# **Supporting Information**

# **Optical Processing of DNA-Programmed Nanoparticle Superlattices**

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# **1** Synthesis and Fabrication

## 1.1 Gold Nanoparticle Synthesis

Gold nanoparticles (AuNPs) were synthesized from an established seeded growth protocol.<sup>1</sup> Briefly, a 500 mL solution of 2.2 mM trisodium citrate dihydrate was brought to a boil. 2 mL of 25 mM HAuCl<sub>4</sub>:3H<sub>2</sub>O was rapidly injected to the solution under vigorous stirring. Within one minute the solution began to darken, and after 15 minutes it stabilized as a deep red color. After the initial injection to synthesize the seeds, the solution temperature was lowered to 90 °C and given 30 minutes to equilibrate. To garner NPs of larger size, further injections of 2 mL of 25 mM HAuCl<sub>4</sub>:3H<sub>2</sub>O were performed, allowing the solution 30 minutes to equilibrate after each. The NPs were characterized by casting onto formvar-coated TEM grids and imaging on a JEOL 2010 Advanced High Performance TEM. Image analysis on images with at least 250 NPs total was performed with ImageJ and used to calculate the mean particle diameter. For this work, NPs with average diameters of 29 nm (11% RSD) were used for all experiments.

## 1.2 DNA Sequences and Synthesis

The following oligonucleotides (Table S1) were purchased from Integrated DNA Technologies (IDT).

Sequence Name	Sequence (5'-3')						
Anchor Strands							
Anchor Y-SH	TCA ACT ATT CCT ACC TAC (EG <sub>6</sub> ) <sub>2</sub> -SH						
Anchor X-SH	TCC ACT CAT ACT CAG CAA (EG <sub>6</sub> ) <sub>2</sub> -SH						
Linker Strands							
Linkor V' 2d20 A'	GTA GGT AGG AAT AGT TGA A TTT AGT CAC GAC GAG TCA						
Linker I -2020-A	TT A TTT AGT CAC GAC GAG TCA TT A TTCCTT						
Linkor V' 2d20 A	TTG CTG AGT ATG AGT GGA A TTT AGT CAC GAC GAG TCA TT						
Linker A -2020-A	A TTT AGT CAC GAC GAG TCA TT A AAGGAA						
Duplexer Strand							
d20	AAT GAC TCG TCG TGA CTA AA						

Table S1. DNA Sequences.



**Figure S1.** Schematic representation of DNA design (consisting of modular sections) that allowed PAEs to bind to other PAEs with the complementary sticky end and to bind to a functionalized substrate.

## 1.3 "Programmable Atom Equivalent" (PAE) Synthesis

DNA "anchor strands" (denoted in black and brown in Figure S1) were thiol-modified to allow for efficient functionalization to gold surfaces using gold-thiol chemistry. These strands consisted of two six-unit ethylene glycol segments separated by phosphate groups (denoted as  $(EG_6)_2$ ) to increase the flexibility of the DNA chains and improve both grafting density and crystallization ability. The next 18 base sequence was unique and hybridized only to the complementary "linker strand." In the naming scheme used in Table S1, the terms X and Y are used to denote these two different 18 base recognition sequences and their complements X' and Y' on the linker strands.

DNA "linker strands" (denoted in blue and red in Figure S2) contained the complementary, 18base recognition sequence to hybridize to the anchors (X or Y). The linker strands contained 20base "duplexer" region(s) designed to hybridize to an additional "duplexer" strand (green in Figure S2) and add overall length to the DNA strand and thus increase the PAE's hydrodynamic radius. Table S1's naming scheme uses "d20" to denote either the sequence of the "duplexer strand" or its complement present in the linker strand. The numbers preceding d20 in the linker names correspond to the number of these units present in the overall linker. Finally, and most importantly, the linkers terminated in a 6-base, single-stranded "sticky end" denoted as A or A' in Scheme 1. (Note that a single, ultimately unpaired adenine base exists between each of the aforementioned sequence sections in the linker strands to add flexibility and improve crystallinity.<sup>2</sup>) Once hybridized to a PAE, these sticky ends allowed PAEs to bind to either the substrate or other PAEs that were functionalized with the complementary sticky end sequence (*i.e.* A and A' sticky ends are complementary). These binding events drove the aggregation of complementary PAEs. <sup>3</sup>

