

Dynamic Investigation of Gold Nanocrystal Assembly Using In Situ Grazing-Incidence Small-Angle X-ray Scattering

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Here we investigate the dynamic self-assembly pathway of ordered gold nanocrystal arrays during the self-assembly of gold nanocrystal micelles, with and without the presence of colloidal silica precursors, using grazing-incidence X-ray scattering performed at a synchrotron source. With silica precursors present, a lattice with rhombohedral symmetry is formed from the partial collapse of a face-centered cubic structure. In the absence of silica, a transient body-centered orthorhombic phase appears, which rapidly collapses into a glassy nanocrystal film. The appearance of face-centered and body-centered structures is consistent with a phase diagram for charged colloidal particles with assembly modulated via Coulomb screening.

Nanocrystals (NCs) have become a highly significant class of nanomaterials, at least in part from the possibility of unique collective behavior obtained through interactions of neighboring NCs within ordered two- (2D) and three-dimensional (3D) arrays readily obtained via a low-cost, rapid self-assembly process.^{1–3} While extensive research has been directed toward the synthesis of novel NC shapes, compositions, and surface functionalization,^{4–6} less effort has been given to examining the self-assembly process used to form well-ordered NC lattices with specified functional properties. Practical integration of these materials into durable coatings and devices will require a fundamental understanding of many technical issues regarding the self-assembly of extended NC structures, including optimization of long-range order,⁷ or the development of pathways to non-close-packed morphologies.^{8,9} To this end, several reports have appeared recently that address the development of thin film structure for highly ordered 2D lattices^{1,7,10} as well as more glassy NC aggregates^{11,12} and NC monolayers formed on a Langmuir

trough.¹³ Although various experimental techniques were employed for these investigations of NC film formation (for example, ex-situ electron microscopy,^{7,10,13,14} or in situ optical measurement of NC island growth at the surface of an evaporating film¹⁴), grazing incidence small-angle X-ray scattering (GISAXS) studies using synchrotron radiation have proven to be a particularly useful method of obtaining direct, real-time structural information during NC self-assembly^{10–13} under ambient conditions. In GISAXS, an X-ray beam is incident upon a sample at an angle greater than the critical angle of the film but less than that of the substrate, thus maximizing the scattering volume inside the film and, coupled with the high photon flux obtained at a synchrotron source, enabling the investigation of fast (on the time scale of seconds) self-assembly phenomena of films as thin as one monolayer.¹⁰ GISAXS has been used to investigate the self-assembly mechanism of Au NC ordering in evaporating drops,^{10,11} as well as to probe the structure of one-dimensional (1D) NC gradient films.¹² However, these studies have all focused on thiol-modified Au NCs that organize into close-packed hexagonal arrays through short-range “hard-sphere” forces. Recently, we developed a new self-assembly method to form ordered NC arrays assembled within a metal oxide matrix.^{1,2} In this method, alkane thiol-capped Au NCs are encapsulated within micelles of ionic surfactants, producing water-soluble NC micelles compatible with the synthesis of metal or semimetal oxides (here we limit our discussion to only the case of silica) from molecular precursors using low-temperature sol–gel chemistry.¹⁵ Solution precipitation from or spin-coating of a NC-micelle/silica precursor solution yields powders or thin films of ordered NC-micelle/silica superlattices with (based upon transmission electron microscopy (TEM) and standard 1D X-ray diffraction (XRD) characterization) a face-centered cubic (fcc) arrangement of NCs.

Here we present the results of a GISAXS study on the structure and self-assembly pathway for ordered Au NC-micelle/silica films deposited using solution casting onto Si substrates. We

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(1) Fan, H. Y.; Wright, A.; Gabaldon, J.; Rodriguez, A.; Brinker, C. J. *Adv. Funct. Mater.* **2006**, *16*, 891–895.

(2) (a) Fan, H. Y.; Yang, K.; Boye, D. M.; Sigmon, T.; Malloy, K. J.; Xu, H. F.; Lopez, G. P.; Brinker, C. J. *Science* **2004**, *304*, 567–571.

(3) Urban, J. J.; Talapin, D. V.; Schevchenko, E. V.; Kagan, C. R.; Murray, C. B. *Nat. Mater.* **2007**, *6*, 115–121.

(4) Murray, C.; Kagan, C.; Bawandi, M. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545–610.

(5) Yin, Y. D.; Rioux, M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. *Science* **2004**, *304*, 711–714.

