Size- and Temperature-Dependent Structural Transitions in Gold Nanoparticles

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Size- and temperature-dependent structural transitions in gold nanoparticles were revealed with morphology statistics obtained by high-resolution electron microscopic observations for thousands of particles annealed in a helium heat bath. We found that gold nanoparticles over a wide size range, 3–14 nm, undergo a structural transformation from icosahedral to decahedral morphology just below the melting points. It was also clarified that the formation of bulk crystalline structures from the decahedral morphology requires the melt-freeze process due to an insurmountable high free-energy barrier.

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Nanometer-size particles in various systems frequently exhibit structures prohibited in the crystallographic translational-symmetry rules, such as icosahedral (Ih) and decahedral (Dh) morphologies with fivefold symmetry axes [1]. It is, indeed, a challenging task in cluster science to explore how their structure evolves from noncrystalline motifs to crystalline structures on a thermodynamic diagram including the size variable [2]. Many attempts until now have been made to observe the size-dependent noncrystalline to crystalline transition during growth of clusters; however, no clear-cut picture has been provided in most cases [3-5]. Because observed features are highly dependent upon growth processes controlled by kinetic factors, rather than by energetics; the system may easily get trapped in a local minimum on the potential energy surface by nonequilibrium processes [1,6,7]. In order to reveal the equilibrium feature of the noncrystalline-to-crystalline transition, it is necessary to anneal nanoparticles up to high temperature and to observe whether structural instability happens or not for different morphologies on a size-temperature map. In this Letter, we report results of our systematic experimental study on structural stability of gold nanoparticles in relation to both size and temperature.

Gold nanoparticles in a size range of 3–18 nm were produced by cooling gold vapor with purified helium gas. They were transported by a steady helium flow through a quartz tube fitted in a furnace for annealing. The present experimental conditions of 2.2 kPa helium pressure and 1.3 s passing time through the annealing zone are sure to bring the particles into equilibrium at the furnace wall temperature; each particle experiences a sufficiently large number of collisions with helium for equilibrium [8], i.e., 1.3×10^{11} times per second in the case of a spherical 10 nm particle. Gold nanoparticles were annealed at 1173, 1223, 1273 K or 1373 K (cf. bulk melting point 1337 K), and then cooled quasistatically to room temperature [9]. They were deposited onto an amorphous carbon film. Structural observations were performed by using a JEOL JEM-2010 electron microscope with a point-to-point resolution of 0.194 nm.

In order to obtain the morphology statistics of a nanoparticle ensemble, i.e., morphology populations as a function of size, we performed high-resolution electron microscopic (HREM) observations for several thousands of particles in each sample prepared at different annealing temperatures. A single HREM image is, however, insufficient to identify and distinguish different morphologies, because particles are located on a substrate with random orientations resulting in complicated images due to their off-aligned symmetrical axes to the observed direction. We took, therefore, at least 20 different micrographs per particle by changing the tilt angle of the specimen holder within $\pm 20^{\circ}$ in an interval of 5° or 10°, combining with the through-focus procedure. By this technique, we were able to obtain a tilt series of high-contrast images for each particle [10], which enabled us to assign more than 90% of the particles by comparing observed images with simulation images calculated for different orientations of Ih, Dh, fcc (truncated octahedral) and twinned fcc structures using the multislice method [11].

Under the present conditions for the particle generation, the major morphology in as-grown particles (i.e., without annealing) was found to be Ih, and the minor one was Dh in faceted pentagonal bipyramid form. Typical HREM micrographs of Ih and Dh particles are shown in Figs. 1(a) and 1(b), respectively. The ellipsoidal outline seen in Fig. 1(b) is due to low sphericity of the as-grown Dh particles. Populations of the different morphologies are shown in Fig. 2(a) as a function of size in the 3–18 nm range. Crystalline particles were hardly found in our asgrown sample even though quite a large number of particles were analyzed, whereas crystalline structures were





FIG. 1. HREM images of gold nanoparticles. As grown (a) Ih and (b) Dh (faceted pentagonal bipyramid) particles. (c) Dh particle formed by annealing at 1273 K. (d) Single-crystalline particle formed by the melt-freeze process. Scale bar, 5 nm.

observed in as-grown samples of some previous studies [1,12]. Morphology populations in the as-grown state are affected by the growth conditions. The high abundance of the (metastable) Ih morphology in the whole size range, as seen in Fig. 2(a), can be explained by the shell-by-shell growth process [7], as discussed in our previous paper [10].