"Programmable Atom Equivalents" (PAEs) were synthesized by functionalizing the synthesized citrate capped AuNPs with a dense shell of one of the thiol-modified DNA ("anchor strands,"

Table S1). The 3'-propylmercaptan protecting group of the thiol-modified DNA sequences was cleaved by treating the sequences with 100 mM dithiolthreitol for 1 hour. The strands were desalted using a size exclusion column (GE Healthcare) and then added to a solution of AuNPs (mixed at roughly 1 OD of DNA per 1 OD of AuNPs). After incubating for 1 hour, the solution was brought up to a concentration of 0.01% sodium dodecyl sulfate and 10 mM sodium phosphate. A salt aging process was used to increase DNA loading by adding phosphate buffer saline (PBS) with 2 M sodium chloride stepwise over the course of several hours until a final concentration of 0.5 M NaCl was reached. After the final NaCl addition, the solutions were set overnight. Unbound DNA was removed by three rounds of centrifugation (13,000 rpm for 70 min for the small NPs and 12,000 rpm for 20 min for the large), removal of supernatant, and resuspension in nanopure water. The final resuspension was done in PBS with 0.5 M NaCl.

"Linker strands" were pre-hybridized by incubating with appropriate number of equivalents of the "duplexer strand" (d20) in 0.5 M NaCl PBS. Stock solutions of 100  $\mu$ M duplexed linkers were incubated at 35 °C for 1 hour to ensure full hybridization and subsequently combined with the corresponding anchor-functionalized AuNPs to yield PAEs. All PAEs created in this project only contained one type of DNA linker. Generally, PAE stock solutions were kept at 200 nM of NPs until needed. In all cases, the concentrations of AuNPs and DNA were characterized using UV-Visible Spectroscopy, monitoring at 520 nm or 260 nm, respectively, and using extinction coefficients calculated by Ted Pella and IDT, respectively.

#### 1.4 Substrate Fabrication and Functionalization

The substrates for PAE thin film deposition were fabricated using standard fabrication techniques at MIT's Materials Technology Laboratory (MTL). Fused quartz slides were purchased from Ted Pella. 2 nm of chromium (Cr) followed by 8 nm of gold (Au) were deposited on the wafer at a rate of 0.2 Å/sec in an AJA eBeam evaporator under vacuum ( $6 \ge 10^{-6}$  Torr). The thin layer of Cr was included to improve the adhesion of the Au thin film to the silicon surface. Au was chosen to enable use of the same thiol attachment chemistry used to functionalize DNA to the nanoparticles. The chip was then diced using a diesaw in 8x8 mm pieces.

DNA functionalization of the substrates was performed by incubating each substrate in a 5  $\mu$ M "anchor strand" solution (Anchor Y-SH) in buffer (0.5 M NaCl PBS) overnight, after the propylmercaptan protecting group of the thiol-modified DNA was cleaved (see SI Section 1.3). To

remove unbound DNA, the substrates were immersed in nanopure water while vortexing, repeated 5 times to ensure complete removal of the DNA. Linkers then were hybridized to the substrates by incubating the substrates in the appropriate 0.5  $\mu$ M "linker strand" solution (Linker Y'-A') at 0.5 M NaCl at 35 °C overnight. Unhybridized linkers were removed by rinsing the solution 5 times in 0.5 M PBS.

#### 1.5 Layer-by-Layer Deposition

The layer-by-layer deposition of amorphous PAE thin films was done rapidly at room temperature. A and A' functionalized PAEs (SI Section 3.1) were diluted with 0.5 M PBS to 10 nM. One functionalized substrate (or a pair of two identical substrates positioned back-to-back) was placed in 1 mL of a solution containing one type of PAE and incubated for 3 hours at room temperature to deposit the first layer. The substrates were then removed, gently washed 5 times in 0.5 M PBS, and placed in the opposite PAE type for the second layer deposition. This process was repeated to generate 5 layers of PAE for each sample.

#### 2 **Instrumentation and Data Collection**



#### Optical processing of amorphous PAE thin films 2.1

Figure S2. Optical setup used to perform experiments. Components, manufacturer, and function listed in table S2.

