Truncated-octahedral copper-gold nanoparticles

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Abstract. Observations of the morphology and behaviour of chemically synthesized Cu-Au nanoparticles using high-resolution transmission electron microscopy are described. Truncated-octahedral (TO) particles, which are the result of a morphological evolution induced by the electron irradiation, are found to be the most stable. They have an fcc structure on a large size range of around 1-12 nm. Aggregation of two TO particles, to form a new TO particle, is observed directly under the electron beam. Modelling performed on 38-atom Cu-Au particles using an empirical-potential genetic algorithm also predicts the existence of fcc single-crystal TO structures.

1. Introduction
Among the various bimetallic nanoparticles which have potential applications in optics, catalysis and nano-electronics [1], Cu-Au nanoparticles have been studied by many research groups since the early 1990s [1-5].

Alloying between Cu and Au is not only well known for bulk systems [6] but also for nano-scale systems [2-5]. The dissolution of copper atoms in gold nanoparticles supported on an amorphous carbon film was observed using Transmission Electron Microscopy (TEM) [2]. Another study indicated fcc-like packing, similar to the bulk alloy phase, for 4 nm-sized stoichiometric (Cu₃Au)₄M (M is the number of Cu₃Au formula units) nanoparticles prepared by dual-source electron beam vaporization [3].

Different morphologies of Cu-Au nanoparticles have been observed. Decahedral and icosahedral Cu-Au alloy particles were produced by an electrochemical method and investigated by TEM [4]. In other work, decahedral and truncated octahedral morphologies were found for 1-4.5 nm-sized Cu-Au nanoparticles produced by laser vaporization of the bulk stoichiometric alloys CuAu, Cu₃Au, and CuAu₃ and then deposition on amorphous carbon and MgO substrates [5]. These nanoparticles all have fcc structures.

In this paper, we describe TEM observations of the morphology and the thermodynamic behaviour of Cu-Au nanoparticles, which are prepared using wet-chemical synthesis.

2. Experiment
Cu-Au nanoparticles were chemically synthesized by a two-phase reaction and galvanic exchange. This chemical method has previously been described in detail [7]. First, Cu nanoparticles capped with dodecanethiol (C₁₂H₂₅SH) are synthesized by NaBH₄ reduction of copper (II) chloride in
toluene/water and then mixed with an Au(I)-4-tert-butylbenzylthiolate solution. The bimetallic particles are formed by a galvanic exchange reaction between Cu and Au(I).

The particles are dispersed in toluene and then deposited on a carbon-coated copper grid for TEM investigation. Conventional TEM and High Resolution TEM (HRTEM) observations are performed on a Philips Tecnai F20 microscope operating at 200 kV. A large condenser aperture and an extraction voltage of 4200 V are used to observe the behaviour of the particles under an adequately high-density electron beam. The image processing software ImageJ 1.40g [8] is used to produce the size-distribution histogram from TEM images and to generate the Fast Fourier Transform patterns (FFT) from HRTEM images.

To study theoretically the structures of Cu-Au particles, modelling of 38-atom Cu-Au particles has been performed. A genetic algorithm code [9], incorporating the many-body Gupta empirical potential [10], is used to find the most stable structures, corresponding to global energy minima, of the particles.

3. Results and discussion

Figure 1 shows a conventional TEM image and the corresponding size-distribution histogram for the Cu-Au particles. The sizes are quite diverse, ranging from around 1 nm to around 12 nm. 2-6 nm sized particles are predominant. Although the capping thiol molecular layers prevent the particles from coalescence in solution [7], particle aggregation may still be observed in during electron microscopy, because the particle concentration is quite high and the capping layers may be vulnerable to the electron beam.

