Supplementary Materials for

Inducing thermodynamically blocked atomic ordering via strongly driven nonequilibrium kinetics

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Supplementary Text

Structural properties of the Bi nanospheres

Additional information about the structural characteristics of Bi nanoparticles is provided here. The spherical morphology of the Bi nanoparticles with good morphological homogeneity is confirmed from the SEM and TEM images (Fig. S1, A and B). The size distribution of the nanoparticle has been characterized (Fig. S3A). Good crystallinity of single Bi nanospheres is evident from the TEM images and electron diffraction patterns (Fig. S1, C and D). The X-ray diffraction (XRD) pattern obtained for the nanoparticles showed pure Bi phase of the nanoparticles in the nominal rhombohedral structure, consistent with the standard XRD pattern of the Bi crystals (Fig. S1E) (JCPDS card No. 05-0519).

Fig. S1. Structure characterization of Bi nanoparticles. (A, B) High quality spherical Bi nanoparticles are observed from SEM and TEM, respectively. (C) TEM image showing high quality crystalline nature of the Bi nanoparticles. (D) Electron diffraction patterns obtained from the TEM experiment visualizes the crystalline nature of the nanoparticle. (E) High purity of the nanoparticles with standard Bi structure is confirmed from the XRD analysis in good agreement with the standard XRD pattern of the Bi crystal in JCPDS.
Quantification of the faceting and data statistics

We quantified the degree of faceting using the anisotropy of the diffraction patterns (Fig. S2A). Anisotropic diffraction patterns with directional streaks reflect the formation of faceted surface deformed from the spherical sample morphology with isotropic diffraction patterns. We defined the anisotropy as \( (C_{\text{max}} - C_{\text{min}})/(C_{\text{max}} + C_{\text{min}}) \), where \( C_{\text{max}} \) or \( C_{\text{min}} \) is maximum or minimum value of angular cross correlation of the diffraction pattern. The angular cross correlation was calculated by \( C(\theta) = \sum_q [(q^\alpha I_0(q)) \cdot (q^\alpha I_0(q))] / \sum_q [(q^\alpha I_0(q)) \cdot (q^\alpha I_0(q))] \), where \( I_0 \) is the diffraction intensity at rotation angle \( \theta \) and \( \alpha \) is the enhancement factor for high-\( q \) signals compensating the decay of intensity as increasing \( q \) (56). The patterns that have the value of anisotropy greater than 1/3 were defined as faceted patterns (Fig. S2B).

**Fig. S2. Temporal evolution of faceting in Bi NPs on melting.** (A) The temporal evolution of the anisotropy noted in diffraction patterns, which indicates the formation of facets with streaks in diffraction patterns. The development of facets started after 10 ps, and fully developed at ~ 40 ps. The patterns which lie above \( e=1/3 \) (horizontal dotted line) were classified as a faceted pattern in (B). The anisotropy from TTMD results (blue) showed good consistency with our experimental results (red). (B) The distribution of faceted or spherical patterns in total measured patterns. The height of each bar represents the ratio of spherical patterns or the ratio of faceted patterns. The number of total measured patterns are displayed at Table S1.
Table S1 shows statistical details of faceting for the whole data sets from three independent XFEL experiments. For each experiment, we sorted out diffraction patterns from a single Bi nanoparticle with its number noted as *Single patterns*. The number of total measured diffraction patterns (*Total No.*) for each delay time was also shown. The number of faceted patterns (*Faceted patterns*) from the *Single patterns* was estimated following the procedures aforementioned with its fraction indicated as ‘*Ratio, %*’. The results are also summarized using the bar graph in Fig. S2B.

Table S1. Statistical information of the faceting in XFEL single-pulse diffraction data

