Polyhedral to nearly spherical morphology transformation of silver microcrystals grown from vapor phase

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Silver microcrystals of various shapes were grown from co-evaporation of Ag2O and SiO powders in the nominal evaporating temperature range (heat source temperature) from 800 to 1200 °C under a reductive atmosphere. With increase in evaporation temperature facets of the (1 1 0)-, (2 1 0)- and (3 1 0)-families come forth successively, that make the Ag polyhedron microcrystals transform into nearly spherical microcrystals. A mechanism based on the recession of {1 0 0} or {1 1 0} steps induced by the solvent SiOx (x ~ 2.0), which modifies the growth kinetics, is proposed to explain the emergence of (2 1 0)- and (3 1 0)-facets at high temperatures. By evaporating at 1200 °C, smooth-looking spherical Ag crystals with 6 nm multi-layered steps on the (1 1 1) facets were obtained. These results are also of significant industry relevance when preparation of noble metal particles with high-index facets is of concern.

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1. Introduction

Crystallization is the most elementary step in shaping a solid. By synthesizing crystals under various conditions in which both thermodynamics and growth kinetics play a role to a varying content simultaneously, amazing complexity and diversity in the crystal shapes can be obtained. The underlying mechanisms for crystal growth have always been an interesting subject worthy of extensive exploration [1–3]. In fact, the design and manipulation of crystal shapes demand more meticulous work, particularly in the cases where the dimension of crystals generally falls in the micrometer range. As for the crystallization of noble metals, considerable amount of researches have been devoted to the growth process and mechanism investigation because of their peculiar physical and functional properties which often rely on the crystal shapes [4,5]. Morphologies ranging from cube, tetrahedron, octahedron, decahedron to icosahedron have been observed for silver, gold and palladium [6–8], where the (1 1 1)-, (1 0 0)- and (1 1 0)-facets dominate the equilibrium shape of crystals at low temperatures (yet higher than half the bulk melting point or so, sic passim). Notably, vaporization deposition is a method often used for mechanism research of metal crystal growth. The relevant researches included the roughening temperature [9], the dependence of morphology on temperature and atomic interaction [10,11], as well as the induction of morphology change by the ambient [12,13]. When an unconventional crystallization process is applied, surprise is ready to occur even for crystals of as simple as fcc metals. In the case of employing evaporation or wet chemistry method, impurities or additives may adsorb at steps and kinks in the growing crystal surfaces, which can modify the relative growth rates of the different facets or even terminate the growth of some planes. This adds a new dimension to the modification of crystal shape. More deliberate research works towards crystal shape control are desirable in order to improve the catalytic and adsorbent properties, mesocrystals of various materials with a designed surface feature are needed.

Silver is a noble metal of very important science and industry relevance, it has been widely used in surface-enhanced Raman spectroscopy [14], electronics [15], catalysis [16], chemical and biological sensing [17,18] and plasmonics, etc. The mechanism research for silver crystal growth is fundamental and can offer clues to other type of crystals. Furthermore, there is a close relationship between crystal morphology and functionality [5]. Consequently, the morphology control and the exploration of the crystallization mechanism for silver have drawn much attention in the last decades. The equilibrium shape of Ag crystal under low evaporation temperatures is generally a regular polyhedron bounded by (1 1 1) facets, and sometimes together with (1 0 0)-facets usually of a smaller area. Under high temperatures approaching its melting point, however, it turns into a spherical morphology showing some high-index crystallographic planes. In both cases, the equilibrium
shape is the result of the minimal surface free energy. Morphology transformation is an essentially important research topic [19–22], in particular when unconventional crystallization processes involving non-thermodynamic influencing factors are engaged. The crystallization pathway for the morphology transformation of silver crystals grown from vapor phase and in the presence of inorganic solvents from the ambient, remains an unsettled problem. In our previous researches, we found that co-evaporation of SiO and Ag₂O powders at high temperature gave rise to the formation of Ag core/SiOₓ shell microstructures which can be used as templates for stress engineering of ordered patterns [23,24]. In the case that less SiO is mixed into the evaporant or a low evaporating temperature (below 1200 °C) is chosen, silver crystals with only negligible amount of SiOₓ solvent on the outermost surface were obtained, which provide a suitable sample for the study of morphology transformation. In the current work, silver single crystals of a few microns in dimension were obtained by co-evaporating SiO and Ag₂O powders in the nominal temperature range from 800 to 1200 °C. Shapes of various truncated polyhedra or in a roughly spherical form were found. The pathways for the tetrahedral/octahedral to spherical morphology transformation can be established. The underlying mechanism for the emergence of high-index facets can be also elucidated. For the Ag microcrystals obtained under the given conditions, the cooling process down to half the melting point lasts less than 3 min. Therefore, they are just in the shape collectively determined by the thermodynamic and kinetic factors. Those crystals having negligible SiOₓ (x < 2) additives at surface can be taken as equilibrium structures. The results are suggestive for the facet control of noble metal crystals.