(6) Zeng, H.; Sun, S. H. *Adv. Funct. Mater.* **2008**, *18*, 391–400.

(7) Lin, X.-M.; Jaeger, H. M.; Sorensen, C. M.; Klabunde, K. J. *J. Phys. Chem. B* **2001**, *105*, 3353–3357.

(8) Kalsin, A. M.; Fialkowski, M.; Paszewski, M.; Smoukov, S. K.; Bishop, K. J. M.; Grzybowski, B. A. *Science* **2006**, *312*, 420–424.

(9) Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. *Nature* **2006**, *439*, 55–59.

(10) Narayanan, S.; Wang, J.; Lin, X.-M. *Phys. Rev. Lett.* **2004**, *93*, 135503.

(11) Roth, S. V.; Autenrieth, T.; Gruebel, G.; Riekel, C.; Burghammer, M.; Hengstler, R.; Schulz, L.; Mueller-Buschbaum, P. *Appl. Phys. Lett.* **2007**, *91*, 091915.

(12) Roth, S. V.; Mueller-Buschbaum, P.; Timmann, A.; Perlich, J.; Gehrke, R. *J. Appl. Crystallogr.* **2007**, *40*, s346–s349.

(13) Schulz, D. G.; Lin, X.-M.; Li, D.; Gebhardt, J.; Meron, M.; Viccaro, P. J.; Lin, B. J. *Phys. Chem. B* **2006**, *110*, 24522–24529.

(14) Bigoni, T. P.; Lin, X.-M.; Nguyen, T. T.; Corwin, E. I.; Witten, T. A.; Jaeger, H. M. *Nat. Mater.* **2006**, *5*, 265–270.

(15) Brinker, C. J.; Scherer, G. W. *Sol–Gel Science*; Academic Press: San Diego, CA, 1990.

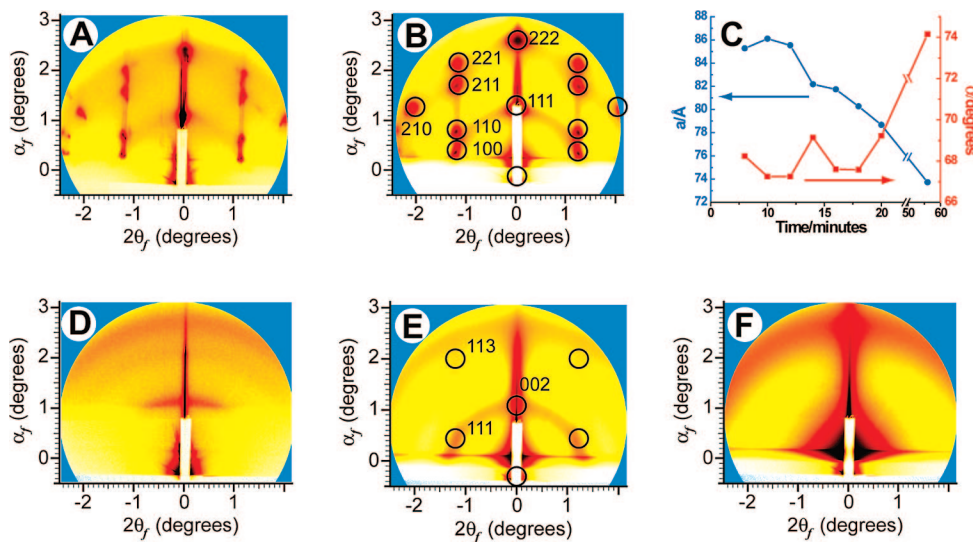


Figure 1. GISAXS data from the self-assembly of Au NC micelles with (A–C) and without (E,F) the presence of silica precursors. (A) Initial NC lattice formed at $t = 8$ min. (B) The same structure at $t = 20$ min. (C) Evolution of unit cell parameters (space group $R\bar{3}m$) over time for this lattice. (D) A layered intermediate observed in the Au NC-micelle system (no silica), followed by (E) a transient orthorhombic (space group $Fmmm$) phase, collapsing upon further evaporation to (F) Au NC-micelles packed in a glassy state. The incident angle is 0.2° .

