Tracing the Surfactant-Mediated Nucleation, Growth, and Superpacking of Gold Supercrystals Using Time and Spatially Resolved X-ray Scattering

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Supporting Information

ABSTRACT: The nucleation and growth process of gold supercrystals in a surfactant diffusion approach is followed by simultaneous small- and wide-angle X-ray scattering (SAXS/WAXS), supplemented with scanning electron microscopy. The results indicate that supercrystal nucleation can be activated efficiently upon placing a concentrated surfactant solution of a nematic phase on top of a gold nanocrystal solution droplet trapped in the middle of a vertically oriented capillary tube. Supercrystal nuclei comprised of tens of gold nanocubes are observed nearly instantaneously in the broadened liquid–liquid interface zone of a steep gradient of surfactant concentration, revealing a diffusion-kinetics-controlled nucleation process. Once formed, the nuclei can sediment into the nanocrystal zone below, and grow efficiently into cubic or tetragonal supercrystals of ~1 μm size within ~100 min. Supercrystals matured during sedimentation in the capillary can accumulate and face-to-face align at the bottom liquid–air interface of the nanocrystal droplet. This is followed by superpacking of the supercrystals into highly oriented hierarchical sheets, with a huge number of gold nanocubes aligned for largely coherent crystallographic orientations.

1. INTRODUCTION

Supercrystals self-assembled from nanocrystals are of broad interest due to their collective and tunable properties outperforming the building blocks in molecule sensing,1,2 catalysis reactions,3–5 and concentrated surfactant solution of a nematic phase on top of a gold nanocrystal solution droplet trapped in the middle of a vertically oriented capillary tube. Supercrystal nuclei comprised of tens of gold nanocubes are observed nearly instantaneously in the broadened liquid–liquid interface zone of a steep gradient of surfactant concentration, revealing a diffusion-kinetics-controlled nucleation process. Once formed, the nuclei can sediment into the nanocrystal zone below, and grow efficiently into cubic or tetragonal supercrystals of ~1 μm size within ~100 min. Supercrystals matured during sedimentation in the capillary can accumulate and face-to-face align at the bottom liquid–air interface of the nanocrystal droplet. This is followed by superpacking of the supercrystals into highly oriented hierarchical sheets, with a huge number of gold nanocubes aligned for largely coherent crystallographic orientations.

formation of supercrystals. Alternatively, by rapidly mixing good solvents and nonsolvents, nanocrystals can be locally condensed and trapped in microemulsions via liquid–liquid phase separation for accelerated supercrystal formation.77–79 The sizes of hence formed supercrystals, however, were limited to the stable sizes of the microemulsions available. Recently, a simple surfactant diffusion approach was developed by our group (parallel to that by Yang et al.10 and Young et al.25) to efficiently form size-tunable and well-shaped supercrystals with high yield from octahedral and rhombic dodecahedral nanocrystals.3,10,30 In the surfactant diffusion approach, a highly concentrated surfactant solution is added on top of an aqueous solution of nanocrystals, allowing fast diffusion of surfactants across the interface toward the beneath nanocrystal regime of a relatively dilute surfactant concentration. Consequently, nanocrystals can form large supercrystals very efficiently with geometric shapes via coordinated actions of surfactant bilayer structures.30 The critical supercrystal formation mechanism of the surfactant diffusion approach, particularly the role of...
liquid–liquid interfacial zone, was not addressed much previously.\textsuperscript{9,10,30}

To trace the formation process of supercrystals from gold nanocubes in the surfactant diffusion approach with \textit{in situ} simultaneous small- and wide-angle X-ray,\textsuperscript{10,19,31–34} we use a thin-wall quartz capillary tube (as better X-ray windows) in sample preparation in this study. Specifically, a concentrated surfactant solution layer is placed on top a gold nanocrystal solution droplet capillary trapped in the middle of a vertically oriented capillary tube for supercrystal formation (Scheme 1).

**Scheme 1.** Schematic of the Scanning SAXS/WAXS along the Height of a Sealed Sample System Capillary Trapped in the Middle of a Vertically Oriented Capillary Tube (with Each Zone Indicated)\textsuperscript{48}

![Scheme 1](image)

“The initial interface of the surfactant solution and the nanocube droplet is marked as $z = 0$."