2. Experimental methods

Commercial powders of Ag₂O (99.7%) and SiO (99.99%) mixed in a mass proportion of 4:1 were evaporated in a closed chamber which had been evacuated and then filled with the gas mixture of 90% Ar and 10% H₂ to a pressure of 3 × 10⁴ Pa (the equipment sketch map is presented in Fig. 1a). In the evaporation temperature range here concerned (from 800 to 1200 °C), deoxidization reaction occurs to Ag₂O, 2Ag₂O → 4Ag + O₂, through which Ag crystals can be obtained from the vapor phase. It also can be further enhanced by the presence of hydrogen in the ambient. Similar deoxidation reaction occurs to SiO only at a temperature much higher than the melting point of Ag (961.78 °C), 2SiO → Si + SiO₂. In the reaction, some SiOₓ (with x ~ 2.0) molecules may resolve in the Ag melt or adsorb to the surface of the Ag crystals. The morphology of silver crystals will be strongly affected by the involvement of the additive SiOₓ molecules.

The growth conditions for the Ag crystals can be specified as follows. A crucible holding the powder mixture, surrounded by tantalum wire, was heated to a required temperature, and maintained at that temperature for 10–15 min before it is cooled down naturally (typical cooling profile is presented in Fig. 1b). The deposits were collected on a silicon substrate (1.0 cm in length) put in the crucible slantways, along which a temperature gradient develops. Temperatures were monitored with thermocouples both at the heat source beneath the crucible and at the top end of the substrate, with the former being the nominal evaporation temperature referred to in this work. The correlation of the temperature measured by the two thermocouples is illustrated in Fig. 1c, which can help make a sense of the temperature gradient along the way from the evaporating surface to the substrate. The deposits, collected on the middle or little down part of the substrate where the temperature can be found at the temperature curve in Fig. 1c, were ex-situ investigated under a field emission scanning electron microscope (FE-SEM, Hitachi S-4800).

3. Results and discussion

3.1. Effect of temperature on morphology

Fig. 2a–c displays the silver crystals obtained under a nominal evaporation temperature of 800, 900, and 1000 °C, respectively,
which are found in a variety of distinct shapes. To enhance the visibility, silver crystals of the same polyhedral appearance are marked with a particular polygonal frame in the SEM micrographs—the correspondence is specified in the figure. We see that the dominant part of the silver crystals obtained at 800 °C in Fig. 2 a is tetrahedral (framed in rectangles), with a feature size of ~300 nm. In addition to the tetrahedrons, decahedral and icosahedral twin crystals, equally bounded exclusively by \{1\ 1\ 1\} facets, are also located, which comprise of tetrahedrons as the basic subunits and exhibit a quintic rotational symmetry—relaxation at the boundaries is of course desirable to cover the angular space of $2\pi$. As the evaporation temperature was raised to 900 °C, most particles thus obtained assume an appearance of truncated tetrahedron or octahedron. The feature size for the average particles also becomes larger, normally at about 1 \(\mu\)m, as shown in Fig. 2b. Notable, the crystals obtained at these low temperatures show sharp edges and corners. At 1000 °C, along with the increase of feature size, roughening transition starts at the edges and corners, through which the polyhedral silver crystals turn to be truncated at these places and seem rounded (Fig. 2c). Or the crystals now intend to assume a more or less spherical appearance, which will be discussed in detail below. A brief tendency for the development of silver crystals with the evaporation temperature is illustrated in Fig. 2d.