| Delay (ps) | Exp. 1 | Exp. 2 | Exp. 3 |
|-----------|--------|--------|--------|
|           | Single patterns (Total No.) | Faceted patterns (Ratio, %) | Single patterns (Total No.) | Faceted patterns (Ratio, %) | Single patterns (Total No.) | Faceted patterns (Ratio, %) |
| Intact    | 105 (2,516) | 0 (0%) | 5 (611) | 0 (0%) | 85 (2,499) | 0 (0%) |
| 3         | - | - | 10 (648) | 0 (0%) | - | - |
| 5         | 6 (144) | 0 (0%) | 26 (864) | 0 (0%) | - | - |
| 7         | - | - | 9 (432) | 0 (0%) | - | - |
| 8         | - | - | - | - | 21 (462) | 0 (0%) |
| 10        | 16 (300) | 0 (0%) | 12 (756) | 0 (0%) | 23 (1,056) | 0 (0%) |
| 15        | - | - | 18 (1,152) | 0 (0%) | - | - |
| 20        | 10 (294) | 0 (0%) | 8 (540) | 1 (13%) | 67 (1,650) | 10 (15%) |
| 25        | - | - | 12 (540) | 4 (33%) | - | - |
| 30        | 7 (324) | 7 (100%) | 7 (216) | 6 (86%) | - | - |
| 35        | 9 (144) | 8 (89%) | 4 (216) | 3 (75%) | - | - |
| 40        | 9 (252) | 7 (78%) | - | - | 133 (5,181) | 111 (83%) |
| 45        | 9 (216) | 9 (100%) | - | - | - | - |
| 50        | 13 (268) | 11 (85%) | - | - | - | - |
| 60        | 6 (213) | 4 (67%) | - | - | - | - |
| 70        | 9 (157) | 8 (89%) | - | - | - | - |
| 80        | 11 (176) | 7 (64%) | 10 (216) | 8 (80%) | 83 (2,046) | 68 (82%) |
| 90        | 15 (160) | 15 (100%) | - | - | - | - |
| 100       | 11 (72) | 10 (91%) | - | - | - | - |
| 120       | 8 (72) | 8 (100%) | - | - | - | - |
| 180       | - | - | - | - | - | - |

* Exp. 1 - 3 : Three independent experiments
* Single patterns (Total No.) : The number of patterns from single Bi NPs with the total number of collected patterns, including patterns from single and multiple particles, indicated in parenthesis.
* Faceted patterns (Ratio, %) : The number of faceted patterns with its ratio to the number of single patterns indicated in parenthesis.
Fig. S3. Size distribution and the expansion of Bi nanoparticles on melting. (A) The particle size distribution was obtained for intact Bi particle images reconstructed from 105 single-pulse diffraction patterns (Fig. S15). The mean diameter is 170 nm. Particle size follows the Gaussian distribution with the standard deviation of 12 nm. (B) The diameter of the Bi nanoparticles on melting showed a similar Gaussian distribution (dashed red and blue curve) of the intact Bi particles (dashed green). (C) The scaled sizes of the Bi nanoparticles are plotted with respect to the diameter of the intact Bi nanoparticle; nanoparticles on higher and lower laser fluence are displayed in red and blue circles, respectively. The expansion speed is ~ 200 m s\(^{-1}\) for the high laser fluence, which is faster than the speed of ~ 50 m s\(^{-1}\) at the low laser fluence.
Fig. S4. Lattice temperature and elastic pressure from TTMD simulations. (A) The lattice temperature of the Bi nanoparticle is calculated from the TTMD for the laser fluence equivalent to the high fluence condition (140-mJ cm$^{-2}$) and the low fluence condition (32-mJ cm$^{-2}$) in experiments. At high laser fluence, the faceting of the Bi nanoparticle was observed at $\sim$ 20 ps corresponding to the lattice temperature of $\sim$ 1000 K, much higher than the bulk melting temperature of Bi at 545 K. (B) The laser induced elastic pressure was calculated near the surface of the Bi nanoparticle from the TTMD simulation. The pressure remained lower than 1 GPa, or mostly less than 0.5 GPa, during the melting, which is much lower than the value required for realizing high-pressure crystalline phase of 10 GPa scale (57).
Fig. S5. Faceting behavior compared with atomic polyhedron models. (A) The polyhedrons on the right composed of (100), (110) and (111) facets reproduce the diffraction pattern and projected density from experiments. The model projected along [100] direction reproduces the observed four-fold symmetry. (B) The projection along [110] also reproduces the four-fold symmetry as observed in the diffraction pattern. Scale bar, 100 nm.
Fig. S6. TTMD simulations displaying the faceting during ultrafast melting of Bi nanoparticles under a high laser fluence. (A) Atomistic structure obtained from the TTMD simulations viewed along the [111] direction shows edged boundaries as the faceting develops. (B) Visualization of the facets for the structures in (A). The surfaces colored in orange, blue and brown display (100), (110), and (111) planes, respectively. (C) Projected density of the structures in (A) is displayed showing inhomogeneous internal density distribution with the melting. The laser fluence for the simulation was 140-mJ cm\(^{-2}\).
Fig. S7. Temporal evolution of the local order parameter calculated for TTMD simulated Bi NP structure. The local order parameter was calculated with the visualization of the value for the structure projected along the [111] direction. Ten independent TTMD simulations were performed to calculate the order parameters. Atoms colored in red show higher ordering compared to the blue ones. The surface and interior atoms show contrasting behavior in that the surface atoms stay ordered while the interior atoms become disordered on melting.
Fig. S8. Bi NPs on melting under the laser fluence of 600-mJ cm$^{-2}$. (A) Single pulse diffraction patterns are obtained at the laser fluence of 600-mJ cm$^{-2}$. Streaks develop for this melting reaction accompanying the faceting. (B) Bi images reconstructed from the single-pulse diffraction patterns in (A). Similar to the results observed for a laser fluence of 140-mJ cm$^{-2}$, the facet formations were accompanied during the melting transition. The melting transition took place faster than that from 140-mJ cm$^{-2}$ case with a higher laser fluence here. The scale bar shows 100 nm.
The spherical and polyhedral Bi NPs used in free energy comparison at 0 K

