



HOKKAIDO UNIVERSITY

Title	Self-assembly of MoO ₃ needles in gas current for cubic formation pathway
Author(s)	Ishizuka, Shinnosuke; Kimura, Yuki; Yokoi, Satoki et al.
Citation	Nanoscale, 9(28), 10109–10116 https://doi.org/10.1039/c7nr02613g
Issue Date	2017-06-20
Doc URL	https://hdl.handle.net/2115/70788
Type	journal article
File Information	Ishizuka_MoO ₃ _Nanoscale_HUSCAP.pdf



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

Shinnosuke Ishizuka^a, Yuki Kimura^{a*}, Satoki Yokoi^b, Tomoya Yamazaki^a, Rikako Sato^a and Tetsuya Hama^a

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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.

1 Introduction

2 Nucleation critically determines the characters (such
3 crystalline size, shape, polymorphism, and crystallinity) of
4 inorganic,^{1–8} organic,^{9–11} proteinaceous,^{12,13} and colloidal^{14,15}
5 materials. In an ideal system, a crystal grows continuously
6 toward its final form by sequential incorporation of growth
7 units.
8 In the last decade, in-situ observations have revealed
9 unexpected nucleation pathways, especially in solution
10 systems. These observations have overridden the previous
11 simple view that nucleation proceeds by monomer-by-
12 monomer incorporation of basic units. Before the stable
13 crystal is formed, intermediates such as polymorphs,
14 amorphous solid particles,³ liquid droplets,^{6,7,12,13} clusters with
15 characteristic structures,^{4,11} and crystals with different
16 chemical compositions from the final crystal² precipitate out
17 metastable phases. The formation sequence sometimes

18 follows Ostwald's step rule, in which the metastable
19 intermediates precipitate due to lower surface energies than
20 the stable phase.¹⁶ This process is complicated by the
21 characteristics of solvent molecules. To approach a kink site
22 and thereby join the crystal, a growth unit in water must
23 dehydrate the hydrated layer that surrounds the material.
24 Dehydration process plays key roles at the early stage of
25 nucleation and growth in solution.^{17,18}

26 In contrast to complex nucleation from solution, nucleation
27 of inorganic particles from a vapor is surface free, so we expect
28 that the result to be comparable to the nucleation theory.
29 Some experimental studies have attempted to unveil the
30 nucleation process. For instance, after thermal evaporation at
31 extremely high supersaturation, metal and metal oxides
32 nucleate homogeneously in the cooling gas.^{19–21} According to
33 nucleation theory, the critical nuclei in manganese nucleation
34 should be several atom/molecules in size, and their surface
35 free energy should be 30% larger than that of the
36 corresponding bulk.²⁰

37 Unexpected pathways in the post-nucleation growth
38 processes have also been proposed. Inter-particle coarsening
39 is thought to determine the resulting characteristics of crystals
40 in some solution systems.²² When coarsening happens
41 selectively between crystallographically equivalent planes, it is
42 known as oriented attachment growth.^{e.g., 2,23–27} For many
43 years, the fusion of two nanoparticles and agglutination by

^aInstitute of Low Temperature Science, Hokkaido University, Hokkaido Sapporo
060-0819, Japan

^bDepartment of Chemical Engineering, Graduate School of Engineering, Tohoku
University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan

[†]Electronic Supplementary Information (ESI) available: Detailed description on the
procedure of the collision simulation and supplementary figures of the
experiment, IR spectra, TEM images and size distribution of the particles are
available. See DOI: 10.1039/x0xx00000x

surface melting has been known to dominate the growth process in vapor phase. These previous studies show nucleation and growth pathways are not simple processes such as continuous incorporation of monomer molecules, are universally more diverse than hitherto predicted.^{26,27} Here we experimentally investigate vapor phase nucleation and subsequent growth of nanoparticles. Our proposed approach captures the early stages of crystallization using *situ* spatial scanning spectroscopy by a transmittance Fourier transform infrared (FT-IR) spectrometer. The *in-situ* IR data (which reflect the chemical compositions, phases, and shapes) of the just-nucleated nanoparticles in the free-flying state is complemented by TEM observations of the collected products. Applied in vapor phase nucleation, this technique demonstrates that morphological evolution of just-nucleated MoO₃ nanoparticles is induced by inter-particle coarsening crystallographically equivalent planes during frequent collisions in the gas current.