Our X-ray scattering results, supplemented by scanning electron microscopy (SEM), evidence a two-step formation process of nucleation and growth. In the nucleation stage, an instantaneously broadened liquid–liquid interfacial zone with a steep gradient of high surfactant concentrations can kinetically trap and supersaturate gold nanocubes for self-assembling into supercrystal nuclei; subsequently, the nuclei can sediment into the beneath nanocrystal-rich zone for efficient growth into large cubic or tetragonal supercrystals. We show that cubic or tetragonal supercrystals hence formed can deposit to the bottom liquid–air interface of the suspended droplet in the capillary tube, to which interface they can face-align and superpack into hierarchical sheets, comprising a huge number of highly oriented nanocrystals.

2. RESULTS AND DISCUSSION

2.1. Nucleation and Growth Process. Figure 1a shows the schematic formation process of cubic supercrystals from gold nanocubes. A surfactant solution of highly concentrated cetyltrimethylammonium chloride (CTAC) micelles (1.0 M) was deposited gently on top of a solution droplet of gold nanocubes (ca. 54 nm size as detailed in the Supporting Information) capillary trapped in the middle of a vertically oriented capillary tube (Scheme 1). The top CTAC micelles instantaneously diffused across the highly asymmetric liquid–liquid interface (in surfactant concentrations) for a broadened interfacial zone with a steep gradient of surfactant concentration. Presumably, the relatively bulky nanocrystals could be kinetically localized and concentrated in the interfacial zone before their slow diffusion into the nanocrystal zone below. Supercrystal nuclei of a few hundreds of nanometers hence self-assembled from the (tens of) trapped and supersaturated gold nanocrystals were evidenced by the SEM image in Figure 1c. The nuclei were, however, isolated and dispersed by densely packed surfactant micelles in the interface zone. After the quick formation, the micelle-confined supercrystal nuclei could sediment into the nanocrystal zone below, where they could grow substantially into large and well-shaped cubic or tetragonal supercrystals, as evidenced by the SEM image (Figure 1d). Matured supercrystals then deposited at the bottom liquid–air interface of the suspended nanocrystal droplet for superpacking into 3D hierarchical architectures (detailed below). The supercrystal formation mechanism via the surfactant diffusion approach has been extensively discussed previously with supporting evidence.\textsuperscript{9,30}

The evolution of the nucleation, growth, and superpacking of the gold supercrystals, occurring sequentially along the sample height inside the capillary tube (containing the top CTAC zone, the interface zone, and the bottom nanocrystal zone), was traced by time and spatially resolved SAXS and WAXS,\textsuperscript{35–39} as illustrated in Scheme 1. Figure 2a gives the SAXS profiles obtained during the first scan, 180 s (limited by the instrumentation used) after placing the surfactant solution on top of the nanocrystal solution droplet (the initial liquid–liquid interface is defined as $z = 0$), exhibiting distinct features for respective zones. At a typical position of $z = -2.0$ mm in the bottom nanocrystal zone, the SAXS profile is mainly contributed by the cubic nanocrystals, and can be well-fitted (Figure 2a) using a cubic form factor with a mean edge length of 53.9 nm and 10% polydispersity (detailed in Table S1, Supporting Information). These features are consistent with the SEM-evidenced nanocube size and shape (Figure S1). The correspondingly collected WAXS data exhibit the characteristic

![Figure 1](image)

**Figure 1.** (a) Surfactant-nanocrystal two-solution system, with the CTAC surfactant solution layer placed on top of a gold nanocrystal solution droplet. Nucleation and growth of supercrystals (SCs) proceed subsequently in the interfacial zone and the beneath nanocrystal zone. At the bottom liquid–air interface (with a surfactant monolayer), precipitated SCs can align and superpack into 3D hierarchical sheets. In the enlarged views for the nucleation and growth zones, small blue dots and yellow cubes denote surfactant micelles and gold nanocubes. The corresponding SEM images of (b) dispersed or small clusters (circled) of gold nanocrystals observed in the CTAC zone, (c) the SC nuclei formed in the interface zone, and (d) the cubic SCs observed near the bottom of the nanocrystal zone.

