

# Kinetics and Structures of Self-assembled Nanocrystal Superlattices Probed by *in situ* Small Angle X-ray Scattering

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## Introduction

Self-assembly of nanocrystals has been considered as one of the most promising candidates for making future electronic and optical devices [1, 2]. However, even for the simplest case of drying a nanocrystal colloidal droplet, a variety of self-assembled structures can be formed. The physical properties of different assemblies can vary dramatically because of the structural difference. Recently, highly ordered two dimensional (2D) gold nanocrystal superlattices (NCSs) with domain size up to tens of microns were demonstrated by evaporating a nanocrystal colloidal droplet containing excess amount of dodecanethiol ligand molecules [3]. The extraordinary degree of ordering and the large domain size indicate the formation of NCSs might occur through an unique mechanism. We have carried out *in situ* small-angle x-ray scattering (SAXS) measurements to elucidate the formation of gold NCSs as the colloidal droplet evaporates [4]. We have shown both the evaporation kinetics and particle interactions with the liquid-air interface are key parameters to tune the structure of nanocrystal superlattices. By varying these conditions, we can form both 2D superlattices or 3D superlattices with high structural ordering.

## Methods and Materials

We used monodispersed dodecanethiol ligated gold nanocrystals with an average diameter of in the range of 5.5-7.5 nm. The particle number concentration was adjusted to be approximately  $10^{13}\text{mL}^{-1}$ , just enough to form a monolayer. The volume concentration of dodecanethiol in the colloidal solution is 0.63%. For *in situ* experiments,  $10\mu\text{l}$  of such colloidal solution was deposited onto a rectangular silicon nitride substrate ( $3\times 4\text{mm}^2$ ). The evolution of scattering pattern was continuously monitored during the solvent evaporation process. The SAXS experiments were conducted at the 1-BM and 8-ID beamline of the Advanced Photon Source (APS). The incident synchrotron x-ray beam was monochromatized to 8.0 keV by a double-crystal monochromator while two sets of horizontal (H) and vertical (V) slits were used to define the beam size to  $0.2\text{ (H)}\times 0.2\text{ (V)}\text{mm}^2$ . The incident beam was positioned at the bottom center of the droplet. The substrate was then tilted  $0.1 - 0.3^\circ$  relative to the incident beam. The scattered x-rays passed through a helium flight path and were collected by either an image plate or a charge-coupled device detector.

## Results

With a high concentration of dodecanethiol ligand, the evolution of scattering patterns demonstrated that nanocrystal superlattices are typically formed at the liquid-air interface (Figure 1a-b). Considering the geometry of our experimental setup, The initial elliptically shaped x-ray scattering patterns, as well as its evolution, can be modeled by the "powder"

diffraction of 2D superlattice domains with varying x-ray incident angles.

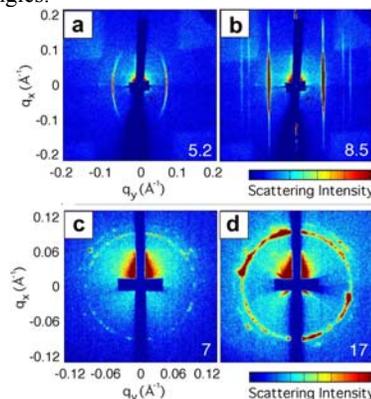


Figure 1. SAXS patterns of 2D (a-b) and 3D (c-d) gold NCSs formation during the evaporation of a droplet. The measurements were done using a same gold nanocrystal colloidal solution. The evaporation rate is the only parameter that control the formation of 2D and 3D superlattices. Numbers in each panel indicate time in the unit of minutes after the droplet was deposited on the surface of a substrate.

The symmetrical scattering patterns (Figure 1b) can only be obtained when the monolayer is at least  $49\mu\text{m}$  above the substrate. A comprehensive understanding of the formation of the 2D gold NCS monolayer can be achieved by comparing the simulated SAXS patterns during the evaporation process with the experimental data.

Two experimental parameters have dramatic affects on the formation of nanocrystals on liquid-air interface. One is the the solvent evaporation rate and the other is the concentration of dodecanethiol ligand in the colloid. While maintaining the same concentration of dodecanethiol, reducing the evaporation rate by a factor of three induces three-dimensional (3D) superlattices formation in the interior of the droplet, whereas the 2D superlattice growth on the interface is greatly suppressed (Figure 1c-1d). These 3D superlattices eventually settle down onto the surface of the substrate. The orientation of the 3D superlattices can also be controlled when the dewetting of the solvent can be delayed as much as possible.

These experiments demonstrated both the evaporation kinetics and the thermodynamics condition such as particle-interface interaction have a significant impact on the structure of nanocrystal superlattices.

## References:

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