Experimental section

Nucleation and subsequent growth experiments of MoO₃ nanoparticles in vapor phase were performed in a stainless steel chamber combined with a FT-IR spectrometer (JASCO-VIR200), as described in our previous study.²⁸ The experimental apparatus for forming nanoparticles in the gas current is schematized in Figure S1a. The thallium bromide (KRS5) viewports provide an optical path for the FT-IR analysis. KRS5 exhibits high transmittance in the 10000–250 cm⁻¹ range. The transmitted IR light was sensed by a detector unit comprising an aperture, an IR filter (LP-8335, IR System Co., Ltd., Tokyo, Japan), a parabolic mirror, and an HgCdTe (MCT) photo-conductive detector (P5274-01, Hamamatsu Co., Shizuoka, Japan). The viewports were fixed to a U-shaped bench on which the FT-IR and detector unit were set at either side of the chamber. The chamber and viewports were connected by flexibly extendable bellows. In addition, the bench was interlocked to withstand a load motor unit (LAS4F40MW-1, Oriental Motor Co., Tokyo, Japan). In this configuration, we could acquire the transmittance FT-IR spectra at different heights from the evaporation source in a single experiment. The measurable region (65 mm along the vertical axis) exceeded the inner diameter of the windows (30 mm). The bench height was measured by a laser measurement sensor (CD22, OPTEX FA Co., Kyoto, Japan). The chamber was connected to a turbo-molecular pump (50 L/s). After evacuating the chamber to below 1.0×10^{-4} Pa, the gate valve was closed and high-purity O₂ (99.9%) and He (99.9999%) were injected. The pressure was first to 4.0×10^2 Pa with O₂ gas, then increased to 5.0×10^3 Pa with He gas. The gas pressure was measured by a crystal ion gauge (M-601GC, ANELVA Co., Kanagawa, Japan) at $<10^{-1}$ Pa, and by a piezoresistive pressure sensor (Pressure sensor 680, Huba Control, Switzerland) at >1 Pa.

The evaporation source was a Mo wire ($\phi = 1$ mm, length = 75 mm, purity 99.95%). The wire was connected to Cu electrodes for rapid electrical-resistance heating. At the starting position

in Experiment A and B, the optical axis of the FT-IR was centered at 10 mm beneath and 7.5 mm above the evaporation source, respectively. The temperature of the evaporation source was monitored during the experiments by a radiation thermometer ($\lambda = 0.8$ – 1.6 μm ; FTZ2, Japan Sensor Co., Tokyo, Japan). In the temperature calculation, the emissivity of the Mo wire surface was assumed constant at 0.3. However, because the emissivity changes by surface oxidation of the Mo wire, the absolute temperature obtained in this study may depend on the oxygen vapor pressure. The evaporation source was rapidly heated to ~ 1900 K by applying an AC voltage to the electrodes, then maintained at this temperature throughout each experiment. Once the temperature had stabilized, the bench was moved toward the vertical axis at 10 mm s^{-1} , until the optical path reached 10 mm and 67.5 mm above the evaporation source in Experiment A and B, respectively. The bench was then returned to its starting position at 10 mm s^{-1} . Smoke formation was confirmed by a CMOS camera (MS-M33WT3, Mosquell Co., Ltd., Tokyo, Japan) as shown in Figure S2. When the U-shaped bench began to move, the convection has become stationary, as confirmed by the shape of the smoke. Several seconds after the bench reached its starting position, the AC voltage was turned off. The changes in temperature of the evaporation source, pressure in the chamber and relative distance between the optical axis and the evaporation source were recorded, and the results are plotted in Figure S3 for the Experiment B.

Surface oxidation on the Mo wire results in MoO₃ formation. As MoO₃ has higher vapor pressure than Mo metal, the oxidized MoO₃ was simultaneously evaporated as molecules from the evaporation source. The gas flowed upward under thermal convection generated by the evaporation source itself, inducing the homogeneous nucleation of nanoparticles. The nucleation was visible as a smoke. By setting the optical path of the FT-IR just above the evaporation source, we could measure the IR spectra of the nascent condensates in the free-flying state. The aperture diameter was adjusted to improve the spatial resolution at a suitable IR signal intensity. At an aperture diameter of 8 ± 1 mm, the beam diameter at the center of the optical axis (where the nanoparticles were nucleated) was calculated as 4.5 ± 0.6 mm. The measurement region was a column of width 5 mm (Figure S1b). The time evolution of the IR spectra was obtained at 24 spectra/s. The background spectra were obtained at each height from the evaporation source, following the procedure just before the experiment. The signal spectra in each 5-mm region were averaged, and the absorbance spectra were then obtained from 7.5 mm to 67.5 mm above the evaporation source. To confirm the consistency of the region-dependent IR spectra in the smoke, the spatial scan spectra were obtained in both outward and homeward directions.