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DOI: 10.1021/acs.langmuir.6b04319

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(111) and (200) powder diffraction rings of a face-centered cubic lattice from the randomly oriented gold nanocrystals in solution. The SAXS profiles measured in the CTAC nematic phase at \( q \sim 0.1 \text{ Å}^{-1} \) (d) exhibit a typical nematic ordering peak of globular CTAC micelles near the scattering vector \( q = 0.11 \text{ Å}^{-1} \) (densely packed rod-like micelles would have formed hexagonal packing), corresponding to a mean spacing of 5.7 nm deduced on the basis of the Bragg law. We note that, estimated with the micelle dimensions observed in lower surfactant concentrations (an ellipsoidal shape of \( \sim 5.8 \) and \( \sim 4.6 \) nm for the major and minor axes),40 the CTAC micelles in the top CTAC zone should be tightly packed. In such a crowded environment, nevertheless, we could observe upward diffusion of the bulky nanocrystals into this CTAC zone, forming ordered clusters of a lamellar packing. The corresponding lamellar spacing is \( d \sim 70 \) nm, as revealed from the periodic but broad (001) and (002) reflections in Figure 2a (cf. Figure S2 and Table S1). Consistently, small clusters of layered nanocrystals were also observed with SEM (Figure 1b). The 1D lamellar packing observed suggests a possible preliminary ordering structure of the nanocubes before formation of 3D-ordered supercrystal nuclei (Figure 1c).

The SAXS profiles collected over the interfacial zone \( (z = -1.0 \) to \( 1.0 \) mm) (Figure S3) exhibit rich ordering peaks of the supercrystal nuclei, and can be indexed by a cubic lattice (Figure 2a). We, however, noticed that these SAXS peaks emphasize the reflections from a 2D structure with a square lattice, implying a better planar ordering of the nanocubes, presumably advanced from the layer packing observed in the top CTAC phase. Such a result is consistent with an incomplete cubic shape of the nuclei evidenced with SEM (Figure 1c). The lattice constant \( a \) and the corresponding coherence length \( \xi \) extracted from the data fitting (Figure S2) based on a cubic lattice, are found to increase from \( a = 70 \) nm to \( a = 77 \) nm and from \( \xi = \sim 100 \) nm to \( \xi = \sim 400 \) nm as the surfactant concentration reduces across the interface zone from 1.0 M at \( z = 1.0 \) mm to 0.15 M at \( z = -1.0 \) mm (Figure 2b). The position-dependent surfactant concentrations along the sample height were estimated using the nematic peak position (indicated in Figure 2c), as detailed in Figure S4.

In the subsequent 2 h of sample incubation, SAXS profiles in the interfacial zone \( (z = -0.5 \) to \( 1 \) mm) are similar in shape (Figure 2c and Figure S3), revealing a largely stable size and structure of the supercrystal nuclei surrounded by the
concentrated surfactant micelles. The intensity of the SAXS profiles with $z = -1$ mm, however, decayed gradually (Figure S3), suggesting that the supercrystal nuclei gradually diffused into the nanocrystal zone below for further growth. In contrast, SAXS profiles measured for the bottom nanocrystal zone at $z = -3.0$ mm evolved significantly from nanocrystal to supercrystal dominance (Figure 2c). SAXS data analysis using a cubic structure (Table S1) shows that the supercrystal size increases steadily to ca. 1 μm within 100 min and then becomes stabilized thereafter, which is accompanied by systematically decreased lattice sizes from $a = 77$ nm to $a = 74.5$ nm for increasingly tighter packing with better long-range ordering (Figure 2d). The decrease of the lattice constant with the growth of the supercrystal size along the evolution is in a same trend as that observed in the evaporation driven assembly, and can be attributed to local structural rearrangements of the nanocubes within supercrystals for enhanced 3D ordering. In contrast, coherent growths in $a$ and $\xi$ values with decrease of the surfactant concentrations over the interface zone (Figure 2b) reveal a different spatially confined packing mechanism for supercrystal nucleation.