Number	Component	Make/Manufacturer	Function
1	532 nm laser	CST-H-532nm 2W / CST	Light source
2	Glass slide	26011/Ted Pella	Beamsplitter
3	Power monitor	PM16-121/Thorlabs	Measurement of split
			incident power
4	Mechanized aperture	SHB1/Thorlabs	Controlling exposure time
5	Focusing optics	Various/Thorlabs	Focusing spot onto sample
6	ND filter	NE510A/Thorlabs	Low-power (ex-situ)
			transmission measurements
7	Cuvette	Hellma	Holding PAE thin film in
			solution
8	Power monitor	PM16-121/Thorlabs	Measurement of transmitted
			power
9	X/Y manual	XYFM1/Thorlabs	X/Y control of processing
	micrometer		region
10	translation stage	KDC101/Thorlabs	Fine X control of processing
			location

T-LL CA 6.41 1 0

Laser power was controlled using TTL modulation of light source (1) and calibrated with direct power measurement using (8). After calibration, incident power was monitored using beam split from (2) and measured by (3). The focal point was measured to have a radius of 60µm, determined via the knife-edge method with an opaque silicon substrate placed in the cuvette filled with 0.5M PBS to account for refraction.

## 2.2 Silica Embedding Procedure

Initial experiments used a sol-gel process<sup>4</sup> that has been shown to adequately preserve the structure of PAE thin films when removed from solution. First, 1.5  $\mu$ L of *N*-trimethoxysilylpropyl-*N*, *N*, *N*-trimethylammonium chloride (TMSPA, Gelest, 50% in methanol) was added to samples submerged in 1 mL of 0.5 M PBS and left to fully associate with the DNA on the deposited film for 8 hours on an Eppendorf Thermomixer R (1400 rpm, 22 °C). Then, 2  $\mu$ L of triethoxysilane (TES, Sigma Aldrich) was added and the sample shaken for another 8 hours. The samples were rinsed by placing them in an Eppendorf tube in DI water and vortexing for 5-10 seconds, repeated 5x. After the fifth rinse, samples were placed in open Eppendorf tubes and allowed to air dry overnight.

## 2.3 Helium Ion Microscopy

Helium Ion Microscopy was performed using a Carl Zeiss scanning-helium-ion at a working distance of 25mm in the Materials Technology Laboratory (MTL) at MIT.

## 2.4 Profilometry of Embedded Thin Films

Profilometry was performed using a Bruker DXT Stylus Profilometer using a 2 µm radius diamond tipped stylus in the Materials Research Laboratory (MRL) at MIT.

# 3 Analysis of Dynamic Thermal Profile and Effects

## 3.1 In-situ Absorptivity Data

Optical processing was performed using in-situ measurement of transmitted power as a function of time. As the hole in the absorbing film formed the transmitted power through the sample increased, resulting in a decreased effective absorptivity of the film.



**Figure S3.** In-situ absorptivity data of films measured during optical processing. The decrease in absorptivity value appears to level off by the first 30 seconds (left of dashed line) but continue to decrease at a slow rate even after several hours (right of dashed line).

Due to the spatial inhomogeneity of both the film and the laser, analysis of the total transmitted power requires analysis of the spatially-varying flux and absorptivity of the system:

$$\phi_T(r) = 10^{-\alpha(r)} \phi_I(r)$$
 (eq S3.1.1)

Where *r* is the radial distance from the center of the illuminated region,  $\phi_T(r)$  is the transmitted flux at *r*,  $\phi_I(r)$  is the incident flux at *r*, and  $\alpha(r)$  is the absorptivity of the film at *r*. The total transmitted power  $T_{tot}$  may then be calculated by integrating over *r*:

$$T_{tot} = \int_0^\infty \phi_T(r) \ 2\pi r \ dr = \int_0^\infty 10^{-\alpha(r)} \phi_I(r) \ 2\pi r \ dr \qquad (\text{eq S3.1.2})$$

For an incident laser with Gaussian profile with total power  $I_{tot}$  and beam width  $\sigma$ :

$$\phi_I(r) = \frac{I_{tot}}{2\pi\sigma^2} e^{-\frac{1}{2}\left(\frac{r}{\sigma}\right)^2}$$
(eq S3.1.3)