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 sweated with ethanol and dried for 1 minute. The particles were observed by TEM (JEM-

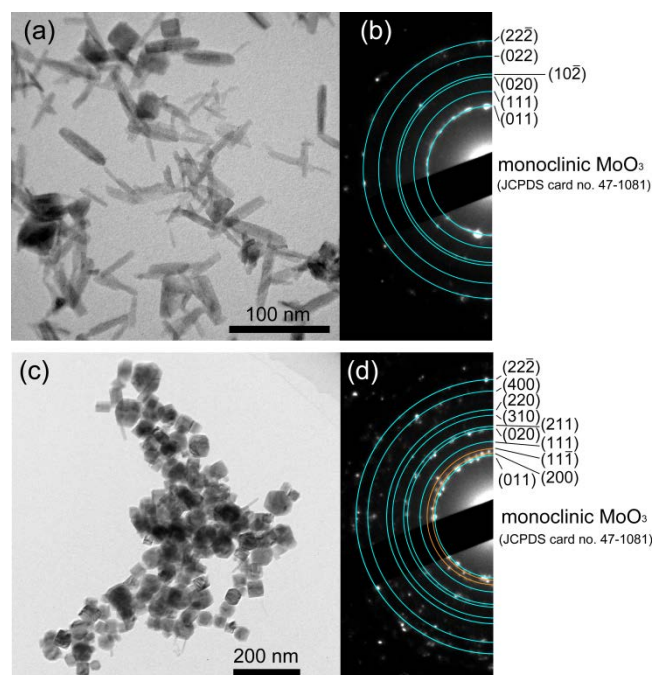


Figure 1. Typical TEM images of the synthesized nanoparticles collected (a) at the height of the evaporation source on the side collector set beside and (c) at the roof collector. (b), (d) electron diffraction (ED) patterns corresponding to (a) and (c), respectively.

2100F, JEOL Co., Japan) at an acceleration voltage of 200 kV. The remaining particles on the collecting sheet were agitated with KBr powder and formed into 10 mm-diameter pellets under a pressure of 8×10^4 N for subsequent FT-IR measurements.

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 total pressure induces frequent collision between the just-nucleated nanoparticles in gas current. These leads increase in size of resulting materials and reduce the time scale for shape evolution.²⁹ We selected relatively low O_2 partial pressure and total pressure conditions (less 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.

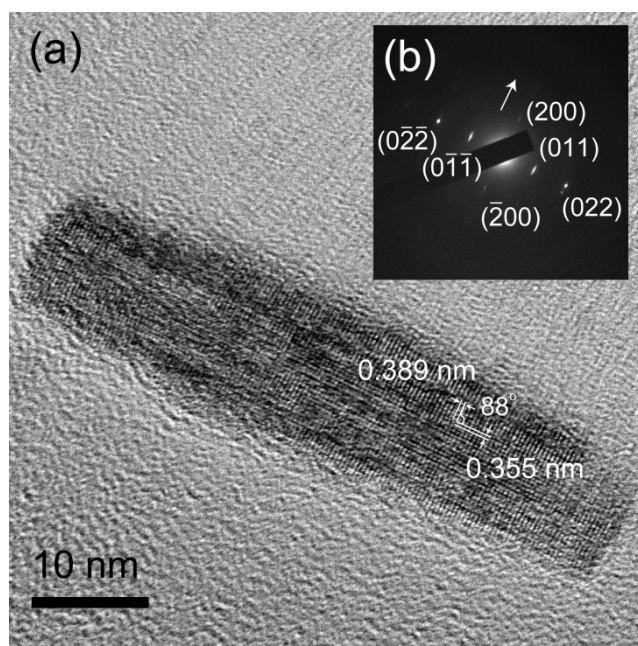


Figure 2. High resolution image of a typical needle shaped particle and (b) its corresponding ED pattern. Streaks along [200] are indicated by the white allow.

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 beside 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 $(11\bar{1})$ and (200) (indicated by the orange lines in Fig. 1d) do not appear in the ED pattern of the needle-shaped particles in Fig. 1b. The needle particles showed well-aligned lattice images of (011) , but frequent defects in the perpendicular planes.