Individual particles were investigated by HRTEM. Their morphologies changed under exposure to the high-density electron beam. Initially, the particles adopted some random indefinable shapes. Some of them seemed to exhibit circular-like or elliptic-like 2D-projections. After irradiating an individual particle with the electron beam for about 2 minutes (with the largest condenser aperture, spot size of 2, extraction voltage of 4200 V), the particle morphology begins to change. It takes approximately 15
minutes for a new stable morphology to be established. As observed, after the morphological evolution induced by the electron irradiation, the particles exhibit hexagonal 2D-projections (see Figure 2a, upper part). These hexagons are unchanged even when irradiated further with the high-density electron beam. In fact, structural rearrangements in gold nanoparticles induced by an electron beam have been reported previously [11]. In another previous work, Cu-Au nanoparticles, which were produced by laser vaporization and deposited on an amorphous carbon film, also exhibited hexagonal 2D-projections under HRTEM [5]. The stable 3D morphology of the particles is identified as a truncated-octahedron (TO) which is geometrically constructed by the uniform removal of six square pyramids from the six vertices of a regular octahedron. Figure 2b (the upper part) shows a larger particle which exhibits a distorted hexagon. This particle is twinned as it is the result of the aggregation of two smaller particles. The shape development of this particle is still in progress.

The morphological evolution of the Cu-Au particles can be interpreted thermodynamically. The initial particles, which are synthesized by chemistry, can be regarded as meta-stable aggregates, corresponding to local energy minima. When stimulated by the electron beam, these aggregates re-crystallize, which causes a transition from the meta-stable state to the thermodynamically preferred structure corresponding to a global energy minimum. Only the TO morphology is observed as the most stable morphology for the Cu-Au particles in this work. The smallest TO particles observed are around 2 nm and the largest TO particles observed are 20 nm. These TO particles are single-crystal fcc. The FFT patterns (see Figure 2a and 2b, lower parts) indicate an [011] orientation. The measurement of the d-spacing of the (111) family of planes gives an estimate of 3.78 Å for the lattice parameter of the two particles in Figure 2. This value is close to the lattice parameter of 3.76 Å for the stoichiometric (Cu$_3$Au)$_M$ nanoparticles in the previous work [5].

![Figure 3](image_url)

**Figure 3.** The aggregation of two TO particles and the formation of a new larger TO particle under the electron beam; the alphabetic order (a-f) corresponds to the time sequence; this process occurs for around 20 minutes.

Figure 3 shows an aggregation of two TO particles. Under the high-density electron beam, the particles behave like liquid drops. They unite with each other to minimize the surface energy of the system. The initial result is a twinned particle but the thermodynamic equilibrium state is eventually reached and a new single-crystal TO particle is formed. The overall process takes around 20 minutes. This confirms that the observed large TO particles (> 10 nm) can be the result of the aggregation of smaller particles when they are irradiated by the electron beam. Previously, the sintering of gold nanoparticles under electron irradiation has been observed [12].

As found from the modelling of Cu$_{38-n}$Au$_n$ nanoparticles, fcc-like TO structures are the most stable structures (global energy minima) for Cu-rich compositions. This has been partially verified (for n = 0-
8) by higher level Density Functional Theory (DFT) calculations [13]. Some of these structures are shown in Figure 4. Au atoms are found to occupy preferentially the centroids of the 8 hexagonal (111) facets of the TO and the TO is slightly distorted when the number of Au atoms is larger than 8. This is also supported by DFT calculations [13]. Relying on the above observed aggregation of two small TO particles (of around 5 nm) forming a larger TO particle, we would like to argue for a possible extrapolation so that the smaller particles, which are below 1 nm in size, might also have the TO morphology. This makes the modelled 38-atom Cu-Au nanoparticles, which are around 0.8 nm in size, relevant to our experiments.

Figure 4. Some TO structures of Cu$_{38-n}$Au$_n$ nanoparticles found by the modelling; from left to right: Cu$_{34}$Au$_4$, Cu$_{29}$Au$_9$, and Cu$_{19}$Au$_{19}$. Au atoms are light grey, Cu atoms are dark grey.

4. Conclusions
Chemically synthesized Cu-Au nanoparticles have been investigated under TEM. The particle sizes are mainly around 2-6 nm. The initial particles are not stable under a high-density electron beam and morphological evolution is observed. The truncated-octahedron is found to be the morphology corresponding to the thermodynamic equilibrium state (global energy minimum) of the particles. TO particles have a single-crystal fcc structure. The aggregation of two TO particles, forming a larger TO particle, is observed under the electron beam. As observed, the TO morphology is predominant over a large range of sizes (approximately 1-12 nm) as the most stable for the Cu-Au nanoparticles. Modelling of 38-atom Cu-Au nanoparticles using a genetic algorithm also indicates a high stability of the fcc-like structures.

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