We tried supercrystal formations with mixing concentrated CTAC (1.0 M) into the nanocube solution; the supercrystals formed in such a mixture without separated nucleation and growth environments tend to be small and irregular in shape. Further, in a reverse-phase case with the nanocrystal aqueous solution placed on top of a concentrated CTAC solution, the supercrystal nuclei hence formed were either trapped in the interfacial zone or sunk into the concentrated CTAC zone below, resulting in more restricted growth of supercrystals, as illustrated in Figure S5. The role of the surfactant concentration gradient established over the interfacial zone in the surfactant diffusion approach becomes evident, because it can regulate the size and number density of the supercrystal nuclei and segregate the nanocrystal zone below for efficient growth of supercrystals. Sedimentation behavior (a directional diffusion) of the supercrystal nuclei from the interface zone into the beneath nanocrystal zone becomes relevant.
2.2. Effects of the Surfactant Concentration Gradient. To illustrate further the effects of the surfactant concentration gradient on the nucleation and growth process of the supercrystals, we compare the supercrystal formation processes with CTAC concentrations of 0.5, 1.0, and 1.5 M on top of similar nanocube solutions. Parallel SAXS/WAXS results indicate that a higher CTAC concentration could create a steeper concentration gradient for a more broadened interfacial zone, as shown in Figure 3a. Such a surfactant concentration gradient reduced slightly with time but could reach a steady state within ca. 30 min, with the nematic phase maintained (Figure S6). We further compared the gap size \( g \) between the nanocrystals in the supercrystal nuclei, deduced from subtraction of the SAXS-determined supercrystal cubic lattice with the nanocrystal size. Interestingly, the hence obtained gap values (Figure 3b) with the top CTAC phases of different concentrations fall on a common dotted line with a slope of \(-4.2 \text{ nm}/[\text{M}]\), suggesting that the gap size is determined mainly by local CTAC concentration in the interfacial zone. A higher CTAC concentration on top, however, leads to a wider interfacial zone and a wider distribution of the lattice size of the supercrystal nuclei, as shown in Figure 3b. The observed tightest packing of the supercrystal nuclei with a nanocrystal gap size of 17.0 nm (or \( a = 71 \text{ nm} \)) corresponds to a local environment of 1.1 M CTAC; the loosest packing of a maximum gap size of 23 nm (\( a = 77 \text{ nm} \)) at 0.15 M CTAC suggests a minimum CTAC concentration in the kinetic formation of the supercrystal nuclei. Moreover, with a 0.5 M CTAC solution on top (for a thinner interface nucleation zone, hence less supercrystal nuclei), supercrystal nuclei could grow faster in size (to ca. 1 \( \mu \text{m} \)) in the nanocrystal zone (Figure 4a). In contrast, with 1.5 M CTAC solution on top for a wider interfacial zone, much more restricted supercrystal size growth to ca. 0.55 \( \mu \text{m} \) was observed (Figure 4b). We note that the supercrystal size evolutions shown in Figures 2d and 4 for a specific height at \( z = -3 \text{ mm} \) of the sample solutions are coupled with accumulated growth along the sedimentation; hence, the comparison can only be qualitative. Without surfactant-mediated nucleation, we found that the nanocrystal concentration used could hardly form supercrystals in a similar time span. These results reveal efficient controls of the size and growth rate of the supercrystals by the CTAC diffusion kinetics across the liquid–liquid interface.

The observed higher and lower limits on the nanocrystal gap size reveal an interplay of long-range attractive and short-range repulsive interactions of the surfactant micelles and bilayers in forming the supercrystal nuclei. After deduction of the CTAC bilayer thickness \( \sim 3.0 \text{ nm} \) (estimated from the SEM image in Figure S1) covered on each nanocube, \(^{41} \) the gap sizes of 17.0–23 nm correspond to a spacing range of ca. 11–17 nm in between adjacent nanocrystals in a supercrystal nucleus. As illustrated in Figure 3c, such large spacing in between neighboring nanocrystals could be stabilized with CTAC micelles. Namely, the supercrystal self-assembly requires sandwiched CTAC micelles to establish a liaison between neighboring nanocubes via associations of the surfactant micelles with the capped surfactant bilayers of the nanocubes. Consequently, the surfactant-mediating strength may be modulated by the number of surfactant micelles/bilayers between the nanocubes for the low and high gap limits. \(^{10} \) Surfactant bilayers in between nanocrystals of a supercrystal were evidenced in our previous reports, \(^{30} \) the in situ observation presented here further illustrates a much larger gap in between the nanocubes during the supercrystal formation than the two surfactant bilayers respectively coated on the neighboring nanocubes, \(^{30} \) suggesting an active role of surfactant micelles in mediating the supercrystal formation.