find that organization of the Au NC micelles into an extended array is consistent with a self-assembly mechanism whereby structural evolution is driven by long-range electrostatic interactions between micelles; the role of the silica phase is primarily that of a “filler”, preventing collapse of the NC lattice during self-assembly. Because the volume of the silica phase is less than that of the empty space in the initial fcc phase, uniaxial shrinkage of the film during evaporation results in a rhombohedral packing arrangement for the NC micelles within the silica matrix. Without the presence of silica precursors, NC micelles form a transient distorted body-centered cubic (bcc) during film evaporation. The appearance of both the fcc and bcc phases is in agreement with a phase diagram for colloidal self-assembly controlled by a screened Coulomb potential.^{16,17}

Stable aqueous solutions of monodisperse gold NC micelles were synthesized using a procedure identical to that reported previously.² Briefly, gold NCs were synthesized according to the preparation route developed by Brust et al.,¹⁸ followed by heat treatment to narrow the size distribution ($\sim 7\%$). An interfacially driven microemulsion process was used to encapsulate NCs within micelles of cetyltrimethylammonium bromide (CTAB). The final solution was indefinitely stable with a concentration of Au NCs in water of ~ 50 mg/mL. For self-assembly into a silica matrix, 0.08 mL of tetraethylorthosilicate was added to 1 mL of Au NC solution, along with 0.05 mL of 0.07N HCl catalyst. For the in situ scattering studies presented here, this solution was further diluted by a factor of 10. GISAXS studies were performed on beamline 8-ID at the Advanced Photon Source, Argonne National Laboratories, using a wavelength of $1.675 \text{ \AA}$ (7.40 keV) and a sample-to-detector distance of 2000 mm. Scattering images were recorded with a 2048×2048 pixel Marr CCD camera. Data fitting was by the use of NANOCELL, a program developed at Purdue University to simulate 2D

diffraction data for nanostructured materials, using the distorted-wave Born approximation.¹⁹

To investigate the self-assembly mechanism of the Au-micelle/silica system, a 0.05 mL drop was cast onto a silicon substrate that had been prealigned with the X-ray beam. Scattering data was obtained every 120 s with an integration time of 30 s; images of significance for the understanding of the self-assembly mechanism are presented in Figure 1A,B, corresponding to data from $t = 8$ and 20 min after solution casting, respectively. Before $t = 10$ min, no demonstrative evidence of a transition structure between an isotropic solution and the lattice seen in Figure 1A was observed. Although data for NC-micelle self-assembly without silica present (*vide infra*) show the presence of a lamellar intermediate, confirmation of short-lived transitional states in the Au NC-micelle/silica system will require further studies using a higher frame rate for data collection. Upon closer inspection of the image in Figure 1A, each reflection is found to be split into two distinct spots, indicating the presence of two lattices sharing the same unit cell symmetry but with slightly different (ca. 8%) lattice constants. In GISAXS, scattering from the beam reflected from the film/substrate interface can also yield a second series of spots at the detector.¹⁹ These features appear at higher α_f relative to the primary scattering pattern, however, while the data in Figure 1A is shifted in both α_f and θ_f . The presence of two lattice spacings could indicate either inhomogeneous evaporation of the film or nucleation at either of the film interfaces; data from this GISAXS study cannot differentiate between these two possibilities, however. At $t = 10$ min (Figure 1B), the doublets coalesce into single spots, forming a pattern that we fit to a rhombohedral space group, $R\bar{3}m$, with $\alpha = 67^\circ$, $a = 8.6$ nm, and the $\langle 111 \rangle$ direction oriented perpendicular to the substrate plane. Figure 1C, fit lattice parameters as a function of time, shows a progressive uniaxial shrinkage of the film from silica condensation. Calculation of the NC–NC distance inside the $\langle 111 \rangle$ plane using the data in Figure 2 shows that significant lateral drying occurs in the cast film; at $t = 10$ min, this nearest-neighbor distance is $120 \text{ \AA}$, quickly shrinking (at 20 min) to $110 \text{ \AA}$ and finally stabilizing at $78 \text{ \AA}$ after ca. 1 h. Another prominent

(16) Kremer, K.; Robbins, M. O.; Grest, G. S. *Phys. Rev. Lett.* **1986**, *57*, 2694–2697.

(17) Sirota, E. B.; Ou-Yang, H. D.; Sinha, S. K.; Chaikin, P. M.; Axe, J. D.; Fujii, Y. *Phys. Rev. Lett.* **1989**, *62*, 1524–1527.

(18) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *Chem. Commun.* **1994**, *7*, 801–802.

(19) Tate, M. P.; Urade, V. N.; Kowalski, J. D.; Wei, T.; Hamilton, B. D.; Eggiman, B. W.; Hillhouse, H. W. *J. Phys. Chem. B* **2006**, *110*, 9882–9892.

