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Can We Solve the Atomic Structure of Small Au clusters by HAADF-STEM?

Z.W. Wang, F. Yin, A. Bruma, and R.E. Palmer

Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, B15 2TT, U.K.

Aberration-corrected scanning transmission electron microscopy (STEM) is a potentially powerful probe of the atomic structure of small clusters and has been successfully applied to the determination of the 3D, atomic structures of supported, size-selected Au_{309} clusters [1]. Small clusters (< 100 atoms) are especially interesting due to the high catalytic activity and selectivity associated with their high surface to volume ratio [2-4]. The geometric structures of the small clusters have been mostly studied in the gas phase, via indirect methods, e.g. photoemission or vibrational spectroscopy or electron diffraction [5-7]. There are no reports of their atomic structure of such small particles on the supports required for applications in catalysis, photonics or biotechnology. The main challenge for STEM is the instability of the small clusters under the electron beam. Quasi-melting or atomic rearrangement/reconstruction have been proposed to explain such behavior [8]. In this paper we report a systematic search for the causes of the instability and solutions which effectively attenuate the structural fluctuations of small clusters.

Size-selected Au_{55} and Au_{58}, the model clusters employed in this study, were deposited onto Cu grids coated with amorphous carbon films using a radio-frequency magnetron-sputtering gas-condensation cluster source. The size-selection was performed with a novel, lateral time-of-fight mass filter with a resolution of $M/\Delta M=20$ [9-11]. High angle annular dark field (HAADF) images were acquired using a 200 kV JEOL instrument (JEM-2100F) with a spherical aberration probe corrector (CEOS GmbH).

Fig. 1(a) shows the serial-acquisition of HAADF images of Au_{55} clusters, from which the change of shape and structure can be clearly seen. The first concern is whether the surface atoms of the small clusters can survive knock-on (i.e. detachment) due to the 200 keV electrons. Thus, we performed an integrated intensity analysis of serial HAADF images of the Au_{55} clusters, as shown in fig. 2. Since no obvious intensity decrease can be seen, this illustrates that the sputtering (detachment) of surface atoms does not occur even in the case of these small Au clusters.

It is believed that beam heating inevitably occurs as a result of inelastic scattering [8]. Thus, we also took the serial images (of Au_{58} clusters) using a cryogenic sample holder (Gatan HC3500), which cools the sample down to -164 °C. The data analysis shows that structural fluctuations can still be observed clearly, which indicates that beam heating is not a major cause of the atomic reconstruction we see.

We conclude that the observed structural fluctuations are mainly the result of the intra-cluster knock-on effects driven by the energy electrons (i.e. momentum transfer). As a result, two methods, reduced (optimal) electron dose and carbon coating, have been developed to minimize the reconstruction of the clusters under the electron beam. An optimal electron dose means the incident electron dose is decreased as low as possible before atomic contrast information is lost. Fig. 1(b) shows that the structural fluctuations can be partially attenuated under the optimal dose conditions.

The stability of the clusters can be further improved when this approach is combined with the carbon-coating method.

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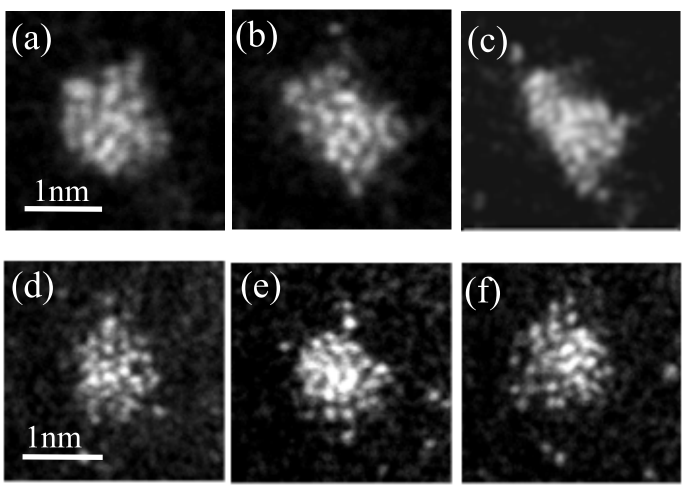

FIG. 1. Serial-acquisition of HAADF-STEM images of Au_{55} clusters. (a), (b) and (c), serial images of cluster A at the normal incident electron dose (6.9×10^4 electrons /Å^2); (d), (e) and (f), serial images of cluster B at the optimal incident electron dose (7.7×10^3 electrons /Å^2).

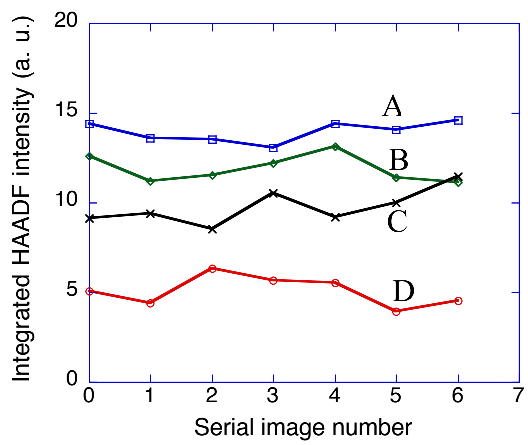

FIG. 2. The integrated intensity for clusters A, B, C and D in the serial HAADF-STEM images of Au_{55} clusters.

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