Observation to ultrafast atomic-scale process of the photo-induced phase transition with multiplexing probe

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Femtosecond-laser pulses drive nonequilibrium phase transitions via reaction paths hidden in thermal equilibrium. It stimulates interest in understanding electron-driven nonthermal and ion-involved thermal processes with a unifying picture, which remained elusive by challenges in resolving accompanied atomic dynamics at relevant space–time resolution. Here, by establishing new femtosecond X-ray multiplexing probe that combines single-pulse imaging and crystal diffraction, we observed sub-picosecond surface-melting proceeding to bulk-melting in photo-excited, surface capped, gold nanoparticles as a model system. Complete process of nonthermal-to-thermal kinetics is uncovered with real-time images and crystal structures at sub-picosecond and Ångstrom-scale resolution. Nonthermal melting from the gold surface is confirmed despite restricting the surface effect. Molecular dynamics simulations confirm the heterogeneous melting through melt-front propagation from surface and grain boundaries along with melt-seed forming homogeneous melting, which proceeds with coexisting liquid-solid phases corroborating experimental results. We establish a comprehensive atomic-scale picture for photo-induced phase transitions explicating nonthermal-to-thermal reactions.

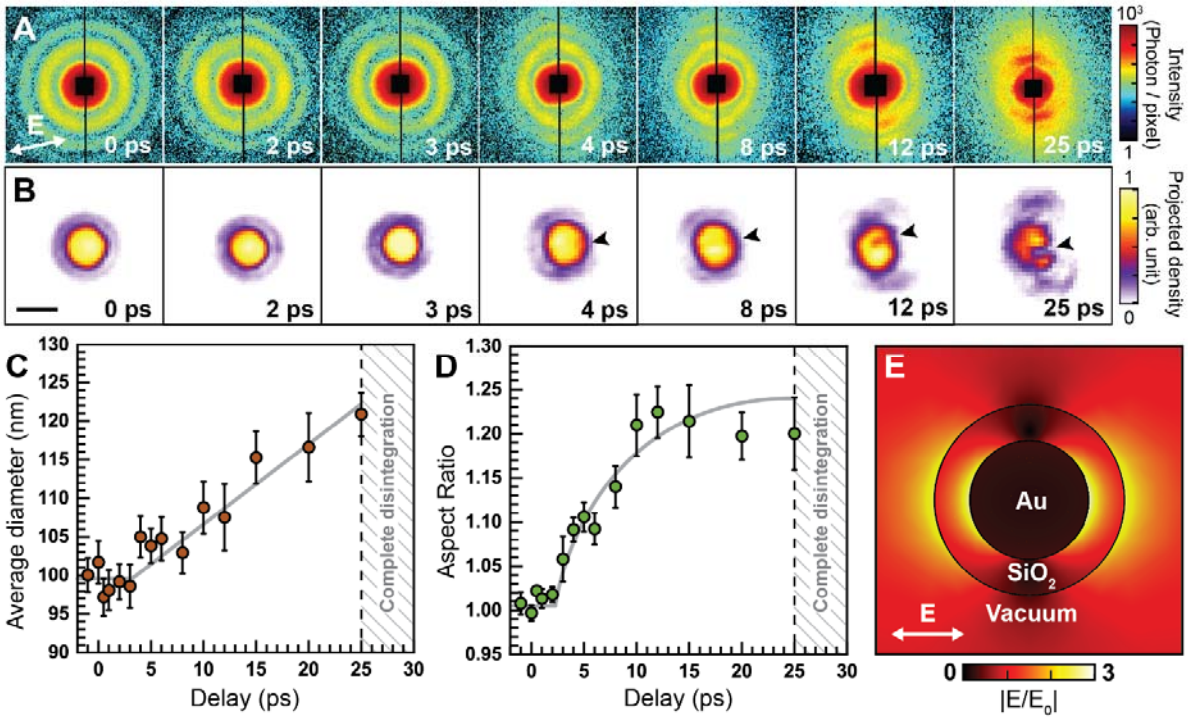

Fig 1. Single-pulse images unveil the ultrafast photo-induced phase–changing process. (A) Single-pulse XFEL diffraction patterns display the temporal evolution of the NP specimen illuminated by single fs-IR laser pulses at 0.6 J cm^{-2}. The diffraction pattern is distorted from the Airy fringe from ~3 ps, implying a morphological change of the NPs due to melting. (B) Reconstructed images display projected charge densities with notable melting reactions from ~3 ps starting from the surface parallel to the laser polarization direction. The void that develops at the surface penetrates the Au NP as the melting proceeds. Scale bar is 100 nm. (C) The average diameter of the Au NPs is obtained with the directional averaging ($\frac{2D_{\perp}+ D_{\parallel}}{3}$) for the diameter perpendicular ($D_{\perp}$) and parallel ($D_{\parallel}$) to the laser field direction. (D) The shape anisotropy caused by polarization-dependent melting is shown by the aspect ratio ($\frac{D_{\perp}}{D_{\parallel}}$). (E) Near field enhancement factors calculated for the core–shell NP.