**Fig. S9. The spherical and polyhedral Bi NP structures.** All-atom structures of the two NPs of 20 nm are constructed to compare the free energy between the spherical and polyhedral Bi NPs. Calculated free energy of the polyhedron per atom was 54 meV lower than that of the sphere as shown in Fig. 3C. Furthermore, the comparison of the free energy of surface atoms (r > 9 nm) showed that the average free energy of the surface atoms of those NP structures was 173 meV lower compared to the spherical NP structure. It clearly confirms that the free energy is lower for the polyhedron structure, and the spherical structure in the beginning is metastable.
MD simulations for equilibrium kinetics-driven melting

The reference structure representing the equilibrium kinetics-driven melting is introduced here. As shown in Fig. 3B, we compared the free energies of the TTMD-simulated structures in Fig. 2A and Fig. 3A with those of reference structures to estimate the effect of the nonequilibrium kinetics-driven structure change on the system free energy. The reference structures represent the equilibrium heating condition, whereas the TTMD represents non-equilibrium laser heating. The equilibrium melting was obtained by slowly heating a 20 nm spherical Bi NP from 300 K up to the target temperatures, i.e. the TTMD-generated temperatures (Fig. S4A), in NVT (N: Number, V: Volume and T: Temperature) canonical ensemble in steps of 50 K. We confirmed that the structure was fully equilibrated at each step by relaxation for additional 10 ps. Under the slow heating condition to represent the equilibrium melting, we obtained disordered structures without facet surfaces (Fig. S10), and we refer to these unfaceted structures as equilibrium kinetics driven structures in comparison with the TTMD-generated structures, which are nonequilibrium kinetics driven.

For each of the TTMD and equilibrium heating simulations, the free energies from ten independent runs were obtained and averaged for comparison. As shown in Fig. 3B, with high laser fluence, the TTMD-simulated structures are at lower free energy states and the free energy difference increases with time until 100 ps, where the faceted structure has a free energy lower by ~141 meV compared to the reference structure. This effect is only mild with low laser fluence, illustrating that the Bi nanoparticle finds lower free energy states more efficiently through nonequilibrium kinetics. Our free energy calculations show that the nonequilibrium kinetics driven melting pathway through ultrashort laser irradiation is lower in free energies than equilibrium kinetics driven ones, and convince that our observations lie on the hidden pathways, which are inaccessible through the equilibrium process.
Fig. S10. Bi NP on equilibrium kinetics-driven melting. All-atom structure of the Bi nanoparticle on equilibrium melting is obtained as reference structures in comparing the free energies for TTMD simulated structures described in Fig. 3B. The temperature labeled below each structure indicates the lattice temperatures from the TTMD simulations under high laser fluence with the corresponding delay time in parenthesis.
Fig. S11. Wide-angle XFEL diffraction patterns of Bi NPs on high fluence melting. (A) Bragg reflections from the Bi NPs on melting were recorded from the single-pulse XFEL experiments using the same Bi NPs. Data cover the diffraction angles between 24° and 33° to detect (0 0 3), (1 0 1) and (0 1 2) Bragg reflections. Red solid lines guide the diffraction circles for the designated Bragg reflections. Many single pulse patterns of the same delay time were added together. (B) The intensity of Bragg peaks obtained from a. The expansion of the lattice on thermalization appeared with the broadening of Bragg reflection to lower diffraction angles (40 ps, for instance). Diffraction pattern collected at 90 ps shows much disordered structure caused by fully progressed melting of Bi.
Bi surface diffusion and the height of the reaction barrier