Populations after annealing at 1173 K are shown in Fig. 2(b). The population of Dh increased drastically in the small size region of 3-6 nm and that of Ih decreased in contrast. The 3-6 nm Ih particles underwent a structural transformation into the Dh morphology during annealing at 1173 K, indicating that the Ih particles gained sufficiently large thermal energy to overcome the activation barrier into the Dh structure.

Figure 2(c) shows populations after annealing at 1223 K. The Ih-to-Dh structural transformations were observed in particles up to 7.5 nm. In the size range smaller than 5 nm, however, coexistence of Ih and Dh was observed, even though the complete transition into Dh was observed at the lower temperature [see Fig. 2(b)]. This suggests that the particles smaller than 5 nm melted during annealing at 1223 K as discussed later.

Figure 2(d) shows populations after annealing at 1273 K. The Ih-to-Dh transitions were observed in large particles up to 14 nm, while particles smaller than 6 nm resulted in a mixture of Ih and Dh, similarly to the case of the annealing at 1223 K. Here the Dh particles showed good sphericity over the entire size range [13], as seen in a typical HREM micrograph in Fig. 1(c). No transformation to fcc from either Ih or Dh was observed.

Figure 2(e) shows populations after annealing at 1373 K over the bulk melting point; all particles were melted and frozen in this annealing process. Here we observed a significantly different population. A large amount of fcc particles was produced; the fcc population was found to increase gradually from 6 up to 18 nm, whereas the Dh population decreased. The two populations cross over at 12.5 nm. In the fcc particles, both single crystalline and lamellar-twinned particles were observed. A HREM micrograph of the former is displayed in Fig. 1(d). A similar result of the lamellar-twinned particle formation from liquid is also found in a molecular dynamics (MD) simulation of lead clusters [14]. On the other hand, populations in the 3–6 nm range showed a mixture of Ih and Dh, similarly to the case of

the annealing at 1273 K. This indicates that the particles in the 3-6 nm range have already melted at 1273 K due to the fall of the melting temperature by the size decreasing [15]. In the same manner, particles in the smaller size range, 3-5 nm, seem to melt even at the lower temperature, 1223 K. We have confirmed the validity of melting points derived from our experiments by comparing with literature values as mentioned below.

From the present data, a structural transition map for the Ih gold nanoparticles has been determined as shown in Fig. 3. The melting curves based on Pawlow's theory [16] and the liquid shell theory for a liquid shell thickness



FIG. 2. Populations of different morphologies of gold nanoparticles as a function of size. Populations of Ih $(-\Phi)$, Dh (-A), and fcc $(\cdots \blacksquare \cdots)$ particles, (a) before annealing and (b) after annealing at 1173 K, (c) 1223 K, (d) 1273 K, (e) 1373 K (cf. bulk melting point 1337 K). The volume-mean size is applied for Dh particles with low sphericity [10].



FIG. 3. A size-temperature structural stability diagram of Ih gold nanoparticles. Melting points (T_m) and Ih-to-Dh transition points $(T_{\text{Ih-Dh}})$ determined in this study are denoted by \bullet and $\cdots \bullet \cdots$, respectively. The solid and dashed curves are melting temperatures predicted by Pawlow's theory [16] and the liquid shell model [17], respectively. Melting points by previous simulation works are plotted by \bigcirc [17], \diamond [18], and \triangle [19], where each value is normalized by the bulk melting temperature.

of 0.5 nm [17], and melting points obtained from recent MD simulations [17–19] are plotted on the same map. The melting points of the Dh morphology determined in our experiments are close to the melting curve by the liquid shell theory, while the Ih-to-Dh structural transition curve is located just below the melting curve. The Dh region is nested between the Ih-to-Dh transition curve and the melting curve; the separation is \sim 70 K at 6 nm and \sim 30 K at 14 nm. We confirmed that the Ih-to-Dh transition occurs over a wide size range, at least from 3 up to 14 nm, i.e., the number of atoms from \sim 500 up to \sim 50 000.