We also tried replacing the top CTAC surfactant solution with a cetyltrimethylammonium bromide (CTAB) solution of a similar surfactant concentration, and found that supercrystals hence formed are of irregular shapes and smaller sizes (Figure S7). CTAB micelles, with more localized Br\(^{-} \) ions compared to Cl\(^{-} \) ions in CTAC micelles, may have a weaker association with the CTAC bilayers of the nanocubes. \(^{32} \) The result implies that efficient supercrystal nucleation and growth requires critical surfactant bilayer interactions to mediate local coordinated actions of surfactant micelles with the surfactant bilayers of the nanocrystals, \(^{43} \) in addition to supersaturated nanocrystals for a sufficient high local concentration.

2.3. Possible Mechanisms for the Proposed Nucleation-and-Growth Process. On the basis of the above results, we summarize the evidence observed for the proposed nucleation-and-growth process of the gold supercrystals. In the developed surfactant-diffusion approach, the nanoparticle solution is of a flexible concentration below the threshold concentration for nucleation, and can be selectively destabilized for heterogeneous nucleation at the liquid–liquid interface with a concentrated surfactant solution on top, via fast interface diffusion of a large amount of surfactant/micelles. Such a heterogeneous nucleation mechanism is similar to the free interface-diffusion nucleation for protein crystallization \(^{44} \) but differs from the homogeneous nucleation of supercrystals in the microdroplets of nanoparticles sealed in a microfluidic platform. \(^{45,46} \) In the latter case, precipitants were slowly diffused into the microdroplets of nanoparticles for very slow homogeneous nucleation (in terms of days). The fast supersaturated gold nanocubes in the surfactant diffusion approach, however, require further delicate local structural alignments into ordered packing of supercrystal nuclei, involving an interplay among electrostatic interactions, van der Waals forces, and entropy. As discussed in our previous reports, \(^{9,30} \) a dominant driving force in the supercrystal formation is attributed to the self-assembly of surfactant molecules to reduce charge interactions for more ordered but stable packing at ultrahigh surfactant concentrations, at the cost of reduced entropy. In general, concentrated ionic surfactant molecules behave on the basis of the same driving force, whether surrounded by nanocrystals or silicate precursors.

Nanocubes of relatively large facets and uniform dimensions (54 nm \( \times \) 54 nm in our case) would provide relatively large flat and symmetric deck surfaces to which small CTAC surfactant micelles (\( \sim 5–6 \text{ nm} \)) can anchor and reorganize into more ordered structures of reduced electrostatic interactions via, for instance, micelle-to-bilayer transformation. \(^{47,48} \)

In the depletion force model, \(^{20,25} \) expelling surfactant molecules from the region between adjacent nanoparticles is suggested to provide a driving force for supercrystal formation in solution. Such a model does not require formation of supercrystals with symmetrical shapes; however, cubic supercrystals missing a corner, that still fulfill the model criteria, have never been observed. In this study, rather than depleting surfactants from the nearby environment of the nanocubes, in situ SAXS elucidates that concentrated surfactants/micelles are necessary to intervene in between nanocubes for formation of supercrystal nuclei. The previously proposed surfactant depletion force explains neither the supercrystal formation

DOI: 10.1021/acs.langmuir.6b04319
Langmuir 2017, 33, 3253–3261
from the assembly of nonspherical nanocrystals nor the need of surfactant micelles in the efficient supercrystal nucleation observed in the surfactant diffusion approach.

