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Probing the Atomic-scale Structure of Monolayer-Protected Au_{38} Clusters

Z.W. Wang,* O. Toikkanen,** B.M. Quinn,** J. Akola,***, O. Lopez-Acevedo,*** H. Häkkinen,*** and R.E. Palmer*

*Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, B15 2TT, U.K.
**Department of Chemistry, School of Science and Technology, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland
***Nanoscience Center, Departments of Physics and Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland

Nanometer-size, thiolate-protected Au clusters may have important applications in future industry, due to their unique physical and chemical properties and facile synthesis on a large scale [1]. The atomic-scale structural determination of very small clusters is critical to understand the dependence of the performance on sizes and synthetic conditions, etc.
Recently the atomic structures of thiolate-protected Au_{102} and Au_{25} clusters have been successfully determined via X-ray crystallography [2-4], which has shed light on the "staple" bonding motif between thiolate ligands (shell) and Au atoms (core) [5-6]. However, the extensive application of X-ray crystallography as a characterization approach has been impeded because the production of sufficiently high-quality cluster crystals from a solvent is very difficult in practice. In this paper, we present the structural characterization of individual monolayer-protected Au_{38} (MP-Au_{38}) clusters using the aberration-corrected scanning transmission electron microscopy (STEM) technique [7]. The obvious benefit of this approach is that cluster monodispersity is not necessary.

The synthesis of hexanethiolate protected Au_{38} clusters, using the optimized Brust-Schiffrin two-phase method, was reported previously [8]. TEM samples were prepared by drop-casting the cluster solution onto Cu grids coated with an amorphous carbon film. The atomic-scale structural investigation was performed using a sub-Ångstrom resolution JEM2100F STEM with spherical aberration corrector (CEOS GmbH). The signal was collected by a High-Angle Annular Dark-Field detector (HAADF), with inner and outer collection angles of 62 and 164 mrad in these experiments.

Fig. 1 shows a representative HAADF-STEM image of MP-Au_{38} clusters. Most of clusters measured have a size of ~1.0 nm in diameter. Mass spectrometry analysis performed via quantitative HAADF-STEM, using size-selected Au clusters as mass standards, shows that they contain 38 ± 2 Au atoms [9]. Large particles, one of them indicated by the arrow, can also be seen, which were shown to be aggregates of the MP-Au_{38} monomers formed during the solvent drying on the TEM grids [9]. A high-resolution image is given in the inset (bottom-right) which displays the atomic-resolution structure of the monomer. However, the precise structural co-ordinates are difficult to obtain because the particles are not stable under the electron beam. The reconstruction/rearrangement of the clusters is found to occur in serial-acquisition experiments.

DFT calculations were performed to find the structures with the lowest potential energies. Based on the motif of "divide and protect", two model structures were considered, which we term " divide and protect" [10] and "dumbbell" [11], respectively. The latter is favored. For comparison, the model structure based on the traditional protection motif was also acquired, called " simple cigar". Based

on the three structural models, we conducted the HAADF-STEM imaging simulation using the multislice method, and found the projections of the "dumbbell" cluster structure contain an aspect ratio of ~1:1.3, which make it easy to be distinguished from the others.

Provided by the calculation and simulation, further structural investigations were performed using experimental conditions optimized to minimize the instability of the clusters under the electron beam. The samples were coated with carbon films, and the STEM investigation was performed at very low incident electron dose (~ 7.7×10^3 electrons /Å^2), with a LN_2 sample holder cooling the sample down to -164 °C. Using these methods, we obtained serial-acquisition images at a fast speed (5 frames /s). By comparing these serial images, we found that most of the clusters retain their shapes between frames. 7 out of 40 clusters were observed to have an elongated shape, consistent with the projection of "dumbbell" structural model. Thus, the theoretically predicted preference for a prolate low-energy structure was confirmed in the experiment. Further work is in process to reconstruct the three-dimensional shape of the clusters.

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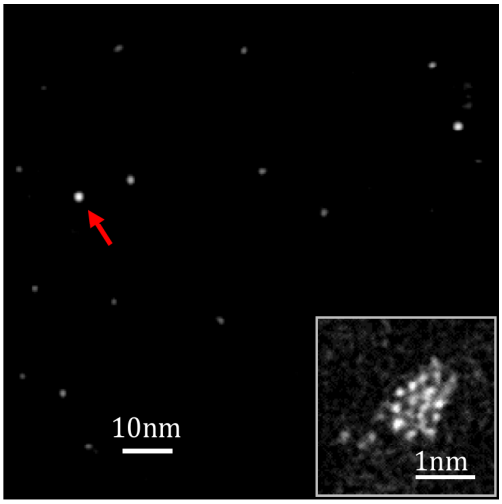

FIG. 1. Typical HAADF-STEM image of MP-Au_{38} clusters. The cluster indicated with the arrow is an aggregate from the monomers. The inset displays a high-resolution atomic structure image of MP-Au_{38} monomer.

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