‘Ex-Situ’ Annealing and Structural Transformations in Gold Nanoparticles

K.E. MacArthur, N.P. Young, J.W. Critchell, A.I. Kirkland
Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK
E-mail: katherine.macarthur@materials.ox.ac.uk

Abstract. The atomic structure and morphology of gold nanoparticles have been studied using High-Resolution Transmission Electron Microscopy (HRTEM). The structural transformations of these particles have been probed through ex-situ annealing experiments, yielding population statistics on structure as a function of particle size and annealing temperature. The results show that for an original structurally heterogeneous particle population, there is a rise in the percentage of particles with the decahedral morphology as annealing temperature is increased. This can be correlated with a reduction in the number of icosahedral particles as a function of annealing temperature. HRTEM imaging following low temperature annealing reveals a range of modified and distorted decahedral particles, giving insight into the temperature threshold of the solid state transformation and the microstructural processes occurring.

1. Introduction

The structure of metallic nanoparticles continues to attract considerable interest due to its fundamental importance in relation to their physical and chemical properties and the application of such properties to technologies such as catalysis. A detailed understanding of the thermodynamics of specific nanoparticle systems is now becoming possible through combined in-situ experiments and detailed structural calculations [1]. However, the behavior of real catalysts under industrially relevant conditions continues to be an area of interest. Factors such as high-temperature annealing, reactive gas environments and contaminants differentiate industrial scenarios from high-vacuum experimental studies on model catalysts or the modeling of idealized free-standing nanoparticles. In the present study we report initial results of variable temperature experiments on gold nanoparticles using ex-situ annealing under argon followed by HRTEM characterisation. This study aims to compare structural transformations initiated through ex-situ annealing with those observed using micro-heater experiments in the TEM [1,2]. Ex-situ experiments also yield better statistics on particle transitions.

2. Experimental Method

Our experiments used colloidal gold particles in the size range 6-20 nm. Colloidal suspensions prepared as described previously [1] were initially size separated into three classes and subsequently studied independently. Particles were drop-cast from aqueous solution onto holey carbon coated copper TEM grids. Ex-situ particle heating was carried out using a tube furnace. Specimen grids were placed in a ceramic boat and inside an alumina furnace tube. The ends of the tube were sealed and the system evacuated using a rotary pump to ~10^-5 psi, prior to the admission of argon gas and
controlled heating. HRTEM was performed using a JEOL JEM-3000F operating at 300kV. Particle structures were initially identified through inspection of the particle outline shape and symmetry. Multislice simulations (using the JEMS software) of particles of different structures in various orientations were also performed to enable comparison with the experimental HRTEM data as an aid to structural classification. There is not space to include the figures here however previously published multislice simulations can be found in [3].

3. Results and Discussion

The sizes of particles from the different colloidal suspensions were first determined from HRTEM images as detailed in the table (1). Size measurements were taken directly from HRTEM images with an average diameter being estimated from multiple measurements of individual particles. Examples of the equilibrium structure of nanoparticles at room temperature are shown in figure 1. All specimens showed a mixture of icosahedral (Ic), decahedral (Dh) and FCC crystalline particles in various orientations. Many of the individual FCC particles were twinned, others were single crystals and some displayed a trigonal lamellar morphology.

|                | Mean Particle Size (nm) | Standard Deviation (nm) | Minimum Size (nm) | Maximum Size (nm) |
|----------------|-------------------------|-------------------------|-------------------|------------------|
| Suspension (A) | 10.8                    | 1.7                     | 6.0               | 16.3             |
| Suspension (B) | 14.2                    | 1.6                     | 10.4              | 21.2             |
| Suspension (C) | 15.8                    | 2.7                     | 7.4               | 22.8             |

Table 1: Summary of the particle sizes witnessed for each colloidal suspension.

![Figure 1: Examples of images of gold nanoparticles obtained during the HRTEM study with multislice simulation image of the same particle orientation (view direction given relative to orthogonal coordinates) inset. All images were taken at room temperature. (a) An icosahedral particle viewed along the <112> axis. (b) A decahedral particle orientated close to the <110> axis. (c) A single crystalline FCC particle oriented along <110>.](image)

