ATOM COUNTING AND ATOMIC STRUCTURE FOR MONOLAYER-PROTECTED GOLD CLUSTERS VIA QUANTITATIVE HAADF- STEM

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Introduction

Nanometre-size, thiolate-protected Au clusters hold great promise for important applications in e.g. catalysis, biosensors and nanoelectronics due to their unique physical and chemical properties [1]. The mass and structural determination of very small clusters is critical to understanding the way the properties depend on cluster size, shape and atomic arrangement. The accurate mass determination of very small nanoparticles has remained challenging. For example, chemically synthesized nanoparticles which were first assigned as $Au_{38}(SC_2Ph)_{24}$ clusters were subsequently reassigned as $Au_{25}(SC_2Ph)_{18}$ clusters after a further investigation using high-resolution electrospray ionization mass spectrometry (ESI-MS) [2]. Moreover, the recent breakthrough in uncovering the bonding motifs of thiolate ligands on Au clusters has provoked particular interest in the structural determination of monolayer-protected clusters, both experimentally and theoretically [3]. So far the main experimental technique used for characterizing the atomic structures of Au nanoclusters is X-ray crystallography; however, its extensive application is restricted by the practical difficulty in obtaining monodispersed, diffraction-quality cluster crystals. Here, we summarize the accurate mass determination of monolayer-protected nominally Au_{38} clusters (MP-Au_{38}) [4] using size-selected clusters as novel mass standards [5], via quantitative high angle annular dark field imaging in the scanning transmission electron microscope (HAADF-STEM). In addition we demonstrate the successful application of the electron microscopic technique, which has no requirements of cluster crystallization and monodispersity, as a subnanometer structural probe of monolayer-protected Au_{38} (MP-Au_{38}) clusters [6].

Experimental

Hexanethiolate-protected Au_{38} clusters were synthesized using the optimized Brust–Schiffrin two-phase method. Size-selected Au clusters were produced with a He gas condensation method and mass-selected by a lateral time-of-flight mass spectrometer (M/ΔM=20). The HAADF-STEM investigation was performed with a 200 kV FEI Tecnai F20 instrument for the mass determination of MP-Au_{38} clusters and a JEOL JEM2100F instrument with spherical aberration corrector (CEOS) to probe the atomic structures of the clusters. For the latter work, to minimize the effect of electron beam irradiation on the stability of the MP-Au_{38} clusters, we developed the optimized imaging conditions as follows: (i) STEM images were acquired with a low electron dose ($\sim 6.9\times10^3$ electrons $Å^{-2}$); (ii) a LN_2 cooling sample holder (Gatan HC3500) was used (down to -164 °C); (iii) the samples were coated with a thin film of carbon to inhibit a beam-induced reconstruction.

Results and Discussion

Our first HAADF investigation of MP-Au_{38} clusters displayed a rather wide size distribution [4]. We performed a statistical integrated intensity analysis for these clusters, which showed that the intensity distribution was consistent with discrete multiples of the intensity of the smallest clusters. This indicated that the large particles were mainly formed as a result of the coalescence of the smallest clusters (monomers). Then, to determine whether the monomers did contain 38 Au atoms, we performed a quantitative HAADF investigation by co-depositing MP-Au_{38} clusters and size-selected Au clusters on the same TEM grid. The statistical integrated HAADF intensities of the two kinds of clusters are shown in Fig. 1. The peak intensity ratio between them was measured, yielding $I_{MP}/I_{Au38} = 1.24$. The equivalent number of Au atoms in the MP-Au_{38} monomers can then be obtained, $1.24 \times (38.0 \pm 1.0) \approx 47.1 \pm 1.2$. We also used size-selected Au_{25} and Au_{55} clusters as mass standards to "weigh" the MP-Au_{38} clusters in this way, which shows that the equivalent number of Au atoms in the MP- Au_{38} monomers is 47.3 ± 1.1 and 46.2 ± 1.2, respectively. However, part of the integrated electron scattering intensity is due to the organic ligands. By utilizing the power law dependence of the HAADF intensity on the atomic number Z, we calculated the contribution of the ligands in the $Au_{38}(SC_6H_{13})_{24}$ clusters (the molecular formula determined by gas phase mass spectrometry). This showed that the intensity due to the ligands was equal to that of 8.7 ± 2.6 Au atoms. Thus, after the

ligands' contribution is subtracted, the MP-Au_{38} monomers were found to contain 38 ± 2 Au atoms on average.

