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Liquid-phase TEM imaging of self-assembly pathways of anisotropic nanoparticles

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Liquid-phase transmission electron microscopy (TEM) has been widely used for probing solution-phase nanoscale dynamics, such as nanoparticle growth/corrosion, electrochemical processes, and aggregation of soft materials (e.g., micelles, proteins) [1]. Among them, one particularly interesting direction is to resolve and understand the self-assembly pathways of nanosized building blocks, namely individual one of them diffuse and interact with each other to form into functional superstructures [2, 3]. The significance is twofold. At the nanoscale, self-assembly behaviors serve as an ideal model system to understand the physical rules for organization and the fundamental interactions complicated by discreteness and nonadditive effects [4]. On the application side, these assemblies are richly relevant, either due to architecture-dependent coupling of quantum-confined properties (e.g., catalytic, optical, electrical, spintronic) of nanoparticles or biological functions enabled by protein organization [5]. However, current liquid-phase TEM studies on the assembly pathways are often limited by practical and technical artifacts [1, 2]. For example, the observed assemblies are often small in size (composed of 20–30 or fewer entities) and not exhibit collective phase behaviors, likely due to the challenge in introducing a large volume and concentration of initial building blocks in a highly confined liquid chamber environment [2, 3]. Moreover, nanoparticles are observed to diffuse slowly in liquid-phase TEM studies, about 10^4–10^7 orders of magnitude smaller than what Brownian motions predict [1]. This sluggish motion, attributed to electron beam and nanoparticle–substrate adhesion, leads to assemblies largely irreversible, thereby hard to allow rearrangement after initial attachment into perfect ordering such as crystalline lattice [6]. Lastly, the illumination electron beam in TEM can cause altering of both solvent conditions and particle surface [7, 8] and it has thus been difficult to correlate self-assembly pathways observed in liquid-phase TEM with practical wet chemistry experiments without TEM [6].

Here we apply low-dose liquid-phase TEM for such self-assembly studies to maximally eliminate beam-induced nanoparticle reactions or ligand damage, and optimize our sample loading protocols to introduce and accommodate a highly concentrated solution of nanoparticles within a liquid volume as small as 0.5 μL so that the nanoparticles can interact to form large assemblies (>100 entities). Nanoparticle–substrate adhesion is screened to allow the generically rapid motions of nanoparticles agitated by thermal fluctuation and the dynamic arrangements of the nanoparticles to efficiently sample over their free energy landscape. We concern a diversity of anisotropically-shaped gold nanoparticles. As shown in the example of gold triangular nanoprisms, time-lapsed snapshots from a continuous liquid-phase TEM movie elucidate that the assemblies are highly dynamic, reversible and large-scale [Figure 1]. The nanoprisms reposition and reorient to change their spatial arrangements in solution and the connection network, which is an essential first-step towards annealing defects and disordered regions into periodic lattices. The observations contrast with our previous study on the same type of gold triangular nanoprisms, where the assemblies are smaller and irreversible as the internanoparticle van der Waals attraction overwhelms the sluggish motions and

"locks" the assemblies in place following their very initial attachments. We foresee our platform which now allows the reversible, large scale assemblies more closely resembling to the diverse nanoparticle superlattice formed outside TEM carry great potentials to fill the gap of real-time and real-space imaging and understanding of the assembly pathways of nanosized objects.

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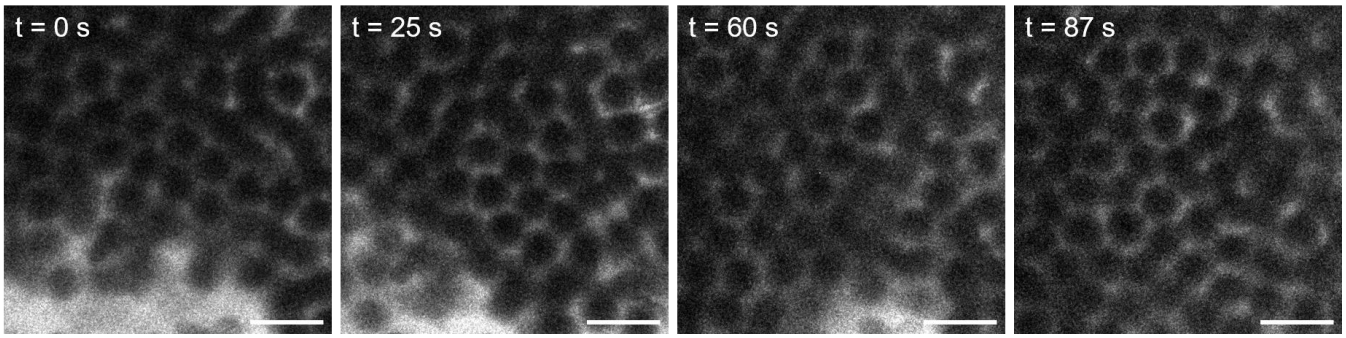

Figure 1: Snapshots of the large-scale, dense and dynamically reversible assemblies from gold triangular nanoprisms in a continuous liquid-phase TEM movie. Scale bars: 200 nm.

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