The lengths of the long and perpendicular (short) axes were measured in samples collected at various heights above the evaporation source (Fig. 3a). The short axis was measured along the middle part of the nanoparticles. The average lengths of the axes (long axis, short axis), measured from at least 126 particles in each sample, were $(24.3 \pm 2.5, 9.9 \pm 0.7)$,

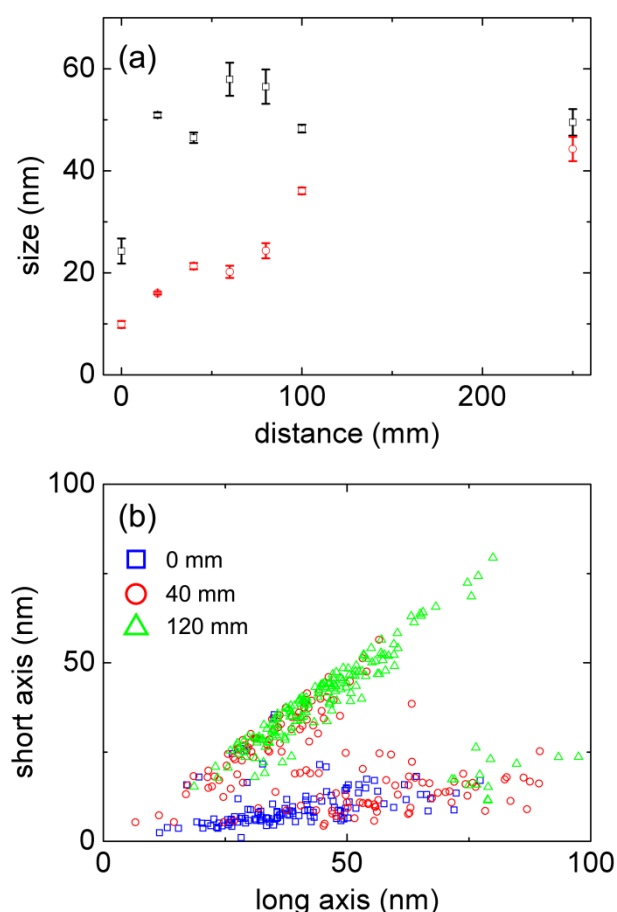


Figure 3. (a) Averaged lengths of the long axis (black squares) and short axis (red squares) of the nanoparticles collected at 0, 20, 40, 60, 80, 120 and ~250 mm above the evaporation source, plotted with their error bars, and (b) the size distributions of samples collected at 0 mm (blue squares), 40 mm (red squares) and 120 mm (green squares).

(50.9 ± 0.5, 16.0 ± 0.3), (46.5 ± 1.0, 21.3 ± 0.6), (58.0 ± 3.4, 20.7 ± 1.5), (56.5 ± 3.4, 24.4 ± 1.5), (48.3 ± 0.8, 36.1 ± 0.7), and (49.5 ± 2.6, 44.3 ± 2.4) nm at collection heights of 0, 20, 40, 60, 80, 120, and ~250 mm, respectively. The longitudinal length of the nanoparticles increased from 0 to 20 mm and thereafter remained nearly constant. In contrast, the short axis increased continuously as the height increased from 0 mm to 250 mm. We show the representative long/short axis ratio of the particles collected at 0, 40 and 120 mm on the side collector in Figure 3b. The ratio of the particles of all sample were summarized in Figure S4. The size evolves because the number of cubic and polyhedral particles increases while the number of needle particles diminishes. Therefore, we measured the absorbance of the floating nanoparticles in the gas current around the evaporation source at different heights, and compared the spectra with the ex-situ IR spectra of the collected particles.

To demonstrate the evolution of the IR spectra of the nucleated molybdenum oxide nanoparticles, we conducted two experimental runs (A and B) under the same conditions. In Experiment A, we surveyed from 10 mm below to 10 mm above the evaporation source (Figure 4A1-5). In Experiment B,

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 is contributed by at least six subtle absorptions (indicated by the blue lines in Figure 4). The combination of these subtle absorptions alters 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.³⁰ 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 MoO₃ 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.²⁹ 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.

