Figure 2a, minimizes the effect of variable electron optical conditions on the measurement precision. Representative HAADF images for size-selected Au₃₈ and MP-Au₃₈ clusters are shown in Figure 2b and c. It can be seen that the size-selected Au₃₈ clusters have a rather uniform size distribution compared with the MP-Au₃₈ clusters as a result of the high-precision mass selection by the cluster source. The quantitative integrated HAADF intensity statistics for the two kinds of clusters are shown in Figure 2d. The data for the MP-Au₃₈ clusters contain only the monomers, an example of which is indicated by the arrow in Figure 2c. The data fits Gaussian functions quite well. We used the peak intensities of the fitting functions instead of averaged intensities in the quantitative analysis, which follows, to effectively attenuate the contribution of the very small proportion of on-axis orientated clusters with non-negligible diffraction contrast. In the case of such MP clusters we must take into account the intensity contribution from the organic ligands. This can be done by utilizing the power law dependence of the imaging intensity on the atomic number *Z*.

As shown in Figure 2d, the integrated HAADF intensity for the MP-Au₃₈ monomers is distinctly larger than that for size-selected Au₃₈ clusters. The peak intensity ratio for MP-Au₃₈ monomers versus size-selected Au₃₈ clusters was measured to be $I_{MP}/I_{Au38} = 1.24$. Thus, the equivalent number of Au atoms in the MP-Au₃₈ monomers is $1.24 \times (38.0 \pm 1.0) \approx 47.1 \pm 1.2$. Size-selected Au₂₅ (Figure 2e) and Au₅₅ clusters (Supporting Information Figure S1) were also used to weigh the MP-Au₃₈ clusters to verify the

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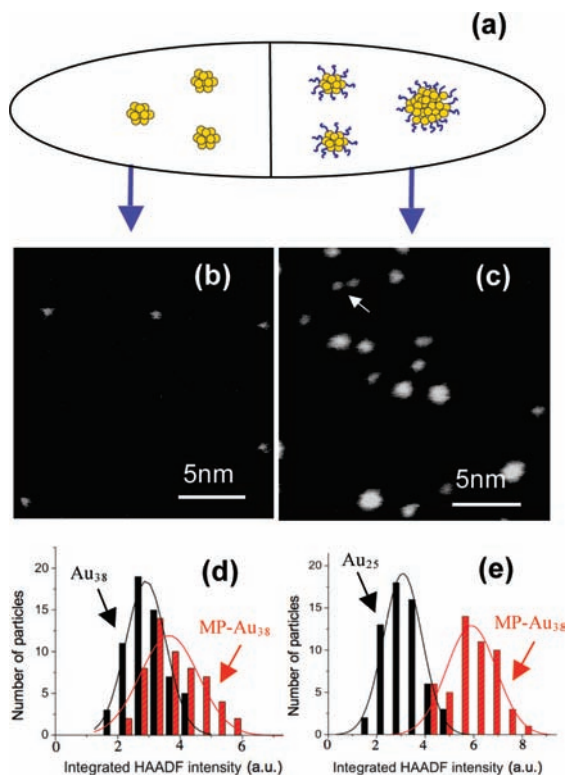


Figure 2. Weighing MP-Au₃₈ clusters using size-selected Au clusters. (a) Both clusters are codeposited on the same TEM grid. Typical HAADF images of (b) size-selected Au₃₈ clusters and (c) MP-Au₃₈ clusters (with a monomer arrowed). Integrated HAADF intensities of (d) MP-Au₃₈ monomers plus size-selected Au₃₈ clusters, (e) MP-Au₃₈ monomers plus Au₂₅ clusters.

measurement. The equivalent numbers of Au atoms in the MP-Au₃₈ monomers thus obtained are 47.3 ± 1.1 and 46.2 ± 1.2 , respectively.

Part of the integrated electron scattering intensities is due to the organic ligands. The molecular formula for the MP-Au₃₈ clusters, as determined by gas phase mass spectrometry, is Au₃₈(SC₆H₁₃)₂₄.^{7a} The relationship between the exponent ‘*n*’ in the *Z*^{*n*} dependent HAADF intensity and the camera length (calibrated for Au and Pd clusters) gives $n = 1.32 \pm 0.12$ for the camera length (285 mm) used in this experiment.⁶ Then the equivalent number (*E*) of Au atoms due to the intensity of the S, C, and H in the ligands is

$$E = N_S \left(\frac{Z_S}{Z_{Au}} \right)^n + N_C \left(\frac{Z_C}{Z_{Au}} \right)^n + N_H \left(\frac{Z_H}{Z_{Au}} \right)^n = 8.7 \pm 2.6 \quad (1)$$

Here, $N_S = 24$, $N_C = 144$, and $N_H = 312$ denote the number of S, C, and H atoms in the molecular formula, and $Z_{Au} = 79$, $Z_S = 16$, $Z_C = 6$, and $Z_H = 1$, the atomic numbers. After the ligands’ contribution is subtracted, the MP-Au₃₈ clusters are found to contain 38.6 ± 2.8 , 38.4 ± 2.9 , and 37.5 ± 2.9 Au atoms, when size-selected Au₂₅, Au₃₈, and Au₅₅ clusters are used as a mass balance,

respectively. Thus, by averaging, we conclude that the MP-Au₃₈ monomers contain $38.2 \pm 1.7 \approx 38 \pm 2$ Au atoms.

In summary, we have determined the nuclearity of deposited, monolayer-protected, nominally Au₃₈ clusters via quantitative HAADF-STEM using size-selected clusters as a mass balance. The assumed 24 hexanethiolate ligands are believed to contribute an electron intensity signal equivalent to 8.7 ± 2.6 Au atoms. On this basis the nominal MP-Au₃₈ monomers contain 38 ± 2 Au atoms. This new method of “mass spectrometry on the surface” also readily discriminates between individual clusters and their aggregates.

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Supporting Information Available: Experimental details and Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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