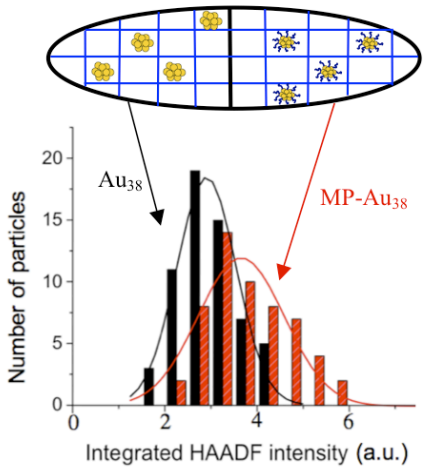

Fig. 1 Statistical integrated HAADF intensities obtained for size-selected Au_{38} clusters and MP-Au_{38} clusters which were co-deposited on the same TEM grid.

The structural investigation of the MP-Au_{38} clusters via aberration-corrected STEM employed optimized experimental conditions (see above). The serial acquisition of HAADF images showed that the projected shape of the clusters is generally retained between frames although structural fluctuations can still be observed, as shown in Fig. 2. Our statistical analysis shows that some clusters display a circular projection shape, like the cluster shown in Fig. 2(a), while, more interestingly, many clusters show a prolate shape with large aspect ratios (up to ~ 1.5), like the one in Fig. 2(b). The prolate shape is found to be consistent with STEM simulations for a "divide and protect" structural model of lowest energy [3]. This calculated structure, which contains a bi-icosahedral Au_{23} core, is also in good agreement with X-ray diffraction results [3]. The calculations also show that similar atomic arrangements of gold-thiolate shell in this model have only slightly different energies. Therefore, the structural fluctuations we observe in the serial HAADF investigations may correspond to structural transitions between these isomers induced by the electron beam.

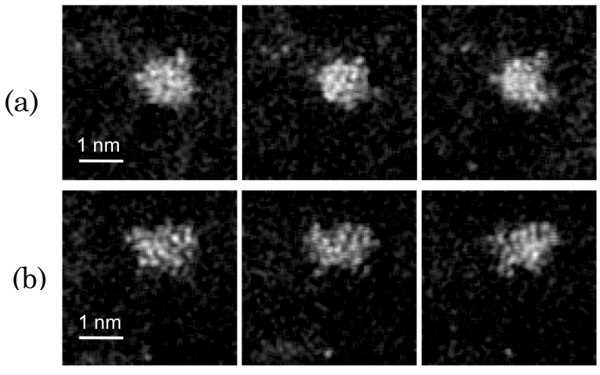

Fig. 2 Representative series of HAADF images (0.2 s/frame) under optimized experimental conditions. (a) shows a cluster with circular projected shape and an aspect ratio of 1.08; (b) shows a cluster with a prolate projected shape and an aspect ratio of 1.52.

Conclusion

In summary, we have determined the nuclearity of (alkanethiol) monolayer-protected nominally Au_{38} clusters using size-selected clusters as mass standards in the STEM. After the contribution due to the ligands is accounted for, the MP-Au_{38} clusters are found to contain 38 ± 2 Au atoms. Further, we have demonstrated the viability of Cs-corrected HAADF-STEM as a sub-nm structural probe of the MP-Au_{38} clusters. The establishment of optimized imaging conditions allowed us to observe directly prolate cluster shapes, in line with theory, as quantified by statistical analysis of the shape population for the MP-Au_{38} clusters.

References

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