The morphology of crystals is determined by many interplaying factors, but for silver crystals prepared at lower temperatures, the SiO impurity in the ambient is less disturbing. Furthermore, at relatively low temperature, the effect of surface relaxation, related to surface energy, could be ignored [25]. Therefore, it is mainly the thermodynamic factor, i.e., the effort to minimize the surface free energy that plays the dominant role. Under this circumstance, the facets of the crystal shape at equilibrium are all close-packed planes which have fewer unsaturated bonds. For fcc metals of silver, we see that the polyhedral crystal shapes, whether in the form of a tetrahedron, an octahedron, a decahedron or an icosahedron, are solely bounded by the \{1\ 1\ 1\}-planes, which are the most close-packed ones, as can be verified in Fig. 2. In Fig. 2b where most particles are in the form of a truncated tetrahedron, it could be found that \{1\ 0\ 0\}-planes begin to appear, which trim the edges of the tetrahedron and leave behind facets in the shape of

![Fig. 2. Morphology statistics for as-synthesized Ag microcrystals. (a–c) SEM micrographs of silver particles prepared at evaporation temperature of 800, 900, and 1000 °C, respectively. In (d) illustrated is the variation tendency of crystal size and morphology with the increasing evaporation temperature. A correspondence between the marking shapes and the marked polymorphs in (a–c) is provided.](image)
a parallelogram. Due to the fluctuation of the local surface super-saturation and particular surface structure, such as defects, some particles are not quite regular, appearing as a prism or an anamorphic polyhedron. Roughly speaking, the particles obtained at \( \sim 800 \, ^\circ\text{C} \) (Fig. 2a) are small in size, and adopt a shape of a regular tetrahedron, a truncated triangular pyramid, a decahedron or a truncated decahedron. Except for the truncated decahedron where a very small area \{1 0 0\}-planes are also present, all these shapes comprise of solely \{1 1 1\}-planes. At 900 \(^\circ\text{C}\), the proportion of \{1 0 0\}-planes increases in the facets, as shown in Fig. 2b, since in this case the specific surface free energies for the \{1 1 1\}- and \{1 0 0\}-planes are competitive. For reference, the data of specific surface free energy for silver from a density function calculation, i.e., 0.553 eV atom\(^{-1}\) for \{1 1 1\}-planes, 0.653 eV atom\(^{-1}\) for \{1 0 0\}-planes, and 0.953 eV atom\(^{-1}\) for \{1 1 0\}-planes, are cited here as a consistent starting point for further discussion [26].

3.2. Transformation pathway to sphere for tetrahedron and octahedron

For nominal evaporation temperatures in the range of 900–1200 \(^\circ\text{C}\), morphology transformation from a regular polyhedron to a spherical particle for the silver crystals can be established from the SEM micrographs of the deposits. Figs. 3 and 4 illustrate the transformation routes that start from a tetrahedron and an octahedron, respectively, where \( a_1-\sim a_6 \) are the SEM micrographs and the colored panels \( b_1-\sim b_6 \) are generated online on a website for crystal growth [27] for a better visualization, roughly reproducing the crystals at different stages of transformation in \( a_1-\sim a_6 \). From a perfectly tetrahedral-looking crystal comprising four primary \{1 1 1\}-planes (Fig. 3a1), one can see that new facets belonging to the \{1 1 1\}_P, \{1 0 0\}, \{1 1 0\} and \{2 1 0\} families emerge in order. Furthermore, the \{1 1 1\}-planes shrink continuously with the emergence of new high-index planes. When the area of the \{2 1 0\} planes is as large as the lower-index ones, these particles look quite rounded. Remarkably, in the transformation that starts from an octahedral shape (Fig. 4a1), the \{3 1 0\} facets are also identified (Fig. 4a6). Taking into account also other observations on particles obtained at below 1000 \(^\circ\text{C}\), it can be conceived that the transformation from a tetrahedron (assuming its four primary surfaces are \{1 1 1\}_P, \{1 1 1\}_T, \{1 1 1\}_II and \{1 1 1\}_I) planes, thus denoted as \{1 1 1\}_P for short in Fig. 3) starts with trimming one or all the corners of the tetrahedron with the other four \{1 1 1\}-planes (denoted as \{1 1 1\}_P in Fig. 3), and proceeds with trimming at the edges with six \{1 0 0\}-planes. For the transformation from an octahedral crystal, the transformation starts with trimming the corners with \{1 0 0\}-planes, and proceeds with trimming at the edges with six \{1 1 0\}-planes, and so forth.