In the lattice model of Flory and Huggins\(^{49,50}\) destablizing a polymer solution for liquid—liquid phase separation (or demixing) is driven by the change of the Gibbs free energy of mixing

\[
\Delta G_m = RT \left[ \sum_{i} n_i \ln (\phi_i) + \sum_{i<j} g_{ij} n_i \phi_i \right]
\]

with the gas constant \(R\) and temperature \(T\) (in Kelvin). The number of moles and the volume fraction of a three-component system \((n = 3)\) of the nonsolvent \((i = 1)\), solvent \((i = 2)\), and polymer \((i = 3)\) are, respectively, \(n_i\) and \(\phi_i\) with the interaction parameter \(g_{ij}\) for the components \(i\) and \(j\). The first and second terms of eq 1 describe, respectively, the ideal entropy of mixing and the enthalpy of mixing of the solution. In our case, with the surfactant diffusion approach (with surfactant as the nonsolvent and nanocubes qualitatively as polymer micelles), the fast and vast mass transfer of the surfactant via interface diffusion can destabilize an originally stable nanocube solution. Specifically, the greatly outnumbered surfactants/micelles enhance the \(n_i \phi_i\) entropy term (of a negative value) of eq 1, favoring ideal mixing; however, the also increased enthalpy of mixing with the \(g_{ij} n_i \phi_i\) term can possibly destabilize the isotropic mixing for liquid—liquid phase separation. In our case, apparently, the gain in the \(g_{ij} n_i \phi_i\) enthalpy reduction with phase separated nanocube-rich domains can compensate the loss of the entropy from ideal mixing, resulting in the observed liquid—liquid phase separation of the solution into surfactant-rich (of a nematic peak) and nanocube-rich domains in the interfacial zone. To form ordered packing of the nanocubes (preordering or nucleation of supercrystals), \(g_{13}\) for the surfactant micelles and nanocubes in the nanocube-rich domains could further reduce via, for instance, a micelle-to-surfactant bilayer transition (through changes of the surfactant headgroup area and ionization factor).\(^{37,49}\) The effective supercrystal nucleation observed here is thus attributed mainly to an efficient reduction of the enthalpy of mixing via the collective effects of liquid—liquid phase separation and ordered packing of the nanocubes for reduction of surfactant charge interactions. The kinetics of the liquid—liquid phase separation presumably can be driven increasingly faster than that of the supercrystal nucleation, via an enhanced rate of the mass transfer driven by a more concentrated surfactant solution on top of the nanocube solution. A consequence might be the formation of increasingly more but smaller supercrystal nuclei (as hinted in Figure 2b).\(^{49}\)

**2.4. Oriented Superpacking at an Inverted Liquid—Air Interface.** With the surfactant-nanocrystal solution droplets stacked and trapped in the middle of a vertically oriented capillary tube, the interface-born supercrystal nuclei can grow substantially during sedimentation toward the bottom liquid—air interface of the suspended nanocrystal droplet. There, matured and large cubic or rectangular supercrystals were first face-oriented along the water—air interface. With an increase of the number density, they could further face—face orient and superpack into massive sheets. Figure 5 demonstrates the global layer-by-layer stacking features in the 3D superpacking of the largely face-oriented supercrystals. The delicate local orientation alignment and coalescence of two supercrystals are also captured, as shown in the inset of Figure 5. The superpacking process of the supercrystals at the suspended liquid—air interface was monitored using time-resolved SAXS/WAXS, as shown in Figure 6. In the beginning, sparsely distributed cubic supercrystals could only align their faces with the liquid—air interface, as evidenced by reflections emphasized in the in-plane and vertical directions (Figure 6a1) for a uniaxial alignment. Gradually accumulated and crowded supercrystals along the development led to further rotational (face-to-face) alignment (with respect to the vertical \(z\)-axis) for enhanced off-axis reflections, as shown in Figure 6a2 and a3. Finally, a highly oriented 2D SAXS pattern (Figure 6a4) could be observed, corresponding to highly face-oriented cubic supercrystals in the superpacking. Figure 6c illustrates the corresponding sharpening process of the azimuthal-dependent SAXS profiles. Consistent with the SEM image for the superpacking with cubic face-aligned supercrystals (Figure 5), most of the brilliant reflections in the 2D SAXS pattern can be indexed with a uniaxial \((\alpha\)-axis) oriented cubic structure (with the crystallographic \(a\)-\(b\) plane parallel to the liquid—air interface), as represented shown in Figure 6a4 and detailed in Figure S8. There are, inevitably, weak reflections from a minority of cubic supercrystals of strayed orientations (Figure S8). Even more amazing is the accompanied sharpening of the (111) and (200) X-ray powder diffraction rings of the gold nanocrystals into arcs (Figure 6b), suggesting a correlated orientation alignment of the nanocrystal facets, as detailed in the evolution of the azimuthal WAXS profiles in Figure 6d. As the individual nanocrystals would hardly perform rotational alignment inside a well-packed supercrystal, such a result implies a prealignment of the nanocrystals during formation of a single supercrystal, before the superpacking. We emphasize a critical role of the suspended liquid—air interface in the alignment of supercrystals for the superpacking; no such oriented superpacking of supercrystals could be observed in the solution slightly above the interface (Figure S9).