The melt-freeze process provides a completely different morphology population as seen in Fig. 2(e). Above 6 nm, we have observed the fcc formation which was not accomplished by annealing Dh particles below the melting points [see Fig. 2(d)]. This indicates that an extremely high free-energy barrier exists between Dh and fcc structures. Presumably there is no direct geometrical conversion route to eliminate multiple twin boundaries in the Dh structure without complete atomic rearrangements, i.e., melting. The morphology population is, in general, determined by the Boltzmann weights of the free energies for different morphologies, if the free-energy barriers between different morphologies were surmountable. The Dh and fcc populations above 6 nm in Fig. 2(e), however, may have been fixed at the freezing temperature because of the insurmountable barrier between the two morphologies. The observed gradual transition from Dh to fcc along the size axis indicates that the difference in their free energies is not so large and changes continuously. The lowest-free-energy motif changes from Dh to fcc at the crossover size of 12.5 nm as the size increases. According to the recent calculation [20], the crossover size at 0 K has been estimated to be ~ 2 nm. The remarkable increase of this size at high temperatures is likely due to the entropic effect [21].

In the small size region of 3-6 nm, the Ih particles were formed by the melt-freeze process [see Fig. 2(e)], even though the Ih-to-Dh transition region locates below the melting curve. This can be explained by taking the supercooling effects into account. Recent studies [14,22,23] revealed that a high degree of supercooling takes place in various molten nanoparticles. In the present case, small Ih particles were likely generated by the freezing of supercooled liquid droplets at temperatures below the Ih-to-Dh transition curve and the population has probably been fixed simultaneously with freezing. As can be seen in Fig. 2(b), the thermodynamic equilibrium between Ih and Dh, which is accomplished above the Ih-to-Dh transition temperature, shows that the free energy of Ih is considerably higher than that of Dh even at 3 nm. Since the freezing point is probably not so much lower than the Ih-to-Dh transition point, the Ih formation by the meltfreeze process cannot be explained only by the free energy. As pointed out in Ref. [24], the Ih potential well is directly accessible from the liquid state due to the polytetrahedral characteristics both in liquid and Ih solid states. A recent MD simulation showed that the Ih form could be efficiently structured by nucleation of an ordered liquid surface with a fivefold symmetry [25]. From these kinetic reasons, metastable Ih paricles have been likely generated from liquid in the present experiment.

The simplest model of the microscopic mechanism for the Ih-to-Dh transitions is to consider a cooperative slip dislocation of {111} planes in the Ih structure, as illustrated in Figs. 4(a)-4(d). The Ih structure can be regarded as two pentagonal bipyramids connected by a common fivefold axis and ten slightly distorted tetrahedrons embedded between the two bipyramids. Cooperative deformation of these ten tetrahedrons transforms Ih into Dh as in the following explanation based on a five-shelled Ih model. We regard one of the ten tetrahedrons as a slightly distorted fcc structure with a ABCABC stacking of {111} planes [see gray-hatched planes from bottom to top in Figs. 4(a) and 4(c)], where its bottom plane is shared with a {111} facet of the bottom pentagonal bipyramid. When each {111} plane in the tetrahedron slips on its underlying plane with a Burgers vector b = a/6(211) (a, local lattice parameter) in the same direction, as denoted by the white arrows in Fig. 4(c), the tetrahedral shape can be deformed to the righttriangular pyramid shape with a ACBACB stacking [see Fig. 4(d)]. With this simple cooperative slip dislocation, two neighboring tetrahedrons merge into a new pyramid segment exposing a {100} plane [see Fig. 4(b)], resulting in the Dh formation. Such a nondiffusive cooperative process is considered to have much lower energy barrier



FIG. 4. A cooperative slip-dislocation mechanism proposed for the Ih-to-Dh transition. Ih model (a) can convert to Dh structure (b) without any atomic diffusion processes, when each of ten central tetrahedral segments within the Ih model cooperatively deforms into a right-triangular pyramid shape. The slip dislocation of each {111} plane on its underlying plane in the tetrahedron (c), with a Burgers vector $\mathbf{b} = a/6\langle 211 \rangle$ (white arrow), brings about conversion into the right-triangular pyramid (d).

in comparison with the case involving diffusion of all atoms. The whole transition process involves 36° twisting of the two pentagonal bipyramids around the common fivefold axis.