The round-off of the crystal morphology at temperatures in this work results from the emergence and stabilization of facets in the order of \{1 0 0\}, \{1 1 0\}, \{2 1 0\} till \{3 1 0\}, which is possible only when these planes attain a decreased specific surface energy under given conditions. It is well known that for fcc metals such as silver, the specific surface energies for the \{1 1 1\}, \{1 0 0\} and \{1 1 0\} planes at low temperatures — less than half the melting point in degree, say — arranges in the increasing order. Following the theoretical calculation in which the multilayer relaxation effect was also considered, this order of specific surface energy, or referred to as stability of the corresponding planes in some literature, may turn reversed at high temperatures (under which surface melting may occur) [25,28]. The \{1 1 0\} facets relax much more intensively than the \{1 1 1\}_P- and \{1 0 0\}-facets to improve their thermal stability — the melting point of facets \{1 1 1\}_P, \{1 0 0\}, \{1 1 0\} for Cu change from 0.840, 0.845, 0.755 to 0.840, 0.914, 0.970 (in unit of bulk melting point), respectively, after surface relaxation [25].

![Fig. 3. Morphology transformation for a tetrahedral silver crystal to the spherical form.](image)

\( a_1-\sim a_6 \) SEM micrographs of as-synthesized silver crystals at different stages of the transformation; \( b_1-\sim b_6 \) schematic illustration of the transformation pathway for a tetrahedral crystal approaching the spherical shape. \{1 1 1\}_P denotes the four primary \{1 1 1\}-facets forming a tetrahedron, and \{1 1 1\}_P; the other four trimming \{1 1 1\}-facets. The evaporation temperature for \( a_1-\sim a_3 \) and \( a_4-\sim a_6 \) are 800–1000 and 1100–1200 \(^\circ\text{C}\), respectively.
The disordering of the (1 1 0) surface with increase in temperature is actualized through the formation of vacancies and adatoms, which enlarges the configuration entropy [29]. Recently, by using the high-temperature transmission electron microscope sublimation technology Wang et al. made an in-situ observation of the morphology variation of silver particles coated with carbon, conforming that the {1 1 0}-plane is more stable than the {1 0 0}- and {1 1 1}-planes at high temperature [30]. Of course, thermodynamics is not the only factor that leads to the formation of the sphere-looking yet faceted particles. The adsorption of impurity, here SiO\textsubscript{x}, also plays a role in stabilizing some planes and thus altering their relative areas in surface [31]. The emergence of the {2 1 0} and {3 1 0} facets that help complete the round-off of the crystal is speculated to be induced from the stable {1 1 0} or {1 0 0} facets by the SiO\textsubscript{x} solvent. More detailed discussion will be given below.

3.3. Growth mechanism of high-index facets

High-index facets, such as {2 1 0} for fcc metal, have larger specific surface free energies compared to the low-index facets. Therefore it is hard to obtain metal particles bounded by high-index facets which deem to have a high step density and a large growth rate. However, since the high chemical activity of the high-index surfaces of noble metals is desirable for catalytic applications, much effort has been devoted to the growth of metal particles with high-index facets and evidenced some progress. Some successful synthesis has been recently reported, such as tetrahedral gold [32] and platinum [33] nanocrystals and trisoctahedral gold nanocrystals [34].

As illustrated in Figs. 3 and 4, high-index planes are desirable to complete the growth of a nearly spherical single-crystalline metal particle, and they do appear on the Ag microcrystals prepared under proper conditions. Since the high-index facets of silver particles have a larger specific surface free energy, adsorption of impurities, here SiO\textsubscript{x}, with \( x \leq 2.0 \) depending on the ambient, is unavoidable. In fact, it is speculated to have played a decisive role in growing sphere-looking Ag crystals from the vapor phase, through passivating the ‘dangling bonds’ to reduce the surface free energy and through modifying the nucleation rate on surface as well as the advancing rate of steps. Notably, just above the eutectic point for the Ag–Si system (~840 °C) it is conceivable that SiO\textsubscript{x} has a negligibly small solubility in Ag melt. Thus SiO\textsubscript{x} molecules that have been captured segregate to the outermost surface. The trace of the growth of the corresponding crystal facets is thus discernible under SEM, by inspecting Fig. 5a and b (also cf. a5 in Figs. 3 and 4) where the crystal shapes can be taken, respectively, as a tetrahedron or an octahedron rounded by {1 1 0}, {2 1 0} and even {3 1 0} facets. Based on the observation that the {2 1 0} and the {3 1 0}-facets appear next to the low-index facets, a mechanism based on the step recession induced by SiO\textsubscript{x} solvent can be figured out, as shown in the schematic representation in Fig. 5c. In the due course of crystal growth from vapor, the advancing steps can be altered either by the local fluctuation of supersaturation or by the adsorption of impurities, here SiO\textsubscript{x}, with the latter being able to reduce the step advancing rate even down to zero. On the other hand, impurities might enhance the nucleation rate at the step terrace. Both factors will result in the seemingly receding at edge of a primary facet when growth proceeds. At some proper balance between the nucleation rate on the terrace and the step advancing rate outward, high-index planes are thus obtained. From Fig. 5c we see that the {2 1 0} and {3 1 0}-facets can be taken as resulting from the recession of a {1 1 0} or {1 0 0}-terrace.