**3. CONCLUSION**

We have demonstrated the surfactant-mediated nucleation and growth process of the supercrystals assembled from the building blocks of cubic gold nanocrystals using the surfactant...
diffusion approach. Placing a concentrated surfactant solution on top of a nanocrystal solution can drive fast interface diffusion of surfactants for kinetically driven supercrystal nucleation. The relative diffusion kinetics of the surfactants and nanocubes (modulated by the surfactant concentration gradient) and the surfactant mediated interactions between the nanocrystals play critical roles in the formation of the size-controlled, well-shaped supercrystals. The supercrystals matured during sedimentation can face-orient and superpack into highly oriented sheets at the bottom liquid–air interface of stacked surfactant-nanocrystal solution droplets suspended in a capillary tube. Most surprisingly, the huge number of cubic gold nanocrystals can align in the superpacking process for largely coherent crystallographic orientations. Such superpacked supercrystals may find applications requiring specific crystal facets or multi-length-scale-ordered nanocrystals for enhanced optical, electric, or thermal-electric properties.

4. EXPERIMENTAL METHODS

Sample Preparation. The gold nanocrystals used in this study were prepared by following our previously reported seed-mediated growth method. Briefly, two 10 mL aqueous solutions, respectively containing $2.5 \times 10^{-4}$ M HAuCl$_4$/0.10 M CTAC and 0.02 M ice-cold NaBH$_4$, were prepared. The HAuCl$_4$ solution was added with 0.45 mL of the NaBH$_4$ solution under stirring. The resulting solution turned brown immediately, indicating the formation of gold particles. The seed solution was aged for 1 h to decompose excess borohydride. Similar growth solutions were prepared in two vials, labeled as A and B. First, 0.32 g of CTAC surfactant and 9.605 mL of deionized water were added into each vial. The concentration of CTAC in the final solution was 0.10 M. The vials were then kept in a water bath at 30 °C. Both vials were added with 250 μL of 0.01 M HAuCl$_4$ solution and 10 μL of 0.01 M NaBr, followed by the addition of 90 μL of 0.04 M ascorbic acid. The total solution volume in each vial was 10 mL. The solution color turned colorless after the addition of ascorbic acid, indicating the reduction of Au$^{3+}$ to Au$^{+}$ species. Next, 45 μL of the seed solution was added to vial A under shaking until the solution color turned light pink. Then, 45 μL of the solution in vial A was well-mixed into vial B. Finally, the solution in vial B was aged for 15 min and centrifuged at 6000 rpm for 10 min to obtain 54 nm cubic gold nanocrystals, as shown in Figure S1a.

Time and Spatially Resolved SAXS/WAXS. SAXS/WAXS measurements were performed at the BL23A end station of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu. Data were collected with a Hamamatsu C9728DK-10 flat penal and Dectris Pilatus 1M-F area detectors, located respectively at 0.15 and 4.9 m from the sample position, to cover WAXS and SAXS $q$-ranges of 2.0–3.5 and 0.003–0.2 Å$^{-1}$ with a 0.5 mm diameter X-ray beam of 15 keV (wavelength $\lambda = 0.8266$ Å). The scattering vector is defined by $q = 4\pi\lambda^{-1}\sin \theta$, with $2\theta$ for the scattering angle. For X-ray scattering from the supercrystals at the liquid–air interface defined in the $x$–$y$ plane with the X-ray incidence in the $x$–$z$ plane, $q = (q_x, q_z)$. The highly oriented SAXS pattern taken at $t = 4$ h can be elaborately indexed to a uniaxial (crystallographic $c$-axis in the $z$ direction) oriented cubic structure (selectively indexed; further detailed in Figure S8). Representative evolutions of the azimuthal profiles of the (c) SAXS and (d) WAXS, illustrating the gradually orientation-focused reflections (as marked) of the supercrystals and nanocrystals, concomitantly.