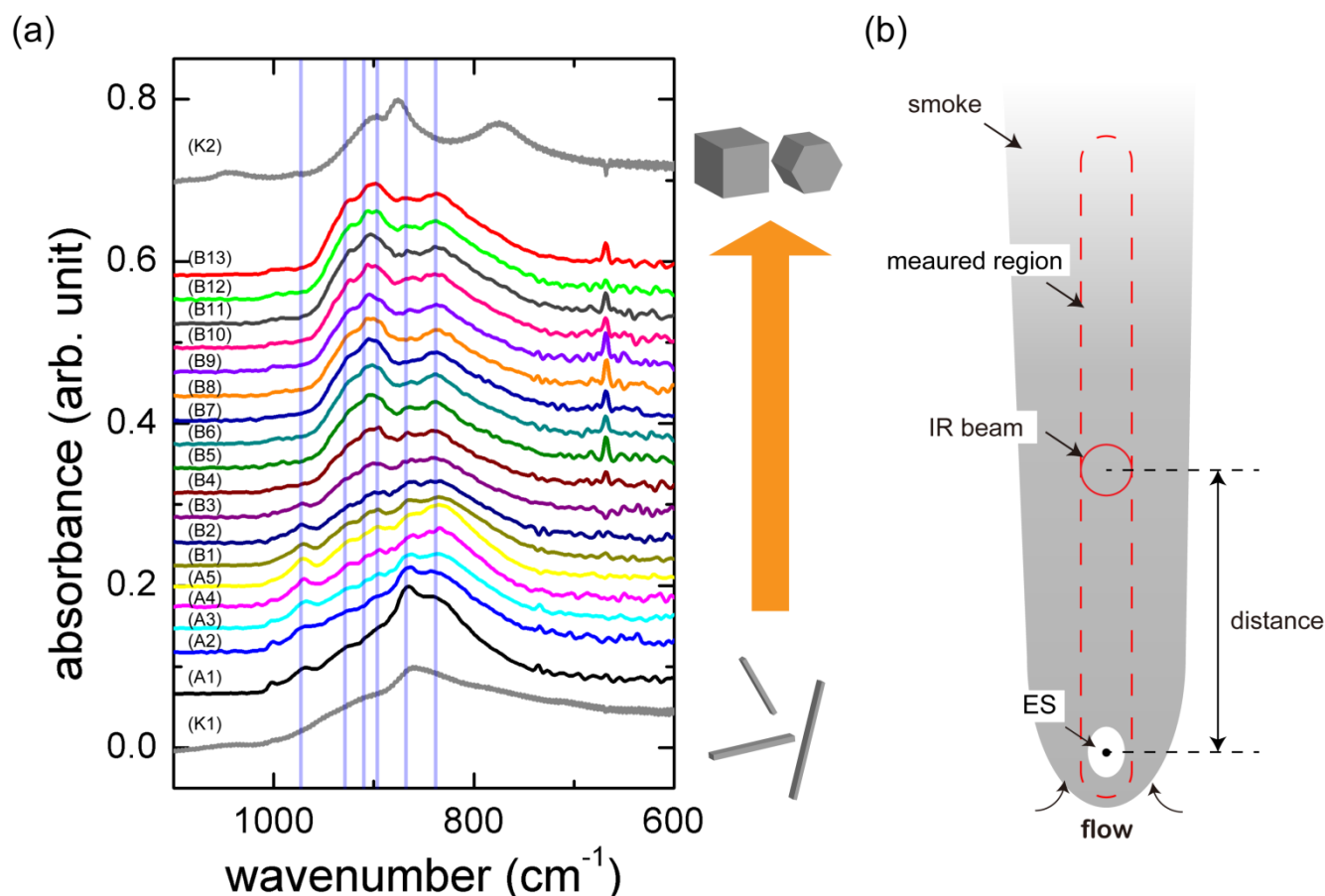


Figure 4. In-situ FT-IR spectra of nucleating and growing nanoparticles in a gas current (a) and a schematic view of the experiment along the evaporation source (ES) (b). In Experiment A, spectra were measured at 10 mm (A1) and 5 mm (A2) beneath the evaporation source, and at 0 mm (A3), 5 mm (A4), and 10 mm (A5) above the evaporation source. In Experiment B, they were measured at 7.5 (B1), 12.5 (B2), 17.5 (B3), 22.5 (B4), 27.5 (B5), 32.5 (B6), 37.5 (B7), 42.5 (B8), 47.5 (B9), 52.5 (B10), 57.5 (B11), 62.5 (B12) and 67.5 mm (B13) above the evaporation source. All spectra were obtained in the downward direction. Blue lines indicate the peaks at 970, 920, 910, 900, 860 and 840 cm^{-1} . The spectra labeled K1 and K2 are the IR spectra of the needle particles and the cubic/polyhedral particles, respectively, measured by the KBr embedding method.

