Self-Assembly of MoO₃ Needles in Gas Current for Cubic Formation Pathway

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Nucleation and subsequent rapid growth are enigmatic due to the unrevealed pathways. Despite the relatively simpler mechanism than nucleation and growth in solution, that in vapor has received little attentions. The largest hindrance to unveiling this process may be observing the rapid and mesoscopic-scale phenomena. To overcome this hindrance, we combine an experimental approach with in-situ spatial scanning Fourier-transform infrared spectroscopy, which reveals the nucleating and growing nanoparticles in vapor. The nanoparticles are then collected at different evolutionary stages and analyzed by ex-situ transmission electron microscopy (TEM). Needle-shaped molybdenum oxide (MoO₃) nanoparticles were formed within ~0.1 s after homogeneous nucleation from a highly supersaturated vapor. Over one second, the needle particles gradually evolved into a cubic shape by fusion in a crystallographically favored orientation in a free-flying state in vapor. The similar sizes of the elongated axes of the needle and cubic structures suggest an additional growth stage, in which the needle particles become the growth units of the cubic particles. The morphology of a final crystal should reflect the formation environment of the particle because growing crystals are sensitive to the formation conditions such as temperature, concentration, and impurities. Although nucleation under very high supersaturation induces anisotropic growth of the needle particles, this information of the initial nucleation environment is lost in the final cubic crystal. These findings enrich our understanding of pathways in the nucleation and growth of nanoparticles and provide new insights into the growth stages driven by oriented attachment.

In contrast to complex nucleation from solution, nucleation of inorganic particles from a vapor is surface free, so we expect that the result to be comparable to the nucleation theory. Some experimental studies have attempted to unveil the nucleation process. For instance, after thermal evaporation at extremely high supersaturation, metal and metal oxides nucleate homogeneously in the cooling gas. According to nucleation theory, the critical nuclei in manganese nucleation should be several atom/molecules in size, and their surface free energy should be 30% larger than that of the corresponding bulk. Unexpected pathways in the post-nucleation growth processes have also been proposed. Inter-particle coarsening is thought to determine the resulting characteristics of crystals in some solution systems. When coarsening happens selectively between crystallographically equivalent planes, it is known as oriented attachment growth. For many years, the fusion of two nanoparticles and agglutination by
surface melting has been known to dominate the growth of nanoparticles in vapor phase. These previous studies show that nucleation and growth pathways are not simple processes. MoO$_3$ nanoparticles are induced by inter-particle coarsening at a rate that is determined by the gas current. The thallium bromoiodide crystal exhibits high transmittance in the 10000–250 cm$^{-1}$ range. The emissivity of the Mo wire surface was assumed constant at 0.3. Some ascending nanoparticles were attached to stainless-steel collecting sheets; one fixed at 10 mm beside the evaporation source, the other fixed at more than 250 mm above the evaporation source. The collected particles were picked up on a standard Cu grid coated with carbon and dried for 1 minute. The particles were observed by TEM (JEM-
Results

Molybdenum (Mo) wire was heated in a regulated gas mixture of reactant oxygen ($P_{O_2} = 4.0 \times 10^2$ Pa) and buffer helium ($P_{He} = 4.6 \times 10^3$ Pa). The oxidation and subsequent evaporation of MoO$_3$ and the nucleation of nanoparticles were confirmed as visible smoke. Convection carries the evaporated MoO$_3$ gas around the evaporation source. Consequently, the gas concentration is highest at the bottom of the evaporation source and nucleation is induced at several millimeters beneath the Mo wire. High $O_2$ partial pressure induces efficient oxidation and evaporation of Mo source. In addition, high $O_2$ pressure induces frequent collision between the just-nucleated nanoparticles in gas current. These leads to frequent collision condition, in order to clarify the particle formation sequences in the spatial resolution of our experimental system. Nucleated MoO$_3$ nanoparticles appear floating in the ascending gas current generated by the hot evaporation source. The MoO$_3$ nanoparticles are then cooled in the convection from nucleation temperature (typically around 1000 K) to room temperature in 1 s. Owing to the rapid heat exchange, the temperature of the nanoparticles in the ascending gas current is similar to that of the surrounding gas.

Figure 1. Typical TEM images of the synthesized nanoparticles collected (a) at the height of the evaporation source on the side collector and (c) at the roof collector. (b), (d) electron diffraction (ED) patterns corresponding to (a) and (c), respectively.

