

The effect of substrate on nucleation of colloidal crystals

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The nucleation of colloidal crystal is affected by the substrate as the same as for the atomic system ^[1]. However, the substrate effect for the nucleation as well as crystal growth has not been quantitatively evaluated for the colloidal crystals as far as our knowledge. We had investigated detailed nucleation process of colloidal crystals on the cover glass ^[2], and revealed occurrence of two different nucleation processes, which is caused by the effect of substrate. To obtain better understandings on the substrate effect on the nucleation of colloidal crystals, two different substrates, cover glass and Pt-coated cover glass, are employed and the nucleation behaviour is investigated.

Crystallization of colloid was induced by the depletion attraction, in which charged polystyrene particles and charged sodium polyacrylate polymer were mixed. 500 nm with green fluorescent polystyrene particles were used. Sodium polyacrylate was added in the solution as depletant to generate attractive interaction, and the concentration is 0.15 g/L. A cover glass and platinum coated cover glass were used as the substrates. Crystallization processes were monitored by optical microscopy.

The grains of a colloidal crystal grown on the different substrate under the same suspension condition are shown in Figure 1 (2.5 hours has passed after mixing solution). The number of grains on the Pt-coated cover glass is less than that on the cover glass. The size of average grain on the Pt-coated cover glass is larger than that on the cover glass.

The nucleation rate, J , is measured for two substrates as shown in Figure 2. The critical size, N^* , is also measured for the different substrate. By fitting the experimental results with J and N^* , $\Delta\sigma$ is obtained based on the classical nucleation theory (CNT). The $\Delta\sigma$ of Pt-coated is found to be larger than that on the cover glass.

In general, the substrate effect is characterized by interfacial free energy change, $\Delta\sigma = \sigma_{\text{sub-solid}} + \sigma_{\text{solid-liquid}} - \sigma_{\text{sub-liquid}}$, where $\sigma_{\text{sub-solid}}$ is interfacial energy between substrate and solid, $\sigma_{\text{solid-liquid}}$ is for solid and liquid interface, and $\sigma_{\text{sub-liquid}}$ is for substrate and liquid. Calculation of van der Waals force between polystyrene particle and each substrate suggests that Pt-coated has larger interaction than that of cover glass. This result leads to large $\sigma_{\text{sub-solid}}$, which is probably consistent with high $\Delta\sigma$ value for Pt-coated cover glass. This study contributes to various application whose colloidal crystals are grown on the substrate.

[1] S.Auer and D.Frenkel, Physical Review letters 2003, 9(1), 015703-1-4.

[2] Suxia Guo, et al., Langmuir 2017, 33, 10543-10549.

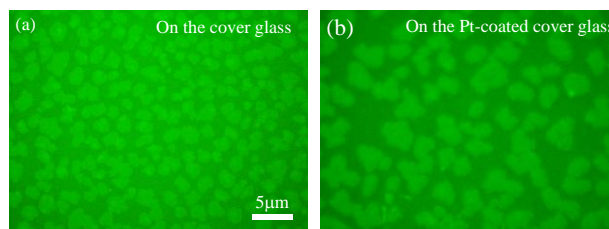


Figure 1 The grains of a colloidal crystal after preparation 2.5h on the different substrate under the same suspension condition. Polystyrene: volume fraction, 0.5%, Polymer: 0.15 g/L of sodium polyacrylate. (a) On the cover glass, (b) On the Pt-coated cover glass.

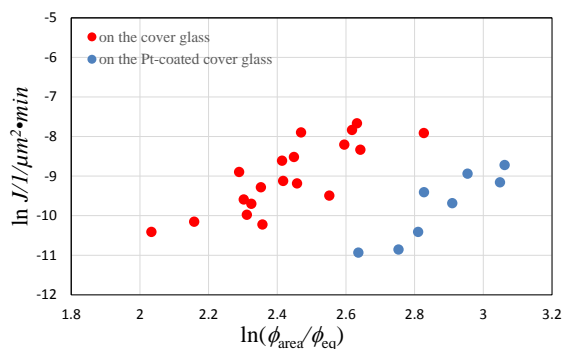


Figure 2 $\ln J$ as a function of $\ln(\phi_{\text{area}}/\phi_{\text{eq}})$ for Pt-coated and cover glass. ϕ_{area} is the area fraction, which corresponds to surface concentration of ad-particles, ϕ_{eq} is the equilibrium area fraction of the colloidal particles on the substrate.