299 Discussions

300 We have questioned how the needle particles transform into
 301 cubic and polyhedral particles in the ascending gas current. In
 302 our experimental set up, the evaporant flowed by convection
 303 and is quenched at temperature gradients $>1000 \text{ K s}^{-1}$. The
 304 observed characteristic features of the just-nucleated
 305 nanoparticles were attributed to the needle-shaped
 306 molybdenum oxide (spectrum A1 in Figure 4). In previous
 307 studies, we determined the partial pressure of the source
 308 molecules at the nucleation point as $\sim 10^{-3} \text{ Pa}$.^{19–21} In such an
 309 atmosphere, a nanoparticle grows to several tens of
 310 nanometers in 10^{-3} s ,^{19,20} with simultaneous consumption of
 311 the vaporized source molecules. The time scale of vapor
 312 growth is several orders of magnitude faster than the time
 313 scale of convection ($\sim 1 \text{ s}$ from the evaporation source to the
 314 top of the chamber, estimated from the convection of visible
 315 smoke). In addition, the MoO_3 vapor pressure at more than 5
 316 mm above the evaporation source, estimated from
 317 temperature fields derived from thermocouple data (Figure
 318 S7), is $<10^{-6} \text{ Pa}$. Thus, the vapor growth by molecular
 319 consumption should finish immediately after nucleation, which

320 initiates within several millimeters of the evaporation source.
 321 The nanoparticles are needle-shaped by anisotropic vapor
 322 growth. In our previous experiments, nucleation of the non-
 323 crystalline precursor was revealed in the IR spectra of Al_2O_3
 324 and TiO_2 .^{28,31} As the IR spectrum of the just-nucleated
 325 nanoparticles already reveals monoclinic crystal formation and
 326 differs from that of non-crystalline particles, the phase
 327 transition from non-crystalline to crystalline form may occur
 328 earlier than the time scale of vapor growth. However, direct
 329 nucleation of crystalline particles from the evaporated vapor
 330 cannot be excluded from the possible formation pathway.

331 In-situ measurement revealed that the needle nanocrystals
 332 evolved into cubic and polyhedral nanocrystals at more than
 333 10 mm above the evaporation source. In addition, the IR
 334 spectral features of the collected nanoparticles transited from
 335 single- to double-swell, even in the 50–250 mm region. The
 336 temperature variation at increasing vertical distance from the
 337 evaporation source (which was maintained at $1900 \pm 100 \text{ K}$)
 338 was measured by a K-type thermocouple (Figure S7). The gas
 339 temperature of the growing region was below 673 K,³² and the
 340 vapor pressure of MoO_3 was below 10^{-6} Pa . The size evolution
 341 along the short axis of the collected nanoparticles also
 342 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 MoO_3 was set to its typical value at the nucleation point (400 Pa). At this pressure, the needle particles were sized at $500 \text{ nm} \times 16.0 \text{ nm}$ and their number density was $3.5 \times 10^{20} \text{ m}^{-3}$. This suggests that the particles are free-flying over a $(300 \times 300) \text{ nm}^2$ area. We carried out a simple 2D random walk simulation (see Supplementary Information). The simulated collision frequency between the needle particles was 10^6 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. This approach minimizes the total free energy of the resulting 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, nor elongated perpendicularly to the $[011]$ direction, over the cubic shape. Despite the most of the resulting particles are transformed to cubic or polyhedral shape, the number of the particles with the intermediate short/long axis ratio (0.4–0.8) were relatively small in all 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 S9) are streaked in the $[200]$ direction, evidencing that stacking

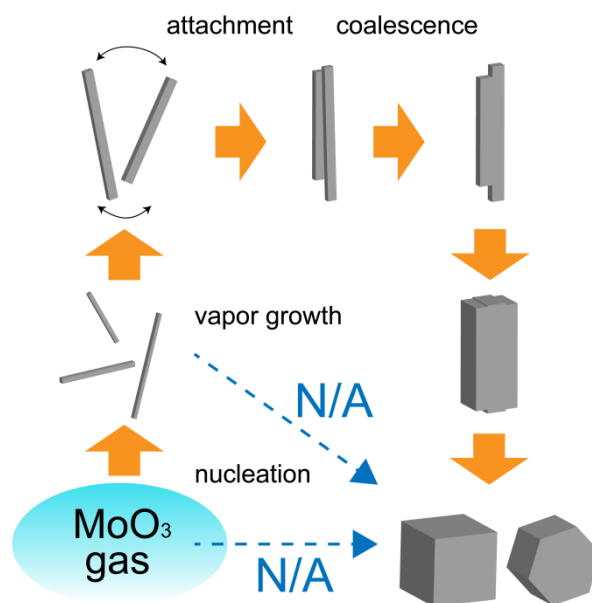


Figure 5. Schematic showing the shape evolution of just-nucleated MoO_3 nanoparticles in an ascending gas current. Previously considered mechanisms shown by dotted arrows (direct nucleation or monomer-by-monomer growth in vapor) are not applicable to the formation of cubic and polyhedral MoO_3 particles.