Our systematic experiments to examine the annealing effects on the gold nanoparticle morphologies revealed the size- and temperature-dependent structural transitions that are strongly ruled by the free-energy barriers between the different structural types. We found that the metastable Ih particles formed in a nonequilibrium growth process undergo the solid-solid transformation into the Dh morphology during annealing at temperatures just below the melting points. The transformations were found to take place over a wide size range, at least from 3 up to 14 nm. We could draw the size-temperature map for the structural stability of the Ih gold nanoparticles. The cooperative slip-dislocation mechanism as a nondiffusive process may be the most probable explanation for the Ih-to-Dh transition. No solid-to-solid transition from the noncrystalline (Dh) to the crystalline structure was observed up to the melting points. This suggests that once the system has been trapped into the noncrystalline (Dh) potential well it cannot escape there without melting due to an insurmountable high free-energy barrier. From a practical point of view, the present results indicate that the thermal annealing is very valuable for the morphological control of gold nanoparticles in order to quantitatively examine structural dependence of various physical and chemical properties such as catalytic activities [26].

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- [1] L. D. Marks, Rep. Prog. Phys. 57, 603 (1994).
- [2] Large Clusters of Atoms and Molecules, edited by T. P. Martin (Kluwer, The Netherlands, 1996).
- [3] J. Farges *et al.*, J. Chem. Phys. **78**, 5067 (1983); **84**, 3491 (1986).
- [4] B. D. Hall *et al.*, Phys. Rev. B **43**, 3906 (1991);
 D. Reinhard *et al.*, *ibid.* **55**, 7868 (1997).
- [5] D. Zanchet, B. D. Hall, and D. Ugarte, J. Phys. Chem. B 104, 11013 (2000).
- [6] B.W. van de Waal, Phys. Rev. Lett. 76, 1083 (1996).
- [7] F. Baletto, C. Mottet, and R. Ferrando, Phys. Rev. B 63, 155408 (2001).
- [8] J. Westergren et al., J. Chem. Phys. 109, 9848 (1998).
- [9] The cooling rate of helium downstream from the furnace exit was measured to be less than 4.0×10^3 K/s. For the quasistatic cooling of a 10 nm particle, the average energy transfer rate of 0.14 μ eV per collision is required. This condition is well satisfied [8] in the present cooling procedure.
- [10] K. Koga and K. Sugawara, Surf. Sci. 529, 23 (2003).
- [11] J. M. Cowley and A. F. Moodie, Acta Crystallogr. 10, 609 (1957).
- [12] S. Giorgio et al., Z. Phys. D 24, 395 (1992).
- [13] The average minor/major size ratio of the as-grown Dh particles larger than 7 nm was found to be ~ 0.7 before annealing. The ratio increased up to 0.8–0.9 after annealing at 1173 K, while no population change was observed [see Figs. 2(a) and 2(b)]. The poor sphericity of the Dh particles was likely improved by the diffusion of surface atoms towards the surface energy reduction.
- [14] S. C. Hendy and B. D. Hall, Phys. Rev. B 64, 085425 (2001).
- [15] Ph. Buffat and J-P. Borel, Phys. Rev. A 13, 2287 (1976).
- [16] P. Pawlow, Z. Phys. Chem. 65, 1 (1909).
- [17] Y.G. Chushak and L.S. Bartell, J. Phys. Chem. B 105, 11605 (2001).
- [18] C. L. Cleveland, W. D. Luedtke, and U. Landman, Phys. Rev. B 60, 5065 (1999).
- [19] F. Ercolessi, W. Andreoni, and E. Tosatti, Phys. Rev. Lett. 66, 911 (1991).
- [20] C. L. Cleveland et al., Phys. Rev. Lett. 79, 1873 (1997).
- [21] J. P. K. Doye and F. Calvo, Phys. Rev. Lett. 86, 3570 (2001); J. Chem. Phys. 116, 8307 (2002).
- [22] L. J. Lewis, P. Jensen, and J-L. Barrat, Phys. Rev. B 56, 2248 (1997).
- [23] R. Kofman et al., Eur. Phys. J. D 9, 441 (1999).
- [24] J. P. K. Doye, D. J. Wales, and M. A. Miller, J. Chem. Phys. 109, 8143 (1998); J. P. K. Doye, M. A. Miller, and D. J. Wales, *ibid.* 111, 8417 (1999).
- [25] H.-S. Nam et al., Phys. Rev. Lett. 89, 275502 (2002).
- [26] G. C. Bond and D. T. Thompson, Catal. Rev. Sci. Eng. 41, 319 (1999).