Amongst several physical mechanisms, the surface self-diffusion may play an important role in determining the height of the reaction barrier for a spherical NP to transform into a faceted polyhedron \((40, 58)\). Transition of the spherical Bi NP into faceted polyhedral nanostructure involves ionic re-arrangement requiring the diffusion of Bi atoms at the surfaces. This self-diffusion is determined by the diffusion coefficient expressed as \( D = D_0 \exp(-Q/k_B T) \) with \( D_0 \) and \( Q \) the pre-exponential constant and activation energy, respectively \((59)\). Here, the activation energy, \( Q \), reflects the formation and migration energy of defects influenced by the binding energy and the activation for Bi is \(~0.12\) eV \((60)\). Both our experiments and TTMD calculations under the high laser fluence showed that the faceting started from 20 ps, at which the lattice temperature reached \(~1000\) K providing a significant amount of thermal energy that is \(~70\) % of the activation energy for surface diffusion to happen. This experimental observation supports that the reaction barrier for Bi NP faceting results from the activation energy of self-diffusion, i.e. energy required for defect formation and migration. This reaction barrier may be overcome by irradiation of high fluence laser. In contrast, under the low fluence laser, the lattice temperature at 20 ps is \(~400\) K, which gives energy about 3.5 times lower than the diffusion activation energy and overcoming the reaction barrier becomes much more challenging. Additionally, the laser illumination also causes photoexcitation of bonding electrons to weaken the Bi-Bi bonding, which helps to facilitate the surface diffusion of Bi atoms by effectively lowering the activation energy.
Detailed process of the image reconstructions and reproducibility

We describe the image reconstruction process from the phase retrieval of measured diffraction amplitude here. The numerical phase retrieval of the diffraction pattern was carried out using the guided hybrid-input-output algorithm (GHIO) as explained in Materials and Methods. The iteration for the phase retrieval started from a random phase with the Fourier amplitude from the experimentally measured coherent diffraction pattern. The square modulus of the diffraction intensity was calculated after subtracting background noises: detector read-out noise, and scattering signal from upstream optical components, etc. We performed phase retrievals for 16 independent random phases, described as 16 seeds in GHIO protocol. The numerical iteration of discrete Fourier transformation (FT) and inverse Fourier transformation (IFT) was carried out between real and reciprocal space while enforcing positivity constraints for the diffraction amplitude and zero-density constraints for image density outside the image boundary. The iteration continued towards minimizing the $R$-factor: the difference between the measured and calculated diffraction pattern, or the Fourier modulus. The measured Fourier modulus and the reconstructed Fourier modulus are displayed in Fig. S12A to demonstrate the good convergence of the iteration. The iteration ran until all the 16 independent reconstructions became consistent. For each random phase, this iteration was performed usually for 3,000 ~ 5,000 times until obtaining a final converged image for each random phase to have 16 independent final images. Among the 16 final images with minimal errors, best image with the lowest $R$-value was selected as a best seed to guide the image reconstruction of the next generations, and we followed the general procedures of the GHIO: details of general GHIO protocols can be found in the published work (47). We performed the whole GHIO reconstruction for the 6th generation to obtain final 16 reconstruction images with good resemblance. Noted difference among 16 reconstructed images was estimated quantitatively to be within 5% confirming the good convergence of the reconstructions (Fig. S12B). Among 16 images, the final reconstructed image was obtained by averaging five best images with smaller $R$-factors (Fig. S12A, middle).

To demonstrate the reproducibility of the image reconstruction, we performed another independent GHIO run with fresh random phases for the same diffraction pattern (Fig. S12C). Reconstructed images from the two GHIO runs were compared explicitly by showing density difference, obtained from the subtraction of the two images, which showed good convergence with only small deviations of less than 5% of density differences. It indicates the fidelity of the image
reconstructions. We also estimated the phase retrieval transfer function (Fig. S13) showing good convergence in phase retrieval with the image resolution better than 10 nm.
Fig. S12. The fidelity of the image reconstructions. (A) Experimentally measured diffraction pattern (left). With the intensity measurement, only the amplitude of the diffraction pattern is collected. After the numerical phase retrieval, the reconstructed image (middle) was obtained from the inverse Fourier transform of k-space with the retrieved phase. The diffraction pattern from the reconstructed image reproduced the measured pattern (right). (B) The histogram of the quantitative difference calculated for the final 16 images of the GHIO reconstruction showed good convergence achieved from our reconstructions. The density difference was estimated as \( \frac{\Sigma_{i,j}|\rho_i(x,y) - \rho_j(x,y)|}{\Sigma_{i,j}|\rho_i(x,y) + \rho_j(x,y)|} \), where \( \rho_i \) is reconstructed images of \( i \)th seed. (C) The reconstructed image from another independent GHIO run. Two independent reconstructions of \( \rho_a \) (A, middle) and \( \rho_c \) (C, top) were compared by the difference map, calculated as \( (\rho_a - \rho_c)/\rho_a \).
Fig. S13. Image resolution from the phase retrieval transfer function. Reconstructed images of single Bi nanoparticles from the single-pulse diffraction patterns achieved sub-10 nm spatial resolution as evidenced by the calculated phase retrieval transfer function (PRTF). The spatial resolution is the full period frequency. All the reconstruction in Fig. 1 is obtained faithfully with PRTF value higher than $e^{-1}$ to the image resolution better than 10 nm.
The Bi nanoparticle structures from ten independent TTMD simulations