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.^{23,25} 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.^{32–34} 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 SnO_2 , nanorods rotate to fit an equivalent plane before inserting into that plane, even in vacuum.³⁵ Such coalescence induced by grain rotation is widely recognized.³⁶ 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 MoO_3 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.²⁶ If the main driving force arises

from thermodynamic requirement, a particle collides at the edge of another particle should be incorporated to reduce energetic disadvantage at free surface. None of the needle 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 ionic 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 in vapor is potentially applicable to industrial synthesis processes, and might explain natural mineral evolution such as cosmic dust aggregation during planet formation.³⁷ In the present experimental setup, we cannot distinguish between free-flying particles that have attached after electrostatic alignment and particles that have randomly attached, then immediately aligned to reduce the misfit. In the previous consensus view, homogeneous nucleation from vapor occurs by a direct monomer-by-monomer process from molecules to crystals. However, our previous works revealed that metal-oxide nanoparticles crystallize by multistep processes.^{28,31,38} The present study reveals a growth pathway of nanoparticles via oriented attachment, which has never been considered in nucleation and subsequent growth processes in vapor. These findings suggest that the versatile nucleation and growth pathways demonstrated in solution systems throughout the past decade also occur in vapor systems.

Conclusions

We measured the IR spectra during the formation of final crystals from homogeneously distributed just-nucleated Meq crystals in a highly supersaturated vapor. The crystals grew by oriented attachment. In the first step, needle particles formed anisotropic vapor growth around the evaporation source. The size of the critical nucleus was estimated as fewer than tens of molecules. The nuclei grew rapidly, forming 10-nm-scale needles in 0.1 s while rapidly exhausting the source gas. The free-flying needle particles collided in approximately 1 s. Finally, the needle particles attached in crystallographically equivalent planes, forming cubic and polyhedral nanoparticles. Attachment in crystallographically favorable orientation, 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.

Acknowledgements

We thank F. Saito, S. Nakatsubo, S. Mori, and K. Shinbori of the Technical Division in the Institute of Low Temperature Science, Hokkaido University, for their help in the development of the experimental system. This work was partly supported by a Grant-in-Aid for a JSPS Fellow (15J02433) and a Grant-in-Aid for Scientific Research(S) from KAKENHI (15H05731).

Notes and references

- S.-Y. Chung, Y.-M. Kim, J.-G. Kim and Y.-J. Kim, *Nat. Phys.*, 2009, **5**, 68–73.
- A. E. S. Van Driessche, L. G. Benning, J. D. Rodriguez-Blanco, M. Ossorio, P. Bots and J. M. Garcia-Ruiz, *Science*, 2012, **336**, 69–72.
- M. H. Nielsen, S. Aloni and J. J. De Yoreo, *Science*, 2013, **218**, 213–218.
- D. C. Gary, M. W. Terban, S. J. L. Billinge and B. M. Cossairt, *Chem. Mater.*, 2015, **27**, 1432–1441.
- J. Baumgartner, A. Dey, P. H. H. Bomans, C. Le Coadou, P. Fratzl, N. A. J. M. Sommerdijk and D. Faivre, *Nat. Mater.*, 2013, **12**, 310–314.
- D. Loh, S. Sen, M. Bosman, S. F. Tan, J. Zhong, C. A. Nijhuis, P. Kral, P. Matsudaira and U. Mirsaidov, *Nat. Chem.*, 2016, 1–10.
- M. K. Bera and M. R. Antonio, *J. Am. Chem. Soc.*, 2016, **138**, 7282–7288.
- C. J. S. Ibsen, D. Gebauer and H. Birkedal, *Chem. Mater.*, 2016, **28**, 8550–8555.
- S. Parveen, R. J. Davey, G. Dent and R. G. Pritchard, *Chem. Commun. (Camb.)*, 2005, 1531–1533.
- K. Harano, T. Homma, Y. Niimi, M. Koshino, K. Suenaga, L. Leibler and E. Nakamura, *Nat. Mater.*, 2012, **11**, 877–881.
- C. Sun and D. Xue, *Cryst. Growth Des.*, 2015, **15**, 2867–2873.
- P. G. Vekilov, *Nanoscale*, 2010, **2**, 2346–2357.
- T. Yamazaki, Y. Kimura, P. G. Vekilov, E. Furukawa, M. Shirai, H. Matsumoto, A. E. S. Van Driessche and K. Tsukamoto, *Proc. Natl. Acad. Sci.*, 2017, **114**, 201606948.
- T. H. Zhang and X. Y. Liu, *J. Phys. Chem. B*, 2007, **111**, 14001–14005.
- J. R. Savage and A. D. Dinsmore, *Phys. Rev. Lett.*, 2009, **102**, 15–18.
- W. Ostwald, *Zeitschrift für Phys. Chemie*, 1897, **22**, 289–302.