Asserting Beer's law pointwise, the absorptivity  $\alpha$  is related to the extinction coefficient  $\epsilon$  and the concentration of particles in the film *c* and the height of the film h(r):

$$\alpha(r) = \epsilon c * h(r) \qquad (\text{eq S3.1.4})$$

Approximating hole in the film as being cylindrical with depth D and height W in a film with initial thickness  $h_0$ , the height profile is given by:

$$h(r) \approx h_0 - D * \Theta(W - r) \qquad (\text{eq S3.1.5})$$

Where  $\Theta$ () is the Heaviside theta step function. Evaluating  $T_{tot}$  for the given  $\phi_I(r)$  and h(r)

$$T_{tot} = \int_0^\infty 10^{-\epsilon c * (h_0 - D * \Theta(W - r))} \left( I_{tot} \frac{e^{-\frac{1}{2} \left(\frac{r}{\sigma}\right)^2}}{2\pi \sigma^2} \right) 2\pi r dr \qquad (\text{eq S3.1.6})$$

$$= I_{tot} 10^{-\epsilon c * h_0} \int_0^\infty 10^{\epsilon c * D * \Theta(W-r)} \left(\frac{e^{-\frac{1}{2}\left(\frac{r}{\sigma}\right)^2}}{2\pi\sigma^2}\right) 2\pi r dr \qquad (eq S3.1.7)$$

$$= I_{tot} 10^{-\epsilon c * h_0} \left( \int_0^W 10^{\epsilon c * D} \left( \frac{e^{-\frac{1}{2} \left( \frac{r}{\sigma} \right)^2}}{2\pi \sigma^2} \right) 2\pi r dr + \int_W^\infty \left( \frac{e^{-\frac{1}{2} \left( \frac{r}{\sigma} \right)^2}}{2\pi \sigma^2} \right) 2\pi r dr \right) \quad (\text{eq S3.1.8})$$

$$T_{tot} = I_{tot} 10^{-\epsilon c * h_0} \left( 10^{\epsilon c * D} \left( 1 - e^{-\frac{1}{2} \left(\frac{W}{\sigma}\right)^2} \right) + e^{-\frac{1}{2} \left(\frac{W}{\sigma}\right)^2} \right)$$
(eq S3.1.9)

The effective absorptivity  $\alpha_{effective}$  of the film and hole is given to be

$$\alpha_{effective} = -\log_{10}\left(\frac{T_{tot}}{I_{tot}}\right) = \epsilon ch_0 - \log_{10}\left(10^{\epsilon c * D}\left(1 - e^{-\frac{1}{2}\left(\frac{W}{\sigma}\right)^2}\right) + e^{-\frac{1}{2}\left(\frac{W}{\sigma}\right)^2}\right) \quad (\text{eq S3.1.10})$$

Since the film is initially at absorptivity  $\epsilon ch_0$ , the change in effective absorptivity is given by:

$$\Delta \alpha_{effective} = -\log_{10} \left( 10^{\epsilon_{c*D}} \left( 1 - e^{-\frac{1}{2} \left(\frac{W}{\sigma}\right)^2} \right) + e^{-\frac{1}{2} \left(\frac{W}{\sigma}\right)^2} \right)$$
(eq S3.1.11)

For qualitative comparison,  $\Delta \alpha_{effective}$  for a hole of either fixed  $\epsilon cD$  or  $\frac{W}{\sigma}$  are plotted in figure S4.



**Figure S4.** Effective absorptivity values for a Gaussian incident light source on an absorbing film with a cylindrical hole which is getting wider at fixed depth (left) or getting deeper at fixed width (right). The graphs were calculated using the non-dimensionalized eq S3.11.

The measured effective absorptivity data appears to match the limiting case of a hole of fixed depth widening (left) compared to a hole of fixed width deepening (right). This is consistent with a hole forming by widening, linear to first order as a function of time.

### 3.2 In-situ Heat Generation Data

Neglecting reflection or scattering, the heat generation of the film Q(t) may be estimated from the measured incident I(t) and transmission I(t) powers at all times t:

$$Q(t) = I(t) - T(t)$$
 (eq S3.2.1)



**Figure S5.** In-situ heat generation data of films measured during optical processing (left axis) and the corresponding melting temperature distance (right axis) as a function of time. Due to the heat-driven motion of the absorbing PAEs. the heat generation of the system is self-limiting, and therefore stabilizes at higher power.

