Polymorph transition-mediated non-classical nucleation and growth in the colloidal heteroepitaxial growth

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Colloidal crystals as a model system have intensively been used to elucidate nucleation mechanisms, for which understanding details of the non-classical nucleation process is critical. We have investigated colloidal heteroepitaxial growth [1], in which we found that polymorph formation and transitions leads to non-classical nucleation and growth. In the present study, nucleation and growth processes associating with polymorph transition are reported, and discussed how they related to the non-classical nucleation and growth.

Colloidal crystallization is achieved by depletion attraction that is induced by added polymers (sodium polyacrylate). A substrate (different particles from that of epitaxial phase) is formed by convective assembly, by which thin colloidal crystal films are fabricated. Typical particle combination for polymorph formation is 790 and 1000 nm for epitaxial phase and the substrate, respectively. By the same particle, two kinds of crystals with different morphologies and orientation against to the substrate are formed (Fig. 1a), which is denoted as α- and β-phase.

Stability of those two phases is found to be dependent on depletion attraction force, which is tuned by polymer concentration (C_p). In the low C_p, α-phase is more stable than β-phase, while it is opposite at high C_p. Polymorph transition were observed at low C_p, where unstable β-phase are dissolved and the particles of which are incorporated into the α-phase to grow.

Non-classical nucleation and growth process were revealed by in-situ observations. To present two phases clearly, positions of each particle are overlapped with colored dots depending on their angle of hexagonal symmetry. Fig. 1b shows β-phase nucleation which went through α-phase cluster as a metastable phase. The α-phase cluster transitioned into β-phase (at 2 min.) which subsequently grow to nucleation size. Also, non-classical growth manner was observed. As growing β-phase, neighboring α-phase cluster is dissolved and absorbed by β-phase (Fig. 1c).

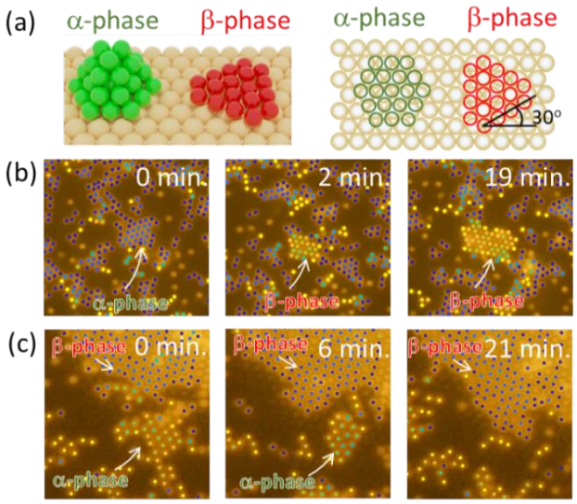

Fig. 1 (a) Two polymorphs formation by the same particle size, α- and β-phase are colored with green and red, respectively. (b) Nucleation of β-phase via α-phase cluster. (c) Growth of β-phase via expense of α-phase.

The colloidal heteroepitaxy has been found to be a good model system for studying non-classical behaviors in nucleation and growth. We will further quantitatively investigate how polymorph transition affects those behaviors.

References

[1] Nozawa J et al. Heteroepitaxial Growth of Colloidal Crystals: Dependence of the Growth Mode on the Interparticle Interactions and Lattice Spacing. J. Phys. Chem. Lett. 2022;13(30):6995-7000.