To identify the size, shape, and polymorph changes of the nanoparticles produced in the ascending gas current, we collected the nanoparticles at different heights from the evaporation source and observed them using a TEM. The floating nanoparticles were attached on SUS sheets set at 10 mm below the evaporation source (side collector) and at ~250 mm above the evaporation source (roof collector) (Figure S1). Nanoparticles collected at the side collector (placed at the height of the Mo wire) are mainly composed of needle-shaped particles, accompanied by a small number of cubic shaped particles (Fig. 1a). Corresponding electron diffraction (ED) patterns (Fig. 1b) and the crossing angle of the lattice fringes (obtained in high-resolution images of a needle particle; see Fig. 2) consistently matched monoclinic MoO$_3$ with a unit cell size of $a = 7.118$ Å, $b = 5.366$ Å, and $c = 5.568$ Å (JCPDS card no. 47-1081). The needle particles were always elongated along [011]. In contrast, most of the samples collected at the top of the chamber were cubic or polyhedral (Fig. 1c). Though clear distinction between cubic and polyhedral particles were difficult because some cubic particles had roundish edges and irregularly deformed outlines, the number of cubic particles was more dominant than polyhedral particles in all samples. The ED patterns of these particles were also consistent with monoclinic MoO$_3$ (Fig. 1d). The rings corresponding to (111) and (200) (indicated by the orange lines in Fig. 1d) do not appear in the ED pattern of the needle-shaped particles in Fig. 1a. The needle particles showed well-aligned lattice images of (011), but frequent defects in the perpendicular planes.

Figure 2. High resolution image of a typical needle shaped particle and (b) its corresponding ED pattern. Streaks along [200] are indicated by the white arrow.
We scanned the growth of nanoparticles in the smoke from 7.5 mm to 67.5 mm above the evaporation source (Figure 4B1-13). Once the temperature of the evaporation source had stabilized, the scan was started in the upward direction. When the scan reached the top in each experiment, it was returned to the starting position and proceeded downward. Figure 4 shows the spectra measured in the downward direction. At any given distance from the evaporation source, the same spectral features were observed in the upward direction (Figure S5).

The IR evolution shows a clear spatial dependence. The spectra measured at 10 mm above the evaporation source in Experiment A (Figure 4A5) were identical to those measured at 7.5 mm above the evaporation source in Experiment B (Figure 4B1). The shape of the IR absorption band continuously changed from 10 mm beneath the evaporation source to 67.5 mm above the evaporation source. The swell in the 1000–750 cm\(^{-1}\) region was contributed by at least six subtle absorptions (indicated by the blue lines in Figure 4). The combination of these subtle absorptions altered the shape of the IR spectra in that region from singly to doubly peaked.

The spectral features were compared with those obtained by ex-situ IR measurements of nanoparticles collected at the same height and embedded into KBr pellets (Figure 4K1, K2; Figure S6). In the ex-situ IR spectrum of the needle particles collected on the side collector at 0 mm, the strongest absorption appears at 860 cm\(^{-1}\). A single swell in the 1000–750 cm\(^{-1}\) region also appears. In contrast, the ex-situ IR spectrum of the cubic nanoparticles collected at ~250 mm exhibits peaks at 880 and 780 cm\(^{-1}\), and a double-swell in the 1000–750 cm\(^{-1}\) region. With increasing collection height, the in-situ IR spectra undergo a transition from the single- to double-swell absorptions, consistent with the ex-situ IR measurements.

Note that the IR spectral features are influenced by electromagnetic interactions between the particles and the embedding KBr medium. Therefore, the peak positions are shifted toward lower wavenumbers, and the band widths are larger, than in IR spectra measured in the free-flying state. Despite these differences, the whole profile of the absorption, including the single and double swells, reflects the shape of MoO\(_3\) nanoparticles. We conclude that the collected particles were frozen and their characteristics were negligibly changed after deposition on the side and top collectors.

The whole profile of the IR spectra is dominated by the superposition of sub-peaks at 1000–750 cm\(^{-1}\), which have been suggested to arise from Mo–O stretching vibrations. The relative intensities of the sub-peaks depend on the crystallographic anisotropy of the nanoparticles. The in-situ FT-IR measurements of the just-nucleated nanoparticles show peak in the 1000–750 cm\(^{-1}\) region, with the strongest absorption at 840 cm\(^{-1}\) (Figure 4). As the nanoparticles cool in the ascending gas current, the peaks at 900 and 910 cm\(^{-1}\) are gradually enlarged, whereas the peaks at 970 and 860 cm\(^{-1}\) in spectrum A1 are reduced in spectrum B13. The characteristic absorptions at 970 and 860 cm\(^{-1}\) of the just-nucleated nanoparticles are attributable to needle particles, and the relatively strong absorptions at 920, 910, 900 and 840 cm\(^{-1}\) are attributable to cubic and/or polyhedral particles.
Discussions