As the incident power increases, the steady-state heat generated appears to level off. This is attributed to higher laser processing causing a greater portion absorbing PAE film to rearrange, forming a larger hole with lower absorptivity, as seen in figure S3, and therefore lower heat generation. This self-regulation of heat generation continues until a thermal profile has been achieved which is incapable of further melting the PAE film, causing the heat generation to stabilize even as laser power is increased. This rapid hole formation is attributed to dewetting of the PAE film which occurs at higher laser power (figure 5).

#### 3.3 Quasi-Static Temperature Profile

The heat generation in the system was approximated by a point source at the laser spot, at the interface between the liquid and substrate. In 3 dimensions, the heat equation for a non-uniform isotropic medium is given by:

$$\rho C_p \frac{\partial T}{\partial t} = \dot{q}_v + \nabla \cdot (k \nabla T) \qquad (\text{eq S3.3.1})$$

Where  $\rho$  is the density of the medium,  $C_p$  is the heat capacity of the medium,  $\dot{q}_v$  is the volumetric heat generation, and k is the thermal conductivity of the medium. First, the steady-state  $\left(\frac{\partial T}{\partial t} = 0\right)$ in either the aqueous medium (denoted i = 1) or the silica substrate (denoted i = 2) was calculated for a hemispherically-symmetric system with volumetric heat generation  $\dot{q}_{v,i} = \dot{Q}_i \delta(r)$ for a point source at r = 0 with constant heat generation rate  $\dot{Q}_i$  entering medium i:

$$0 = \dot{q}_{v_i} + k\nabla^2 T = \dot{Q}_i \delta(r) + k_i \frac{1}{r^2} \frac{d}{dr} \left(\frac{r^2 d}{dr}\right) T_i \qquad (\text{eq S3.3.2})$$

In medium i = 1,2, the solutions are given by:

$$T_i = A_i + \frac{B_i}{r} \tag{eq S3.3.3}$$

Where  $A_i$ ,  $B_i$  are dependent on the boundary conditions of the system, solved for below. For continuity of temperature at the interface,  $T_i(r) = T_i(r)$ :

$$T_i = T_j = A + \frac{B}{r} \tag{eq S3.3.4}$$

To satisfy the boundary condition that the temperature approaches the ambient temperature  $T_0$  for large r:

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$$T = T_0 + \frac{B}{r}$$
 (eq S3.3.5)

To enforce conservation of energy, the total power flowing out of both mediums 1 and 2 must sum to  $\dot{Q}$ , the total heat generation of the system. At a distance r from the source, the flux  $\phi_i$  through medium i = 1,2 is given by:

$$\phi_i = -k_i \,\nabla T = k_i \frac{B}{r^2} \tag{eq S3.3.6}$$

And the total power through a hemisphere in medium *i* of distance r from the source is given by

$$\dot{Q}_i = \frac{1}{2} 4\pi r^2 \phi_i = 2\pi B k_i$$
 (eq S3.3.7)

By conservation of energy, the total energy through both hemispheres is given by the heat generation of the point-source:

$$\dot{Q} = \dot{Q}_1 + \dot{Q}_2 = 2\pi B(k_1 + k_2) \rightarrow B = \frac{\dot{Q}}{2\pi(k_1 + k_2)}$$
 (eq S3.3.8)

Therefore, the steady-state temperature profile for a point source with fixed heat generation is given to be:

$$T(r) = T_0 + \frac{\dot{Q}}{2\pi(k_1 + k_2)r}$$
(eq S3.3.9)

For this system, in which the heat generation changes with time, the temperature profile was approximated using the quasi-static approximation, such that the temperature profile at time t is approximate given by the steady-state profile for the instantaneous heat generation rate:

$$T(r,t) \approx \frac{\dot{Q}(t)}{2\pi(k_1+k_2)r} + T_0$$
 (eq S3.3.10)

From this temperature profile, it is possible to solve for the radial distance at the melting temperature is achieved (Figure S5, right axis), which is directly proportional to the rate of heat generation:

$$r_{melt} \approx \frac{\dot{Q}(t)}{2\pi (k_1 + k_2)(T_{melt} - T_0)}$$
 (eq S3.3.11)

This value allows us to predict the size of the hole in the PAE film, assuming that the film in regions  $r < r_{melt}$  are melting and therefore unstable.

