Supporting Information for

"*In Situ* Observations of Nanoparticle Early Development Kinetics at Mineral-Water Interfaces"

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Summary

Total four SI pages, containing details of experimental setup figure and data analysis, one figure, and references

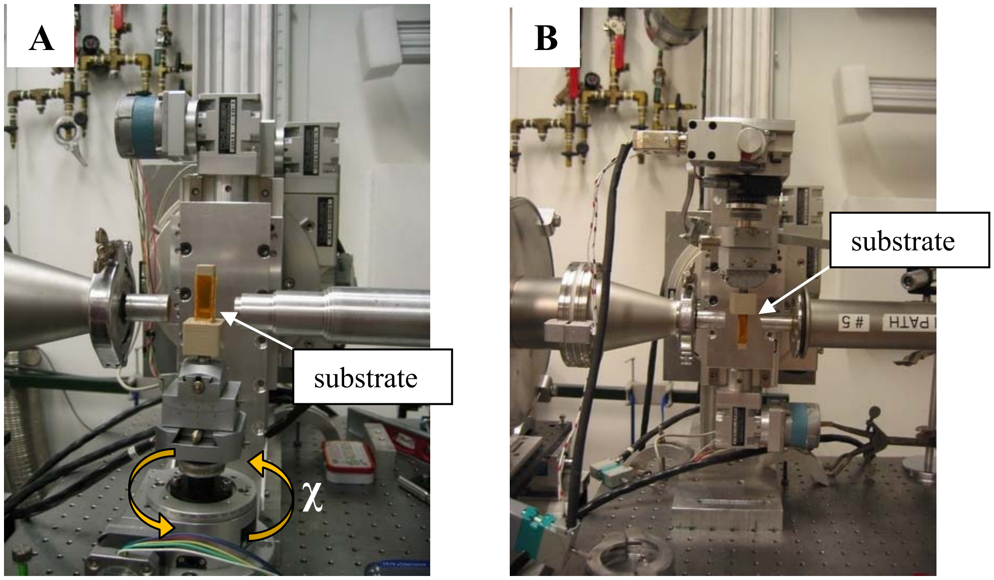

Figure S1. *In situ* time-resolved simultaneous SAXS/GISAXS setup at the Advanced Photon Source, sector 12ID-C. (A) Regular operation mode. (B) Bottom-up test setup to test for collection by gravitational settling of homogeneously nucleated nanoparticles.

GISAXS Data Analysis

GISAXS Structure Factor Calculations: For structure factor calculations, the assumption of the 2D paracrystal (1) is made because the early formed nanoparticles are likely to have significant numbers of crystal imperfections in their structure. In the 2D paracrystal model, while short-range order is maintained, the long-range order is gradually reduced according to a probabilistic way when atoms or islands can be found. Hence, this model is usually used for intermediate cases between regular lattice and fully disordered structures (2-3).

The structure factor for 2D paracrystals was adopted from refs (2-3) is as follows:

$$S(q)=\frac{1-e^{2q^2\sigma_D^2}}{1-2e^{2q^2\sigma_D^2}\cos(qD)+e^{2q^2\sigma_D^2}} \qquad (2)$$

where D and σ_D stands for the interparticle distance and the Gaussian width of the distance distribution of particle position. Note that $I_{GISAXS,\,p}(0) = I_{GISAXS,\,p1}(0) + I_{GISAXS,\,p2}(0) = N_{p1} \times (\Delta\rho)^2 \times V_{p1}^2 + N_{p2} \times (\Delta\rho)^2 \times V_{p2}^2$. In the time range of this work $I_{GISAXS,\,p2}(0)$ is at least 3 orders of magnitude smaller than $I_{GISAXS,\,p1}(0)$ even at the latest stage of growth. Thus, $I_{GISAXS,\,p}(0) \sim I_{GISAXS,\,p1}(0)$.

