Formation of Novel Self-organized Periodic Precipitation Pattern by pH-induced Gold Nanoparticles Aggregation

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Spontaneous pattern formation under far-from equilibrium condition is driven by self-organization via reaction-diffusion processes. So far, it has attracted many researchers because chemical and mathematical modeling of such phenomena being ubiquitous in nature lead to help understanding the pattern formation mechanism in nature. Liesegang pattern (LP) is one of the chemical models for the self-organized patterns. So far, most of its formation mechanisms are limited to discussion of spatially heterogeneous precipitation driven by a diffusion concentration gradient of material for precipitates. Because of this limitation, the universality of LP as the model for natural pattern formation is limited.[1,2] In this study, we tried to form the novel LP based on an idea mimicking another condition in nature which is driven by that a gradient inducing instability was imposed to the reaction medium dispersed precipitation precursors uniformly. In detail, the pH gradient was imposed into a hydrogel doped with gold nanoparticles (Au NPs) to trigger their aggregation and pattern formation.

Au NPs were synthesized by chemical reduction with citric acid and modified by 11-mercaptoundecanoic acid (MUA) through a surface ligand exchange in NaOH aq. soln.. Then, 0.5 w/w% agarose gel doped with this deprotonated MUA-Au NPs was prepared in a test tube. Subsequently, HCl aq. soln. was poured on the top of the gel, then the pH gradient was evolved toward the bottom due to the diffusion of H^+. Figure 1a shows the pattern formation by pH-induced aggregation of MUA-Au NPs, where MUA-Au NPs aggregate at the position showing a slightly deep red color. To make it more clearly, a gray scale of Figure 1a is shown as Figure 1b, in which four darker discrete bands consisting of aggregates of MUA-Au NPs are observed. Between each band, aggregates were almost absent, and an inter-band spacing increased geometrically. This unique feature is good agreement with the characteristic geometrical feature of LP. Finally, its novel mechanism was discussed by simulation considering the phase transition from dispersion to aggregation states, and consistent results were obtained. As a conclusion, we succeeded novel LP formation from the uniform distribution and revealed its detailed mechanism, which could make LP a universal model for various periodic structure with geometric series in nature.

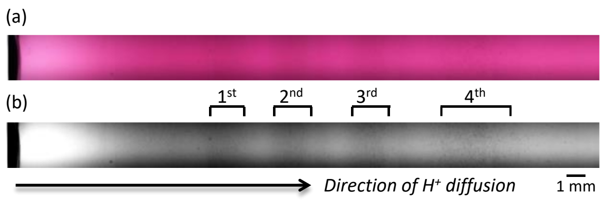

Figure 1. Pattern formation by pH-induced aggregation of MUA-Au NPs: [MUA-Au NPs] = 4.0 nM, [agarose] = 0.20 w/w%, $[HCl]_0 = 1.5 \times 10^{-4}$ M. (a) original and (b) gray scale.

1) **M. Itatani** et al., *J. Phys. Chem. C*, **2018**, *122*, 3669-3676.
2) **M. Itatani** et al., *J. Phys. Chem. B*, **2020**, *124*, 8402-8409.