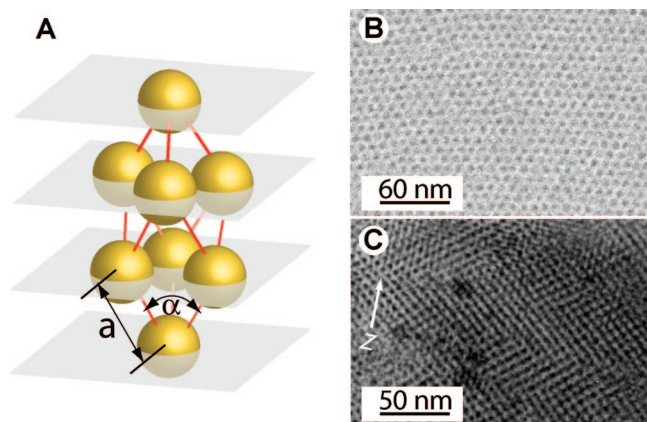


Figure 2. (A) Schematic of an $R\bar{3}m$ unit cell showing the relationship between this space group and an fcc structure (each gray plane representing a close-packed NC layer, stacked in an ABC motif). (B) Plan-view TEM image of a Au NC-micelle/silica cast film showing the hexagonal packing of the (111) plane. (C) Cross-sectional TEM image of a Au NC-micelle/silica cast film (the z direction of the film is indicated by the inset arrow).

characteristic of the data in Figure 1A,B is the presence of a diffuse ring connecting the (111) reflection with the out-of-plane peaks; we ascribe this feature to imperfect orientation of NC lattice domains.

In-situ GISAXS data of Au-micelle self-assembly without the presence of silica is shown in Figure 1D–F. Here, it is clear that self-assembly of the NC lattice proceeds through a lamellar intermediate (Figure 1D). A transient mesophase appears (Figure 1E), which then collapses to a nonordered, glassy state upon further evaporation (Figure 1F). Although fitting of the scattering pattern in Figure 1E is hampered by the limited number of reflections present as well as the diffuseness of the scattering features, we find that the data is best described using a [020] oriented $Fm\bar{3}m$ phase (face-centered orthorhombic) with $a = 5.3$ nm, $b = 6.7$ nm, and $c = 7.2$ nm. Again, a diffuse ring is present in the data, indicating the presence of nonoriented or poorly ordered domains. The bcc NC lattice collapses upon further film evaporation, yielding a glassy state with interparticle spacing of ca. 3–4 nm (Figure 1F). It is not known whether this disordered structure is a result of insufficient physical dispersity of the NC-micelles or the specific self-assembly pathway, or a combination of the two.

These observed lattice symmetries can be rationalized by using a phase diagram for colloidal self-assembly controlled by screened Coulomb interactions along with the recognition that $R\bar{3}m$ and $Fm\bar{3}m$ symmetries can describe partially collapsed fcc and bcc lattices, respectively.²⁰ Figure 2A illustrates a unit cell for NCs arranged in a rhombohedral lattice formed from layers of hexagonally packed NCs (gray planes) stacked in an ABC motif, showing the relationship between this unit cell and fcc packing; if $\alpha = 60^\circ$, then the space group $R\bar{3}m$ is isomorphic with the fcc structure.¹⁹ TEM data of a NC-micelle/silica cast film is consistent with fcc-type packing: a plan view (Figure 2B) confirms the 6-fold symmetry of the (111) plane, while cross-sectional data (Figure 2C) is in agreement with ABC-type stacking of NC layers (the (110) plane). Similarly, the space group $Fm\bar{3}m$ is equivalent to bcc packing when $a = b = c$. Significantly, both fcc and bcc packing are found in the phase diagram for colloidal self-assembly controlled by “soft” electrostatic interactions:^{21,22} at low screening potentials (e.g., conditions of low ionic strength, such as those found in the Au NC-micelle system without silica), non-close-

packed bcc organization is favored, while a close-packed fcc structure appears at higher ionic strength (contributed by the presence of ionized silica precursors and acid catalyst in the Au NC-micelle/silica system).¹³ Although undistorted fcc or bcc structures are not directly observed in this study, we conjecture that these phases are formed initially in the self-assembly pathway, but rapidly collapse during solvent evaporation. The presence of silica precursors stabilizes the fcc structure before complete disruption of the NC lattice; because the volume of silica produced by these precursors is less than the free volume of the pure fcc phase, however, distortion of the unit cell can still occur, producing an NC lattice with lowered symmetry. Subsequent condensation of the silica matrix further induces unit cell deformation. In the case of the bcc phase, the absence of stabilizing silica precursors allows for complete collapse of the lattice.