3.4. Facet development on spherical crystal

Fig. 6 displays the spherical-like crystal synthesized at the evaporation temperature of 1200 °C. The facets on those crystals
surface comprise of multi-layered steps, as shown in Fig. 6a–c. By inspecting a \{1 1 1\}-facet under high magnification (Fig. 6d), we see that the facet is composed of rather conformal multi-layered steps which assume a circular periphery. From Fig. 6c, the circularity of the steps’ periphery can be confirmed with confidence. Remarkably, the crystallite displayed in Fig. 6b results from twin growth, which displays perfect mirror symmetry as a whole. And its facets can be identified by the difference in the affinity to adsorbates between the \{1 1 1\} and \{1 0 0\} facets. Whether these facets comprising multiple steps are formed via 2D nucleation or screw dislocation initiated growth is hard to resolve in the current work.

The facets start out close to the special crystallographic directions. Fig. 6d displays the local magnification of a \{1 1 1\}-facet in Fig. 6c. It clearly demonstrates the multilayer growth in the face center. The macrosteps which comprise a host of atomic layers \[3,35\] have a depth height of \(\sim 6\) nm. The emergence of multilayer
step is a character of growth at high temperature [36]. The initial nucleus forms at the center of the uppermost layer where the supersaturation is higher than other places and nucleation is thermodynamically favorable. It could act as the primary source of the steps. Once the nucleus exceeds the critical size, it becomes stable and lateral growth will continue. The emergence of the multi-layered steps can be ascribed to the effect of dense SiO$_2$ adsorbrates onto step fronts, which is actualized at the given temperature. With the presence of the impurity SiO$_2$, the advance rate of a layer may be slowed down whereas the nucleation thereupon, which contributes some to the growth of that layer, may be enhanced. Consequently the growth front of an overlayer can catch up the underlying layer, leading to the merging of proximate layers. The formation of a multi-layer step would further reduce its advance rate, thus the mono-atomic layer atop can catch up with it at ease, leaving behind a multi-layered macrosteps.

4. Conclusion

Polyhedral to spherical morphology transformation was established for silver crystals grown from vapor phase by co-evaporating the Ag$_2$O and SiO$_2$ mixture, in particular the pathways starting from the SEM micrographs of the deposits. Evaporation temperature that determines the partial pressure, supersaturation and substrate temperature plays a key role in determining the final shape of the silver crystals. At evaporation temperatures between ~800 and ~1000 °C, the particles are usually polyhedrons bounded by {1 0 1} and {1 0 0} facets with smaller specific surface energies, and thermodynamics is the predominant factor in determining the crystal morphology. At evaporation temperatures from ~1000 °C up to ~1200 °C, high-index facets appear. With the concurrent presence of {1 1 0}-, {2 1 0}- and {3 1 0}-facets in the surface, the silver crystals ultimately assume a roughly spherical shape. Or briefly, the polyhedral to spherical transformation of morphology for silver crystals is a process in which the facets of higher specific surface energies (at room temperature) appear in succession at elevated temperatures. The {2 1 0}- and {3 1 0}-facets evolve through the recession of steps on a {1 0 0} or {1 1 0}-terrace. Adsorption to the Ag surface of the impurity SiO$_2$ can play a role in the formation and fade-out of multilayer steps, but the underlying microscopic mechanism cannot be resolved from the current experiment. To our best knowledge, this is the first time that the morphology transformation process for silver crystals has been recognized from SEM micrographs of crystals frozen in the intermediate stages of the transformation. As findings here can be instructive for growing noble metal particles of larger high-index facets which are pretty desirable in the catalytic applications, they are also of considerable practical significance.

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