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Visualizing Nanoscale Assembly in Solution Using *In Situ* TEM

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The assembly process of nanoparticles from individual atoms, and nanostructures from nanoparticles in solution is fundamental for materials engineering and "bottom-up" fabrication of functional nanodevices.

Using dynamic in situ TEM imaging [1-4] in liquids, I will describe how nanoparticles form in solution and how these nanoparticles interact with each other. First, I will discuss how phase separation of a solution containing Au ions into solute-rich and solute-poor phases leads to formation of Au nanocrystal through a pathway that does not follow classical nucleation theory (CNT). Namely, I will show that there are multiple steps that lead to formation of nuclei from which nanocrystal grow (Figure 1A). These steps are: 1) phase separation of liquid solution into solute-poor and solute-rich phases, from which 2) an amorphous nanoparticles which serve as a precursor for nuclei emerges. This is followed by 3) crystallization of amorphous nanoparticle into a crystalline nuclei.

Next, I will highlight the role of intermolecular forces between nanoparticles in solution and describe their role in the assembly of nanostructures from individual nanoparticle building blocks [5]. Specifically, I will show how the balance between repulsive hydration force and attractive van der Waals (vdW) force results in a metastable nanoparticle-pair which promotes their subsequent attachment to each other (Figure 1B-C) [5]. I will also describe the role of capillary forces in the assembly of nanoparticles at liquid-liquid interface [6]. We found that during nanoparticle assembly at fluid-like interfaces capillary forces provide torque that aids in the alignment of interface-bound nanoparticles. I will conclude by showing how chemistry and mechanical constraints can be used in aiding the self-assembly of nanoparticles.

These findings highlight the role of solvent mediated physical and chemical forces in material synthesis and self-assembly of nanoparticles. Our observations also emphasize the importance of direct nanoscale observation in uncovering previously unknown intermediate states that are pivotal for synthesis and self-assembly [7].

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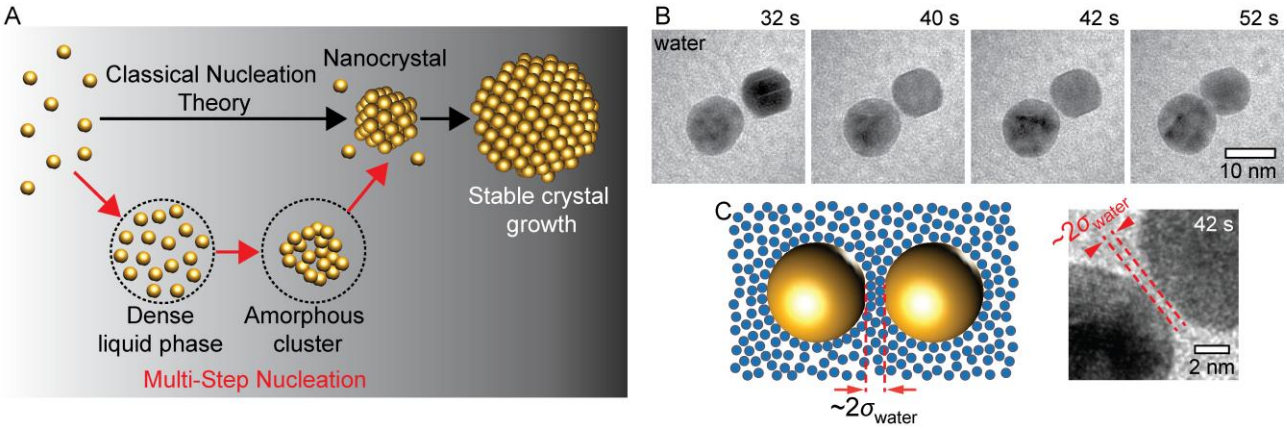

Figure 1. (**A**) Multistep nucleation of gold nanocrystals. (**B**) Attachment of gold nanoparticles in water. (**C**) Nanoparticles are surrounded by hydration layer which is one water molecule thick. Steric repulsion due to this hydration layer balances the attractive vdW force between nanoparticles and results in a metastable nanoparticle-pair. Attachment shown in (B) occurs only when the water between nanoparticles is drained (Ref [5]).

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