Breaking the symmetry: probing two-dimensional nanocrystal self-assembly in real time

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Nature uses self-assembly to form the physical world around us. This paper investigates the phenomenon, using in-situ small-angle x-ray scattering experiments to show how nanocrystals can self-assemble to form highly ordered super-lattices at the liquid-air interface of an evaporating droplet of fluid.

Self-assembly is an important protocol nature adopts to form the physical world around us. Modern biology has shown that one of most efficient ways to create living organisms is by using atoms and molecules to form nanometer-scale objects, such as DNA and proteins, and then to use these building blocks to form macroscopic biological systems. For material scientists, mastering the self-assembly process using nanoscale building blocks offers a new way to tailor material composition and properties.

Over the past decade, various types of nanocrystals have been synthesized using colloidal chemistry. Individual nanoparticles have many unique physical properties including quantum size effects, Coulomb charging effects and low coordination of surface atoms. New collective phenomena might emerge if the self-assembly of these nanocrystals could be controlled. However, manipulating large numbers of particles, on the scale of $10^{13}$ particles/ml, has turned out to be a daunting task. For example, the simple evaporation of a nanocrystal colloidal droplet (see Figure 1), has resulted in a variety of self-assembled structures.

![Figure 1. (a, b) Small-angle x-ray scattering setup at 1-BM beamline of the Advanced Photon Source (c-e). The evaporation process of a colloidal droplet. The black bar indicates the size of x-ray beam.](image-url)
These range from random aggregates and fractals to three-dimensional (3D) and two-dimensional (2D) lattices with various degrees of ordering.\textsuperscript{6, 7}

One major problem lies in the fact that the crystallization process is dependent on concentration. Thus, when the solvent is evaporated to a certain degree, single particles (3D super-lattices and super-lattice aggregates) can coexist in a concentrated droplet.\textsuperscript{8} The dynamics of solvent flow during evaporation and the solvent dewetting process add further complexity to the formation of nanocrystal assemblies.\textsuperscript{9, 10}

This is why it was such a surprise when we found that dodecanethiol-ligated gold nanocrystals (∼ 6nm) spontaneously organized into highly ordered 2D super-lattices using this simple droplet evaporation process.\textsuperscript{11} What set that experiment apart from previously-published work was the high degree of ordering obtained—with single domain size extended to more than 20–30μm—and the pure 2D nature of the lattices. Because the typical interaction between nanocrystals is isotropic, the formation of pure 2D lattices requires the symmetry to be broken by confining the self-assembly process at an interface. So the question became, “Does this occur at the liquid-air interface or at the liquid-substrate interface?”

We decided to carry out \textit{in-situ} small-angle x-ray scattering (SAXS) experiments to monitor the formation of highly-ordered nanocrystal super-lattice monolayering during colloidal droplet evaporation.\textsuperscript{12, 13} The experiments were performed at sector 1 (1-BM) and sector 8 (8-ID) beamlines at the Advanced Photon Source at Argonne National Laboratory. Figure 1 shows the experimental setup at 1-BM and the relative size of x-ray beam used, compared with the size of colloid droplet. Figure 2(a-d) shows a typical time series of the SAXS patterns after the droplet is deposited on the substrate. An elliptically shaped diffraction ring was observed after two minutes: see Figure 2(a). It gradually evolved into the scattering pattern shown in Figure 2(d). The evolution of scattering patterns demonstrated that nanocrystal superlattices were formed at the liquid-air interface, beginning at the early stage of the droplet evaporation. When the liquid film was completely dried and the super-lattices were deposited on the substrate, the downward scattering was suppressed by absorption and total external reflection by the substrate. The elliptically-shaped diffraction ring observed in the early stage of evaporation was also due to 2D super-lattice domains at

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the liquid-air interface, which had a large incident angle ($\alpha$) relative to the x-ray, see Figure 2(f). These experimental data can be easily reproduced from a simulation based on the concept that super-lattices form at the liquid-air interface, Figure 2(g-j).

The findings of these experiments are in sharp contrast with the traditional notion that the self-assembly process occurs predominantly on the liquid-substrate interface.\textsuperscript{14, 15} Our experiments also indicate that the presence of both ligand and evaporation kinetics plays an important role in inducing the formation of 2D super-lattices at the liquid-air interface. The 2D superlattices only form when the evaporation rate is high enough to accumulate nanocrystals at the liquid-air interface. The presence of a dodecanethiol ligand significantly increases the tendency for 2D super-lattice formation, possibly due to the reduction of the interfacial energy of the liquid-air interface. Our experiments have shed new light on controlling the self-assembly process, and may have a significant impact on the bottom-up approach to forming materials based on colloidal nanocrystals.

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References

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