The percentage of particles in each main structural category was calculated for the three different colloidal preparations by analysis of single particle HRTEM images. A sample of images of 100 particles prior to heating and after each annealing temperature was recorded. Preliminary investigations of the particle dispersion on the holey carbon support membranes ensured that single particles were well separated. This is particularly important to avoid particle coalescence, interaction and ripening during the annealing stages. Each specimen was then heated in the tube furnace to 100°C under an atmosphere of argon. The total annealing time was 250 minutes after which specimens were removed and new images recorded. This process was also repeated for an annealing temperature of 250°C for 350 minutes. Figure 2 shows plots of the percentage of particles from each colloidal sample for particular morphology as a function of annealing temperature. A clear increase in the occurrence of decahedral particles is evident in figure 2(a) and an increase in the number of particles adopting this
structure as a function of temperature was identified for all three sets of colloids. Figure 2(b) shows a decrease in the occurrence of icosahedral particles across all three sets of colloids during the same heating program. The percentage increase in decahedral particles and decrease in the percentage of icosahedral particles observed are comparable in magnitude (within statistical errors) for any one colloidal preparation across the temperature range studied. Figure 2(c) shows a subset of decahedral particles taken from figure 2(a) and discriminates between those decahedral particles which display a clear, ordered decahedral structure and those which are modified or distorted. Modification, in this study, is defined as a significant deviation from the accepted conventional decahedral structure of five distorted FCC tetrahedral units sharing a common vertex. The more commonly observed distortions and modifications included a five-fold axis shifted from the centre of the particle towards one edge, additional twining of a decahedral particle, the occurrence of bi-decahedral particles with two separate axes of five-fold symmetry, and particles showing co-existing icosahedral and decahedral symmetry. Examples of modified decahedral particles are shown in figure 3.

![Figure 2](image)

**Figure 2:** Percentage of the particle population studied which take a particular crystallographic structure as function of annealing temperature. (a) Decahedral particles, (b) Icosahedral particles, (c) percentage of the decahedral subset which display modified structures, (d) FCC particles.

The increase in the percentage of decahedral particles in the size and temperature range studied is consistent with previous in-situ experiments and the calculated phase diagram for nanogold [1]. Our ex-situ annealing studies also show that the decahedral morphology is energetically favorable in an argon atmosphere and the larger population statistics act as confirmation of the previous limited single-particle in-situ studies. Further annealing at discrete temperatures and subsequent cooling back to room temperature for HRTEM observation has identified some of the processes occurring during the transformation from icosahedral to decahedral structures. Annealing temperatures up to 250°C are below the melting point for gold particles of this size and thus, suggests that any transformation must occur in the solid state. A plausible microscopic mechanism has been suggested by Koga [4] based on cooperative slip of the \{111\} planes in the icosahedral structure, allowing realignment of
crystallographic planes and twisting of the 5-fold axis to form a decahedron. However, the energy barriers for such a process are poorly defined and thus the work presented here provides an approximation for the annealing temperature required to overcome such energy barriers.

Figure 3: HRTEM images of modified decahedral particles. (a) Decahedral particle with additional parallel \{111\} twinning. (b) Bi-decahedral particle sharing a common \{111\} twin plane. (c) Particle displaying both decahedral and icosahedral symmetry with a common \{111\} twin plane. (d) Decahedral particle with a non-central 5-fold symmetry axis. Such structures are often formed after incomplete transformations from icosahedra.

Close inspection of decahedral particles present after annealing at 100°C reveals that many of these decahedra adopt a modified structure in comparison to the surveys at room temperature and at 250°C. At 100°C incomplete Ic to Dh transformations are evident as shown by an increased number of decahedral particles showing additional \{111\} twinning, shifted 5-fold axes, or bi-decahedral [5] or combined Dh-Ic symmetry. Figure 2(d) also shows a relatively constant percentage of FCC particles indicating that transformation of the FCC to Dh structure is not favorable at the temperatures used in this study.

Conclusions

The structure of gold nanoparticles in the size range 6 – 20 nm has been investigated through HRTEM and ex-situ annealing under an argon atmosphere. Annealing of particles at 250°C revealed an increase in the percentage of decahedral particles and a correlated reduction in the number of icosahedral particles across all particle sizes studied. This indicates a solid-state structural transformation from the icosahedral to the decahedral structure. Particle annealing at 100°C revealed many decahedral particles with a modified structure including increased \{111\} twinning, shifting of the 5-fold axis to the periphery of the particle and the formation of bi-decahedral particles. This suggests the onset of structural transformation occurs at 100°C or lower, but is not completed until higher temperatures are reached.

References

[1] A.S. Barnard, N.P. Young, A.I. Kirkland, M.A. van Huis, H. Xu, ACS Nano, 3 (2009) 1431
[2] N.P. Young et al. Journal of Physics: Conference Series, 241 (2010) 012095
[3] J.A. Ascencio et al. Surface Science, 396 (1998) 349-368
[4] K. Koga, T. Ikeshoji, K. Sugawara, Physical Review Letters, 92 (2004) 115507
[5] K. Koga, Physical Review Letters, 96 (2006) 115501

Acknowledgements

Colloidal specimens were supplied by Dr. H. Xu of the University of Wisconsin-Madison. K.E.M. thanks Prof. Roy Johnston and Mr Andrew Logsdail of the School of Chemistry, University of Birmingham for providing nanoparticle coordinate files used in the multislice simulations in this work. N.P.Y. acknowledges JEOL (UK) Ltd and EPSRC for financial support.