Variable Temperature Investigation of the Atomic Structure of Gold Nanoparticles

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Abstract. The characterisation of nanoparticle structures is the first step towards understanding and optimising their utility in important technological applications such as catalysis. Using newly developed in-situ transmission electron microscopy (TEM) specimen holders, the temperature dependent atomic structure of gold nanoparticles in the size range 5-12 nm has been investigated. In this size interval, the decahedral morphology has been identified as the most favourable structure at or above room temperature, while particle surface roughening becomes evident above 600°C. An icosahedral transition has also been identified at low temperature in particles under 9 nm in diameter. These experimental results are consistent with recently published temperature dependent equilibrium phase maps for gold nanoparticles.

1. Introduction

The structure of metallic nanoparticles continues to attract considerable interest due to its fundamental importance in relation their physical and chemical properties. These properties are crucial to the commercial exploitation of nanomaterial based technologies in heterogeneous catalysis. However a rigorous understanding of the structure of metallic nanoparticles, particularly as a function of particle size and temperature proves elusive. This situation has arisen through a number of factors pertinent to the physics of nanoparticles; primarily the sensitivity of small particles to the experimental conditions under which they are produced, often yielding non-equilibrium structures, and also the possibility of multiple stable structural configurations for any given size and temperature scenario. Such structural isomers may be closely related in terms of total energy, yielding structurally poly-dispersed populations, making interpretation difficult. Finally, the size of such particles makes experimental verification a challenge in terms of high-resolution in-situ imaging. In the present study we report results of variable temperature experiments on gold nanoparticles using newly designed in-situ TEM holders and compare our findings with contemporary theoretical calculations.
2. Experimental Method

Our methodology employs gold colloids prepared by the reduction of dilute solutions of tetrachloroauroic acid, using maltodextrin to prevent aggregation. Particles are formed in a size range of 5 nm to 12 nm in diameter and were drop-cast from aqueous solution onto suitable TEM supports. For the heating experiments an advanced MEMS micro-hotplate type holder with SiN support membrane was used [1] in combination with a Philips CM300-UT field-emission transmission electron microscope. The low heat capacity of the micro-hotplate allows the temperature of the chip to be varied quickly and with high precision, while producing minimal specimen drift within the microscope. Temperature changes can be controlled with an accuracy of 0.1°C through feedback electronics, while the absolute uncertainty in temperature is estimated at ±30°C due to possible local temperature variations of the substrate and induced beam heating. To investigate particle cooling, a newly designed TEM cryo-holder [2] was used in combination with a JEOL JEM-2200MCO aberration-corrected microscope.

3. Results and Discussion

The first question we address is the equilibrium structure of nanoparticles at room temperature. This was investigated by selecting particles in clearly identifiable crystallographic orientations and steadily heating to ca. 400°C in the CM300-UT microscope whilst recording images at regular temperature increments. The temperature range used was expected to provide sufficient energy for the particles to thermodynamically equilibrate, regardless of their initial structure that may have resulted from kinetic trapping. An example of such a transition is shown in figure 1, where a 7.2 nm diameter particle, with an initial icosahedral structure (figure 1(a)) is heated to 400°C.

![Figure 1](image.png)

**Figure 1:** *In-situ* heating of an individual 7.2nm gold nanoparticle in the CM300-UT. (a) The initial icosahedral structure, close to a <112> projection, at room temperature. (b) The structure observed at 400°C, which corresponds to a decahedron close to a <110> projection. (c) Cooling the particle back to room temperature the decahedral structure is observed to be stable.