## 3.4 Transient Temperature Profile of Heating System

In general, the transient case at boundary does not have an analytical solution<sup>5</sup>, so for this analysis the transient behavior at the interface was approximated by treating the medium as homogenous medium with thermal conductivity of  $k = \frac{1}{2}(k_1 + k_2)$ , in order to enforce consistency with the calculated steady-state temperature profile. For a spherically symmetric system, the time-dependent homogenous heat equation:

$$\rho C_p \frac{d}{dt} T = k \frac{1}{r^2} \frac{d}{dr} \left( \frac{r^2 d}{dr} \right) T \qquad (\text{eq S3.4.1})$$

Can be solved via separation of variables:

$$T(r,t) = \tau(t)R(r), \ \alpha \frac{\tau'(t)}{\tau(t)} = \frac{\frac{d}{dr}\left(\frac{r^2d}{dr}R(r)\right)}{r^2R(r)} = -\lambda^2 \qquad (\text{eq S3.4.2})$$

Where  $\tau(t)$  is a time-dependent function, R(r) is a radially-dependent function,  $\lambda$  is an eigenvalue of the ODE independent of both time and radial distance, and  $\alpha = \frac{\rho c_p}{k}$  is the thermal diffusivity of the medium. For a given eigenvalue  $\lambda$ , the corresponding eigenfunction solution is given by:

$$T_{\lambda}(r,t) = \left(A(\lambda)\frac{\sin(\lambda r)}{r} + B(\lambda)\frac{\cos(\lambda r)}{r}\right)e^{-\alpha\lambda^{2}t}t \qquad (\text{eq S3.4.3})$$

To enforce even parity at the origin,  $B(\lambda) = 0 \forall \lambda$ 

Then, the transient behavior of a homogenous system with known initial state  $T_0(r)$  is given by:  $T(r,t) = \frac{1}{r} \int_0^\infty A(\lambda) \sin(\lambda r) e^{-\alpha \lambda^2 t} d\lambda, \quad A(\lambda) = \frac{2}{\pi} \int_0^\infty r' T_0(r') \sin(\lambda r') dr' \quad (\text{eq S3.4.3})$ 

Due to the linearity of the heat equation, the transient behavior of the inhomogenous system with known initial state  $T_0(r)$  and steady state profile  $T_{ss}(r)$ :

$$T(r,t) = \frac{\left(\int_0^\infty A_0(\lambda)\sin(\lambda r)e^{-\alpha\lambda^2 t}d\lambda\right)}{r} + T_{ss}(r) - \frac{\left(\int_0^\infty A_{ss}(\lambda)\sin(\lambda r)e^{-\alpha\lambda^2 t}d\lambda\right)}{r} \qquad (\text{eq S3.4.4})$$

$$A_0(\lambda) = \frac{2}{\pi} \int_0^\infty r' T_0(r') \sin(\lambda r') dr', \ A_{ss}(\lambda) = \frac{2}{\pi} \int_0^\infty r' T_{ss}(r') \sin(\lambda r') dr' \qquad (\text{eq S3.4.5})$$

Substituting  $T_0(r) = T_0$ ,  $T_{ss}(r) = \frac{\dot{Q}(t)}{2\pi(k_1+k_2)r} + T_0$ :

$$T(r,t) = T_0 + \frac{\dot{Q}}{2\pi(k_1 + k_2)r} \left( 1 - Erf\left(\frac{r}{2\sqrt{\alpha t_0}}\right) \right) \qquad (\text{eq S3.4.6})$$

Where Erf() is the error function. From this equation, the dimensionless parameter  $\frac{r}{\sqrt{\alpha t}} = \sqrt{\frac{\tau_D}{t}}$ may be interpreted as the extent of diffusion, with characteristic timescale for diffusion timescale  $\tau_D = \frac{r^2}{\alpha}$ . For  $r \sim 500 \mu m$  (the extent of the area of effect) and  $\alpha \sim \frac{\alpha_{H_2O} + \alpha_{SiO_2}}{2} = 0.66 \frac{mm^2}{s}$ , then  $\tau_D \sim 400 ms$ .