Sample Size Corrections in GISAXS Intensity: The surface particle scattering intensities, $I_{GISAXS}(q=0)$, for both the horizontal and vertical cuts, were corrected to consider any overshooting of the x-ray beam (i.e., larger beam size than the substrate dimension). All the calculations were conducted under the following considerations: When the substrate is aligned parallel to x-ray beam and rotated to the incidence angle (α_i) of measurement, the downstream intensity (i.e., the intensity of the photodiode, which was located close to the beam center) should be 0 for an ideally narrow beam (4). When the length of a substrate in the beam direction is not long enough to cover the whole footprint of x-ray beam, there will be some intensity overflowing the substrate in such a way that the sum of two times of the overflow intensity and intensity exposed on to substrate equals the incident intensity. The surface area correction factors were calculated by $I_{\alpha i=0}/(I_{\alpha i=0} - I_{\alpha i=0.1\ \mathrm{degree}})$, where $I_{\alpha i=0}$ is the intensity at half cut of x-ray condition, and all the GISAXS data were multiplied by their surface area correction factors. Because the same sample geometry and water path length were used during all experiments, we can directly compare the total net scattering among all cases.

GISAXS intensity including the intensity enhancement phenomena at the Yoneda wing has been successfully described by the distorted wave Born approximation (DWBA) using two scattering vectors, $\mathbf{q_t} \equiv (q_x, q_y, q_{t,z})$ and $\mathbf{q_r} \equiv (q_x, q_y, q_{r,z})$, where the former and the latter are scattering vectors defined with respect to the transmitted beam and reflected beam, respectively. The z components of these scattering vectors are $q_{t,z} = k_{f,z}-k_{i,z}$ and $q_{r,z}=k_{f,z}+k_{i,z}$, and thus $\mathbf{q_t}$ is identical to the conventionally defined scattering vector. $k_{f,z}$ and $k_{i,z}$ are z components of wave vectors of the scattered and incident beams, respectively. The scattering amplitude of GISAXS using the DWBA therefore reads (5)

$$F(\alpha_i,\alpha_f,2\theta_f) = T_iT_fF_p(q_{xy},q_{t,z}) + T_iR_fF_p(q_{xy},-q_{r,z}) + T_fR_iF_p(q_{xy},q_{r,z}) + R_iR_fF_p(q_{xy},-q_{t,z}) \tag{S1}$$

where T_i, T_f, R_i, and R_f are the amplitudes of transmitted (T) and reflected (R) wave fields of incoming (i) and outgoing (f) wave on a substrate surface, F_p is the scattering amplitude of a particle, and scattering angles α_i, α_f, and $2\theta_f$ are defined in Figure 1A and elsewhere. Then, GISAXS intensity is

$$I_{GISAXS} = |F|^2 \tag{S2}$$

When the particle of interest is small ($4\pi\alpha_i$ R < 4.5λ; R < 23nm in this work) and polydisperse, the complex GISAXS intensity equation including 16 terms could be drastically simplified to equation S3 (5)

$$I_{GISAXS} = |\Psi_i(\alpha_i)|^2|\Psi_f(\alpha_f)|^2|F_p(\mathbf{q_i})|^2 \tag{S3}$$

where $\mathbf{q_i} \equiv (q_x, q_y, \surd(k_{f,z}{}^2+(2k_o\alpha_i)^2/4)) \sim (q_x, q_y, k_{f,z})$. Ψ_i and Ψ_f are the x-ray wave amplitude on a substrate and each is a function of the incident angle and exit angle, respectively. The value of $|\Psi_i(\alpha_i)|^2|\Psi_f(\alpha_f)|^2$ can be directly obtained from the enhancement of intensity at the Yoneda wing, which is about 3.5, 3.1, and 2.9 at IS = 1, 10, 100 mM, respectively, in our experiment.

SAXS and GISAXS Scattering Intensity Comparison: As long as particles on substrate is randomly oriented and distributed, both the invariants of SAXS and $|\Psi_i|^2|\Psi_f|^2$ corrected GISAXS provide the same physical quantity. Since I(0) is proportional to NV^2 and Q is NV, Hence, $Q_{SAXS} = I(0)_{SAXS}/V_p$ and $Q_{GISAXS}/(|\Psi_i|^2|\Psi_f|^2) = I_{GISAXS}(0)/(V_p\cdot|\Psi_i|^2|\Psi_f|^2)$ provides identical quantities, and both the former and latter provide the relative units of total nanoparticle volumes formed in a solution and on a substrate, respectively. In this work, we compared Q_{SAXS} vs $I_{GISAXS}(0)/(V_p\cdot|\Psi_i|^2|\Psi_f|^2)$ due to technical reasons: the background subtraction for GISAXS might not be as good that for SAXS. I(0) is less sensitive to level of backgrounds than Q is.

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