Fig. S14. The Bi nanoparticle structures from ten independent TTMD runs. The structures generated by TTMD simulations that started from ten different initial configurations are captured at 100 ps. Facets of \{100\}, \{110\}, and \{111\} planes are colored with orange, blue and brown, respectively, which shows that the faceting behavior is commonly observed with small variations.
Single pulse images of Bi nanoparticles in intact condition
Fig. S15. Single pulse diffraction patterns & images of intact Bi nanoparticles. Images were reconstructed from single-pulse XFEL diffraction patterns taken before the fs laser illuminations.
Single pulse images of Bi nanoparticles on melting under high fluence
**Fig. S16. Single-pulse images of Bi NPs on melting under high laser fluence.** Images of single Bi nanoparticles on the melting process at high laser fluence of 140-mJ cm\(^2\) are shown. The formation of facets as well as the internal void is clearly noted as the melting proceeds.
Single pulse images of Bi NPs on melting under low fluence
Fig. S17. Single-pulse images of Bi NPs on melting under low laser fluence. Images of single Bi nanoparticles on the melting process at a low laser fluence of 32-mJ cm$^2$ are shown. The melting proceeds with the formation of internal void. The faceting observed for the high laser fluence melting is not noted here.
Movie S1.

(‘movie_S1.mp4’) **Bi nanoparticle on melting under high laser fluence viewed along the [111] direction.** Single-pulse diffraction patterns and reconstructed images displaying the melting transition of Bi nanoparticles collected from XFEL experiments with the IR laser fluence of 140-mJ cm$^{-2}$. The solid-liquid transition proceeded with the facet formation and internal density variation to form a central void. The structures are viewed along the [111] direction.

Movie S2.

(‘movie_S2.mp4’) **Bi nanoparticle on melting under high laser fluence viewed along the [100] direction.** Same as movie S1 except for the view direction along the [100] direction.

Movie S3.

(‘movie_S3.mp4’) **Bi nanoparticle on melting without faceting under a lower laser fluence.** Experimentally measured single-pulse diffraction patterns and reconstructed images of Bi nanoparticles on melting under a low laser fluence of 32-mJ cm$^{-2}$. The solid-liquid transition proceeded without forming the facet. Internal density variation is accompanied while forming a central void.

Movie S4.

(‘movie_S4.avi’) **Atomic scale movie of Bi melting under high laser fluence in a cut-away view from TTMD simulations.** A cutaway view movie of the ultrafast structural transformation of the bismuth nanoparticle driven by high fluence IR laser ($F_{\text{inc}} = 140$-mJ cm$^{-2}$) obtained through two-temperature molecular dynamics simulation. The structures are viewed along the [111] direction.
Movie S5.

(movie_S5.mp4) Temporal evolution of the projected density of Bi nanoparticles under high laser fluence from TTMD simulations. The temporal evolution of the bismuth nanoparticle atomic densities projected along [111] direction (high laser fluence case).

Movie S6.

(movie_S6.mp4) Atomic scale movie of Bi melting under a low laser fluence in a cut-away view from TTMD simulations. A cutaway view movie of the ultrafast structural transformation of the bismuth nanoparticle driven by low fluence IR laser (F_{inc} = 17-mJ cm^{-2}) obtained through two-temperature molecular dynamics simulation. The structures are viewed along [111] direction.

Movie S7.

(movie_S7.mp4) Temporal evolution of the projected density of Bi nanoparticles under a low laser fluence from TTMD simulations. The temporal evolution of the bismuth nanoparticle atomic densities projected along [111] direction (low laser fluence case).
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