- 541 17 D. Chakraborty and G. N. Patey, *J. Phys. Chem. Lett.*, 2013,
542 **4**, 573–578.
- 543 18 J. Ihli, W. C. Wong, E. H. Noel, Y.-Y. Kim, A. N. Kulak, H. K.
544 Christenson, M. J. Duer and F. C. Meldrum, *Nat. Commun.*,
545 2014, **5**, 3169.
- 546 19 Y. Kimura, H. Miura, K. Tsukamoto, C. Li and T. Maki, *J.*
547 *Cryst. Growth*, 2011, **316**, 196–200.
- 548 20 Y. Kimura, K. K. Tanaka, H. Miura and K. Tsukamoto, *Cryst.*
549 *Growth Des.*, 2012, **12**, 3278–3284.
- 550 21 Y. Kimura, K. K. Tanaka, T. Nozawa, S. Takeuchi and Y.
551 Inatomi, *Sci. Adv.*, 2017, **3**, e1601992.
- 552 22 N. T. K. Thanh, N. Maclean and S. Mahiddine, *Chem. Rev.*,
553 2014, **114**, 7610–7630.
- 554 23 R. L. Penn and J. F. Banfield, *Science*, 1998, **281**, 969–971.
- 555 24 J. F. Banfield, *Science*, 2000, **289**, 751–754.
- 556 25 D. Li, M. H. Nielsen, J. R. I. Lee, C. Frandsen, J. F. Banfield
557 and J. J. De Yoreo, *Science*, 2012, **336**, 1014–1018.
- 558 26 H. Zhang and J. F. Banfield, *CrystEngComm*, 2014, **16**,
559 1568–1578.
- 560 27 M. Raju, A. C. T. Van Duin and K. A. Fichthorn, *Nano Lett.*,
561 2014, **14**, 1836–1842.
- 562 28 S. Ishizuka, Y. Kimura, T. Yamazaki, T. Hama, N. Watanabe
563 and A. Kouchi, *Chem. Mater.*, 2016, **28**, 8732–8741.
- 564 29 M. Kurumada and C. Kaito, *J. Phys. Soc. Japan*, 2006, **75**, 2–
565 6.
- 566 30 C. F. Bohren and D. R. Huffman, *Absorption and Scattering*
567 *of Light by Small Particles*, John Wiley & Sons., New York,
568 United States, 1983.
- 569 31 S. Ishizuka, Y. Kimura and T. Yamazaki, *J. Cryst. Growth*,
570 2016, **450**, 168–173.
- 571 32 C. Kaito, *Jpn. J. Appl. Phys.*, 1978, **17**, 601–609.
- 572 33 C. Kaito, *Jpn. J. Appl. Phys.*, 1985, **24**, 261–264.
- 573 34 O. Kido, H. Suzuki, Y. Saito and C. Kaito, *Jpn. J. Appl. Phys.*,
574 2003, **42**, 5705–5708.
- 575 35 C. Ribeiro, E. J. H. Lee, T. R. Giraldo, R. Aguiar, E. Longo and
576 E. R. Leite, *J. Appl. Phys.*, 2005, **97**, 24313.
- 577 36 D. Moldovan, V. Yamaev, D. Wolf and S. R. Phillpot, *Phys.*
578 *Rev. Lett.*, 2002, **89**, 206101.
- 579 37 S. Okuzumi, M. Momose, S. Sirono, H. Kobayashi and H.
580 Tanaka, *Astrophys. J.*, 2016, **821**, 82.
- 581 38 S. Ishizuka, Y. Kimura and I. Sakon, *Astrophys. J.*, 2015, **803**,
582 88.
583