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In-situ Observation of Nanoparticle Self-Assembly Formation and Migration at the Solid-Liquid-Gas Interface

Arixin Bo[1] and Niels de Jonge[1,2]

[1] INM – Leibniz Institute for New Materials, Saarbrücken, Germany.
[2] Department of Physics, Saarland University, Saarbrücken, Germany.

Nanoparticle (NP) self-assembly is an important process for bottom-up development of versatile nano/micro-structures. Self-assembly of NPs from a colloid dispersion is a complex process that involves, *e.g.*, particle interactions, Brownian motion, packing constraints, and liquid surface tension [1]. Dynamic imaging the self-assembly process in liquid aims at achieving a better mechanistic understanding. Using liquid-phase electron microscopy (LP-EM), chemical and physical behaviors of the NPs can be observed at a close resemblance to their native colloidal environment [2]. It was shown in previous work that evaporation-induced liquid behavior posed a strong role in NP transport, causing structural variations [3]. However, there is lack of information on the interactions taking place at the liquid front movement in forming NP superlattices.

In this work, we imaged the formation and migration of self-assembled gold (Au) NP superlattices at the interface between substrate, liquid, and air. AuNPs (NANOPARTZ Inc., USA) of 50 nm diameter with negative charges were deposited (0.2 µL) on the surface of the bottom microchip of the liquid enclosure as shown in Figure 1a. The assembled microchips were transferred into a LP-EM holder, which was connected to a microliter syringe pump (Figure 1b). Before starting liquid flow, the outlet of the holder was sealed to maintain a certain pressure during liquid immersion and prevent rapid liquid diffusion between the chips by capillary force. H_2O infusion started when the window area was located and the electron microscope was adjusted for optimal imaging conditions. When the liquid edge entered the window area, pumping was immediately stopped and reversed so that the liquid boundary was maintained within the field of view (Figure 1c). The deposited AuNPs prior to wetting are shown in Figure 1d. As H_2O slowly infused into the holder (2 µL/min), liquid immersion occurred as is evident from the brighter background signal, and particle motions (Figure 1e). A fraction of the deposited AuNPs were redispersed by the infusing H_2O, their motions were captured as faint, white stripes under scanning transmission electron microscopy (STEM).

Reversing the pumping direction induced retracting of the liquid boundary. Here, we observed AuNPs self-assembly of superlattices at the liquid edge that were of different configuration than the initial structure (Figure 2a-d). Different self-assembled structures were observed such as a quasi-crystal [4] (Figure 2c), and hexagon close packing (*hcp*, Figure 2d inset). The AuNPs first landed on the substrate and migrated along with the liquid boundary. The relative positions of the deposited AuNPs were changing when dragged by the hydrodynamic force, causing the assembled pattern change. From the *in-situ* dynamic observations, we understood that the assembled double-layer patterns could switch between quasi-crystal and *hcp*, instead of having a cluster of fixed patterns gliding over the substrate. This is likely caused by individual AuNPs rotating on the substrate instead of gliding. The role of electron beam in the redispersion, subsequent deposition, and self-assembly process requires more understanding for the NPs at the liquid boundary. The movement style of NPs could relate to the substrate-NP and NP-NP interactions that posed an impact on the assembled structure at the liquid boundary.

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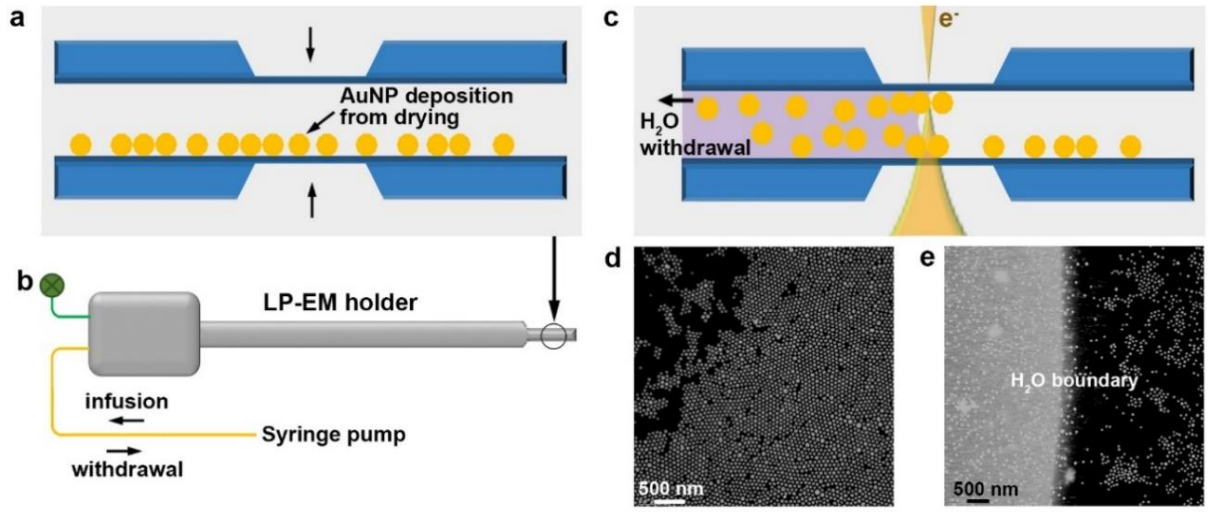

Figure 1. Experimental setup to record AuNP self-assembly at the liquid boundary. (a) Schematic illustration of microchips with deposited with AuNPs at the bottom one. (b) Liquid-phase electron microscopy (LP-EM) holder connected to a microfluidic pump system. The liquid outlet is sealed. (c) Imaging the liquid boundary motion using scanning transmission electron microscopy (STEM). (d) STEM image of deposited AuNPs on SiN microchip in dry state. (e) STEM image of AuNPs at H_2O boundary.

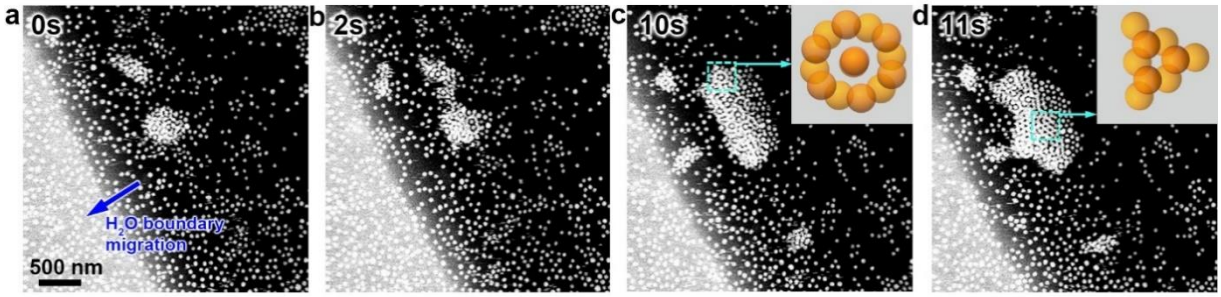

Figure 2. STEM image sequence capturing AuNP deposition and migration of self-assembled AuNP superlattices at the solid-liquid-gas interface. Electron dose: $0.1e^-/Å^2$. (a) Initial image showing the water front and the onset of self-assembly. (b) Two structures approaches. (c) A double layer quasi-crystal. The inset shows a model of the structure. (d) Another structural element visible was the hexagon close packing with a model shown in the inset.

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