We have questioned how the needle particles transform into cubic and polyhedral particles in the ascending gas current. In our experimental set up, the evaporant flowed by convection and is quenched at temperature gradients >1000 K s\(^{-1}\). The observed characteristic features of the just-nucleated nanoparticles were attributed to the needle-shaped molybdenum oxide (spectrum A1 in Figure 4). In previous studies, we determined the partial pressure of the source molecules at the nucleation point as ~10\(^{-3}\) Pa.\(^{19-21}\) In such an atmosphere, a nanoparticle grows to several tens of nanometers in 10\(^{-3}\) s,\(^{19,20}\) with simultaneous consumption of the vaporized source molecules. The time scale of vapor growth is several orders of magnitude faster than the time scale of convection (~1 s from the evaporation source to the top of the chamber, estimated from the convection of visible smoke). In addition, the MoO\(_3\) vapor pressure at more than 5 mm above the evaporation source, estimated from temperature fields derived from thermocouple data (Figure S7), is <10\(^{-6}\) Pa. Thus, the vapor growth by molecular consumption should finish immediately after nucleation, which initiates within several millimeters of the evaporation source. The nanoparticles are needle-shaped by anisotropic vapor growth. In our previous experiments, nucleation of the non-crystalline precursor was revealed in the IR spectra of Al\(_2\)O\(_3\) and TiO\(_2\).\(^{28,31}\) As the IR spectrum of the just-nucleated nanoparticles already reveals monoclinic crystal formation and differs from that of non-crystalline particles, the phase transition from non-crystalline to crystalline form may occur earlier than the time scale of vapor growth. However, direct nucleation of crystalline particles from the evaporated vapor cannot be excluded from the possible formation pathway.

In-situ measurement revealed that the needle nanocrystals evolved into cubic and polyhedral nanocrystals at more than 10 mm above the evaporation source. In addition, the IR spectral features of the collected nanoparticles transited from single- to double-swell, even in the 50–250 mm region. The temperature variation at increasing vertical distance from the evaporation source (which was maintained at 1900 ± 100 K) was measured by a K-type thermocouple (Figure S7). The gas temperature of the growing region was below 673 K,\(^{32}\) and the vapor pressure of MoO\(_3\) was below 10\(^{-6}\) Pa. The size evolution along the short axis of the collected nanoparticles also revealed that growth proceeded under extremely low vapor
pressure conditions. This strongly suggests that the growth and transformation are induced by coalescence, because no growth units remained in the vapor at such low temperatures.

According to the size distributions of the particles collected at different heights, the number of needle particles decreased at higher collection points, while the number of cubic/polyhedral particles increased. This indicates an evolution from smaller to larger particles with increasing distance from the evaporation source (Figure 3b and Figure S4). Here particles with short/long axis ratios above 0.8 and below 0.4 were defined as cubic/polyhedral and needle-shaped, respectively. Cubic or polyhedral particles with a relatively larger long axis than that of needle particles were not observed. In addition, the number of smaller cubic/polyhedral particles did not decline, suggesting negligible growth by monomer attachment. All of these results are consistent with the coalescence of needle particles into cubic and polyhedral nanocrystals.

To compare the attachment number of the needle particles required to construct a cubic crystal (~10 particles) with the collision number in the free-flying state, we then estimated the collision frequency between the needle particles in a simple simulation, ignoring the decreased number density of the needle crystals during coalescence. The partial pressure of MoO₃ was set to its typical value at the nucleation point (400 Pa). At this pressure, the needle particles were sized at 50.9 nm × 16.0 nm and their number density was 3.5 × 10²⁰ m⁻³. This suggests that the particles are free-flying over a (300 × 300) nm² area. We carried out a simple 2D random walk simulation (see Supplementary Information). The simulation collision frequency between the needle particles was 10⁻¹² s⁻¹, implying that the number of collisions between the needle particles is several orders of magnitude larger than the number of attachments required to grow a cubic nanocrystal from the needle particles. This implies that the needle particles incorporate into the crystal only when their approach direction aligns with the crystallographically equivalent planes. An approach minimizes the total free energy of the result particle, suggesting that newly approaching needle particles preferentially incorporate into a kink site, as occurs in typical crystals.

Needle particles were never randomly attached, aggregated, or elongated perpendicularly to the [011] direction, over the cubic shape. Despite the most of short/long axis ratio (0.4-0.8) were relatively small in samples (Figure S4). Attachment probability of an intermediate particle composed of several needle particles may be higher than that of single needle particle because the intermediate particle should have kink sites, or a few nanometer steps between attached needle particles due to inhomogeneity of the size of monomers (needle particles).