At this temperature the structure changes to the decahedral form shown in figure 1(b). No further structural transitions were observed and following gradual cooling back to room temperature the decahedral structure persists. The transition to the decahedral phase was the overwhelming trend in all of our heating experiments, whether this occurred from either an icosahedral, single crystalline or twinned starting structure. Statistically (from 33 individual, isolated particles tracked over a range of temperatures), 88% of the equilibrated nanoparticles adopted a decahedral morphology after heating to 350 - 400°C, while for 12% the as grown structure (almost exclusively icosahedral) persisted. These results indicate that the decahedral phase is energetically preferred at intermediate temperatures around 400°C and also as the room temperature equilibrium structure for gold particles in the size range investigated.
The structure of particles at high temperatures is of particular relevance for catalytic applications where changes in the surface periodicity have a strong correlation with catalytic performance. In order to investigate this, a range of pre-equilibrated particles were heated to around 650°C, with a representative heating series shown in figure 2. Evidence for the formation of re-entrant {111} facets at the particle vertices is shown in 2(c). The onset of this change in surface structure was routinely observed in our study in the temperature range 350°C – 400°C. We propose that the formation of these facets lowers the overall surface energy, offsetting contributions from internal strain and allowing the ordered decahedral motif to persist to higher temperatures. Heating the particle further reveals the onset of additional changes to the surface structure. Figures 2(e) and (f) show the particle at 600°C and 650°C respectively. At these temperatures the particle interior retains discernable decahedral features, while the particle perimeter becomes increasingly smoothed. Since the terminal layers of gold atoms have fewer neighbours, the surface is the likely location for the first signs of melting. While a full liquid melt is not suggested by the current data, the surface is certainly less ordered and resembles an amorphous layer in some locations. On cooling to room temperature, the particle did not recover a pristine decahedral structure; rather it retained the highly distorted shape presumably since insufficient kinetic energy was then available for a further transformation.

**Figure 2:** Controlled heating of a 10.2 nm decahedral particle in the CM300-UT. (a) Room temperature, (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C, (f) 650°C.

A quantitative phase map for gold nanoparticles, based upon relativistic *ab-initio* thermodynamics has been constructed [3], and provides an ideal comparison for the experimental data presented here. The key predictions of the phase diagram in terms of structure of gold particles as a function of temperature are summarised in table 1 below. Particle sizes studied in our experiments are predicted to adopt a decahedral morphology between room temperature and 400°C. The phase diagram predicts surface roughening of particles at 600°C, which is defined as a general deterioration of the surface structure; including melting, defect formation and growth of solid amorphous gold shells. Figure 2(f) shows such effects and is the topic of our continued research.

Having investigated particles at elevated temperature and found good agreement with the above published calculations, we have chosen to investigate the low temperature behavior of the gold particles. Figure 3(a) shows a decahedral nanoparticle imaged at room temperature. The specimen is
then cooled in-situ, and the same particle imaged at the holder base temperature of -173°C. At this temperature this 9 nm particle is seen to revert to an icosahedral morphology. We have reproduced this for similarly sized small particles, however we have also observed that larger decahedra are structurally stable against transitions at low temperature in agreement with the predictions of the phase diagram.

**Table 1:** Summary of results from a recent quantitative phase diagram for gold particles [3] (Ic: Icosahedral, Dh: Decahedral, FCC: single crystalline FCC or twinned, M: Molten, QM: Quasi-molten, SR: Surface roughening)

| Temperature / °C | Size / nm Structure | Temperature / °C | Size / nm Structure |
|------------------|---------------------|------------------|---------------------|
| -200             | 0 – 9 Ic            | 200              | 0 – 2 Ic            |
|                  | 9 – 14 Dh           |                  | 2 – 18 Dh           |
|                  | 14 – 30 FCC         | 18 – 30 FCC      |                     |
| Room Temperature | 0 – 4 Ic            | 400              | 0 - 1.5 Ic          |
|                  | 4 – 15 Dh           | 1.5 – 16.5 Dh    |                     |
|                  | 15 – 30 FCC         | 16.5 – 30 FCC    |                     |
|                  | 600                 | 0 – 2.5 M / QM   | 2.5 – 30 SR        |

**Figure 3:** (a) 9 nm decahedral gold particle, (b) the same particle imaged at -173°C where the structure has changed to an icosahedral structure.

**Conclusions**

The structure of gold nanoparticles in the size range 5 nm – 12 nm has been investigated using variable temperature HRTEM. Heating of particles revealed the decahedral morphology to be preferred between room temperature and 400°C independent of the initial structural configuration. Heating to higher temperatures revealed the onset of surface roughening. Cooling of small particles showed an icosahedral transition. These results provide an experimental verification of a recently published theoretical phase diagram, with the methodologies employed being easily extendable to other systems of catalytic importance.

**References**

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