Figure 6. Time-resolved (a1–a4) SAXS and (b1–b4) WAXS patterns taken simultaneously during sedimentation of the supercrystals to the bottom water–air interface of the sample solution suspended inside a capillary tube. Gradually intensified on-axis followed by off-axis SAXS reflections reveal an alignment sequence of face-orientation to the liquid–air interface followed by in-plane rotational alignment of the supercrystals in superpacking. The highly oriented SAXS pattern taken at $t = 4$ h can be elaborately indexed to a uniaxial (crystallographic $c$-axis in the $z$ direction) oriented cubic structure (selectively indexed; further detailed in Figure S8). Representative evolutions of the azimuthal profiles of the (c) SAXS and (d) WAXS, illustrating the gradually orientation-focused reflections (as marked) of the supercrystals and nanocrystals, concomitantly.
resolution, over the sample height from for the cubic gold nanocrystals were position of the sample solution in the capillary. SAXS data measured measurements could provide parallel structural evolutions at each the cubic lattice size matured supercrystals were modeled with a 2D square lattice or a using the software SasView for the shape, size, and size polydispersity a wider zone from scan step of 0.5 mm. In the following 90 min, data were collected over nanoparticle solution droplets was de droplet. This initial contact interface of the CTAC and the after placing the CTAC solution on top of the gold nanocrystal sample preparation procedure, the filling, the capillary tube applicable for capturing the sample solution. With the above time-consuming was sealed from the top by epoxy. The sample solution hence sealed successive stages, at an ambient temperature of 3.5 mm sample height. The sample solution was sealed top of the nanocrystal solution for adding another sample over the measurements. With the above time-consuming sample preparation procedure, the first SAX scan was done 180 s after placing the CTAC solution on top of the gold nanocrystal droplet. This initial contact interface of the CTAC and the cubic gold nanocrystals were fabricated with a cubic form factor μL was deposited gently on the capillary tube orientation. An aqueous samples for the superpacking of the supercrystals were transferred from the corresponding zones and reaction times of a similar sample section at 90°. Time and spatially resolved SAXS/WAXS measurements were conducted in two In the first stage of 30 min, SAXS/WAXS data were collected with 1 s time resolution, over the sample height from z = −2.0 to 3.5 mm, with a scan step of 0.5 mm. In the following 90 min, data were collected over a wider zone from z = −5 to 4 mm with a larger scan step size of 1.0 mm. With the time and spatial resolutions, the SAXS/WAXS scanning measurements could provide parallel structural evolutions at each position of the sample solution in the capillary. SAXS data measured for the cubic gold nanocrystals were fabricated with a cubic form factor using the software SasView for the shape, size, and size polydispersity of the nanocrystals. SAXS profiles measured for supercrystal nuclei or matured supercrystals were modeled with a 2D square lattice or a cubic lattice using the software Scatter. The cubic lattice size a = 2π/ q0 is extracted using the first reflection peak position q0 of the corresponding SAXS profile. Typical fitting results are shown in Figure S2, with the fitted parameters shown in Table S1. Scanning Electronic Microscopy. SEM samples were retrieved from the corresponding zones and reaction times of a similar sample solution parallel to that in the SAXS/SAXS measurements. The SEM samples for the superpacking of the supercrystals were transferred onto a silicon wafer from the bottom liquid—air interface of a capillary trapped sample solution.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b04319.

SEM images; SAXS data, fitting models, and parameters; and indexing of 2D SAXS pattern (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Dr. W. T. Chuang for the help in structural analysis. This work was supported by the Ministry of Science and Technology of Taiwan (MOST 104-2119-M-007-013-MY3 and 104-2633-M-007-001).

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