Aggregates of multiple needle particles with the same crystallographic orientation were frequently observed in samples collected at 20–80 mm above the evaporation source (Figure S8). The ED patterns of single needle particles (Figure S8) are streaked in the [200] direction, evidencing that stacking faults formed on (100). Owing to the attachments of the needle particles, these stacking faults were periodic. Increased structural defects caused by imperfect alignment during oriented attachment has been reported in previous studies. Therefore, cubic and polyhedral particles probably form by coalescence between the needle particles in planes perpendicular to [011] in the ascending gas current.

The role of coalescence during frequent collisions in the smoke of just-nucleated nanoparticles has been already reported in the size evolution of metal and metal-oxide nanoparticles. These collisions are thought to form connected nanoparticles at surfaces, indicating that the molecules at the surface of just-nucleated nanoparticles has significant mobility. The surface molecular diffusion may form the faceted shapes. Attachment in crystallographically favorable orientations was previously recognized in limited temperature regions, but was never thought to majorly affect the morphology of nanoparticles. At the bulk surface of SnO₂, nanorods rotate to fit an equivalent plane before inserting into that plane, even in vacuum. Such coalescence induced by grain rotation is widely recognized. We conclude that selective coalescence at the crystallographically equivalent planes of the just-nucleated nanoparticles, namely, oriented attachment, strongly influenced the resulting morphology in our experiments. The formation sequence of cubic and polyhedral MoO₃ particles in vapor is schematically illustrated in Figure 5.

Oriented attachment growth is suggested to proceed by three driving forces; a thermodynamic driving force that reduces the energetic disadvantage at the surface, Coulombic (electrostatic) interactions, and van der Waals interactions. Competition between these forces, which depend on the orientation and surrounding medium, obscures the driving force of coalescence growth. If the main driving force arises
from thermodynamic perspective, a particle collides at the edge of another particle should be incorporated to reduce energetic disadvantage at free surface. None of the needle-like particles aggregated in random orientations or in inequivalent planes suggests collision among particles always occurs at the central part of another particle. In contrast, Coulombic force interacts between particles and may attract each other at the central part, leading attachment at the near center. In aqueous solution, Coulombic interactions between particles decay exponentially with distance, as they are mediated by the ion screening effect. Elimination of interfacial solvent molecules also influences the growth process. In addition, the surface energy differences between the planes are reduced in aqueous solution. In some simulation studies, the coalescence mechanisms of nanoparticles clearly differed in vacuum and solution.\(^{26,27}\) Comparisons between these processes might elucidate the driving force of oriented attachment. In our experiments, large differences of surface energy between the fresh planes of the just-nucleated nanoparticles were expected and the Coulombic forces should extend over much larger distances than in aqueous solution.

We present the first experimental report on the oriented attachment of free-flying nanoparticles in vapor. Such self-assembly growth around the evaporation source. The oriented attachment. In the first step, needle particles form by crystals from homogeneously distributed just-nucleated MoO\(_3\) molecules. The nuclei grew rapidly, forming 10-nm-scale anisotropic vapor growth. The nuclei collided at the near center. In aqueous solution, Coulombic interactions between particles decay exponentially with distance, as they are mediated by the ion screening effect. Elimination of interfacial solvent molecules also influences the growth process. In addition, the surface energy differences between the planes are reduced in aqueous solution. In some simulation studies, the coalescence mechanisms of nanoparticles clearly differed in vacuum and solution.\(^{26,27}\) Comparisons between these processes might elucidate the driving force of oriented attachment. In our experiments, large differences of surface energy between the fresh planes of the just-nucleated nanoparticles were expected and the Coulombic forces should extend over much larger distances than in aqueous solution.

**Conclusions**

We measured the IR spectra during the formation of final crystals from homogeneously distributed just-nucleated MoO\(_3\) crystals in a highly supersaturated vapor. The crystals grew by oriented attachment. In the first step, needle-like particles formed, anisotropic vapor growth around the evaporation source. The size of the critical nucleus was estimated as fewers than ten molecules. The nuclei grew rapidly, forming 10-nm-scale needles in 0.1 s while rapidly exhausting the source gas. Finally, the needle particles attached in crystallographically equivalent planes, forming cubic and polyhedral nanoparticles. Attachment in crystallographically favorable orientations, which has not been previously recognized in nanoparticle formation in vapor, critically determines the properties of the resulting particles and is comparable to the typical growth process of macromolecular crystals. In this case, the growth units are the needle particles. This result provides new insights into the control of chemical compositions, morphologies, and polymorphs of industrial nanomaterials, and assists our understanding of cosmic dust aggregation in early solar systems.

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**Notes and references**