Assuming an approximate Au-micelle radius of 2 nm, the lattices found in Figure 1B,E occur at a volume fraction of ca. 25%, higher than the range for bcc and fcc stability measured for macroscopic colloids.¹⁷ However, the rhombohedral and orthorhombic phases described here occur after partial film collapse, beyond the range where the pure lattices would appear; transformation into the glassy state predicted from the (equilibrium) phase diagram in Sirota et al. may be kinetically slow. Also, vigorous volume fraction calculations for Au NC-micelle solutions will require careful measurement of the thickness of the thiol/surfactant layer surrounding the Au core to obtain a true particle radius.

Contrasting the results obtained in this study with those obtained previously for hard-sphere assembly of Au NCs in cast films, it is evident that lattice formation and orientation occurs through a mechanism other than concentration and nucleation at the liquid/air interface.^{10,14} First, no evidence of monolayer formation at the surface of the evaporating drop is observed, as indicated by the lack of scattering features consistent with 2D lattice formation. Second, comparison of cast and spin-coated films shows that increased evaporation rate *decreases* the net orientation of the self-assembled lattice; in 2D lattices formed from concentration of NCs at the liquid surface during solvent evaporation, increased evaporation rate has the opposite effect, suppressing the growth of nonoriented NC lattice crystallites.¹⁴ Combining these observations with the phase behavior seen during our in situ GISAXS experiments suggests a mechanism of self-assembly whereby lattice formation is driven by bulk concentration of Au-NCs during solvent evaporation. We hypothesize that preferential orientation of the lattice is induced by confinement between the liquid/solid and liquid/air interfaces; during slow evaporation, the relative rates of structure formation and NC diffusion may allow for lattice reorganization into a more stable orientation, while the rapid kinetics of self-assembly in spin-coated films freezes domain orientation before this reorganization can occur.⁶ Because self-assembly of Au-NCs is observed without the presence of silica, the self-assembly process is clearly driven by long-range (nonspecific) forces.²³ Addition of silica precursors (along with acid catalyst) does modify the self-assembly pathway, but in a manner consistent with Coulomb screening rather than specific close-range interactions. Without silica, the Au NC lattice collapses upon completion of solvent evaporation, further demonstrating the function of silica as primarily that of a structural “filler”.

(21) Robbins, M. O.; Kremer, K.; Grest, G. S. *J. Chem. Phys.* **1988**, *88*, 3286–3312.

(22) Sirota, E. B.; Ou-Yang, H. D.; Sinha, S. K.; Chaikin, P. M.; Axe, J. D.; Fujii, Y. *Phys. Rev. Lett.* **1989**, *62*(13), 1524–1527.

(23) Israelachvili, J. *Intermolecular and Surface Forces*; Academic Press: San Diego, CA, 1992.

(20) Urade, V. N.; Hillhouse, H. W. *J. Phys. Chem. B* **2005**, *109*, 10538–10541.

We anticipate that future GISAXS studies of Au NC-micelle/silica self-assembly using a faster data collection rate will enable us to elucidate in more detail the mechanism of lattice orientation. In addition, extension of these studies to other NC micelle systems²⁴ (such as those with semiconductor²⁵ or magnetic cores²⁶) and NC composite systems²⁷ as well as nonspherical shapes and variable interaction potentials will further advance the fundamental understanding of self-assembly processes, enabling the design of NC lattices with tailored function and properties.

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(24) Fan, H. Y. *Chem. Commun.* **2008**, 12, 1383–1394.

(25) Fan, H. Y.; Leve, E. W.; Scullin, C.; Gabaldon, J.; Tallant, D.; Bunge, S.; Boyle, T.; Wilson, M. C.; Brinker, C. J. *Nano Lett.* **2005**, 5, 645–648.

(26) Fan, H. Y.; Leve, E. W.; Gabaldon, J.; Wright, A.; Haddad, R.; Brinker, C. J. *Adv. Mater.* **2005**, 17, 2587–2590.

(27) Fan, H. Y.; Chen, Z.; Brinker, C. J.; Clawson, J.; Alam, T. *J. Am. Chem. Soc.* **2005**, 127, 13746–13747.

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