**Figure S6.** Solution to the transient heat equation for a point source in a homogenous medium initially at uniform temperature (eq. S3.4.6). As time increases, the temperature profile approaches the steady-state solution with  $\frac{1}{r}$  dependence.

#### 3.5 Transient Temperature Profile of Cooling System

If the optical power is shut-off, the system no longer generates heat, and the temperature profile decreases as the local heat dissipates into the medium. The transient behavior of a system illuminated for time  $t_0$  and then allowed to dissipate by solving the homogenous heat equation, with initial conditions  $T_0$  dictated by the transient temperature profile at time  $t_0$ :

$$T_0(r) = T_0 + \frac{\dot{Q}}{2\pi(k_1 + k_2)r} \left( 1 - Erf\left(\frac{r}{2\sqrt{\alpha t_0}}\right) \right), \ T_{ss}(r) = T_0 \qquad (\text{eq S3.5.1})$$

$$T(r,t) = T_0 + \frac{\dot{Q}}{2\pi(k_1 + k_2)r} \left( Erf\left(\frac{r}{2\sqrt{\alpha t}}\right) - Erf\left(\frac{r}{2\sqrt{\alpha(t+t_0)}}\right) \right)$$
(eq S3.5.2)



**Figure S7.** Solution to the transient heat equation for a homogenous medium immediately after being heated by a point source until  $\alpha t_0 = 1$ , and allowed to cool in the absence of a heat source (eq S3.5.2). As time increases, the temperature profile rapidly drops as heat dissipates.

#### 3.6 Effect of Pre-Nucleation site density on Grain Size

In general, the average crystalline grain size  $A_G$  is related to the density of crystalline nucleation sites  $N_{Tot}$  by the relation:

$$A_G = \frac{1}{N_{Tot}} \tag{eq S3.6.1}$$

In the limiting case where grains nucleate exclusively at the pre-nucleation sites with density  $N_0$ , the effect of decreased prenucleation sites is straightforward:

$$A_G \approx \frac{1}{N_0} \tag{eq S3.6.2}$$

However, if nucleation occurs concurrently with growth,  $N_{Tot} > N_0$ , and the effect of changing  $N_0$  is partially mitigated on the final grain size of the sample. This may be analyzed via the JMAK framework for a 2D system with constant nucleation rate  $\dot{N}$ , growth rate  $\dot{G}$  in a sample with total area A. First, the extended crystalline area  $A_{XL}^e$ , which neglects impingement of growing nucleation sites, is calculated to be:

$$\frac{A_{XL}^e}{A} = \pi \dot{G}^2 t^2 N_0 + \frac{\pi}{3} \dot{G}^2 \dot{N} t^3 \qquad (\text{eq S3.6.3})$$

Where the first term  $(\pi \dot{G}^2 t^2 N_0)$  corresponds to the uninhibited growth of the initial nucleation sites, while the second term  $(\frac{\pi}{3} \dot{G}^2 \dot{N} t^3)$  corresponds to the established solution for uninhibited growth of the sites which nucleate concurrent with the growth process for a 2D system. The growth of the extended area may be used to estimate the growth of the crystalline area  $A_{XL}$  by accounting for impingement via an area-fraction term in the differential equation:

$$dA_{XL} = \left(1 - \frac{A_{XL}}{A}\right) dA_{XL}^e \to \frac{A_{XL}}{A} = 1 - e^{-\frac{A_{XL}^e}{A}} = \frac{A_{XL}(t)}{A} = 1 - e^{-\left(\pi \dot{G}^2 t^2 N_0 + \frac{\pi}{3} \dot{G}^2 \dot{N} t^3\right)} \quad (\text{eq S3.6.4})$$

This time-dependent crystal growth may be used to determine the total number of nucleation sites which form throughout the growth process:

$$N_{tot} = N_0 + \int_0^\infty \dot{N} \left( 1 - \frac{A_{XL}}{A} \right) dt = N_0 + \dot{N} \int_0^\infty e^{-\left( \pi \dot{G}^2 t^2 N_0 + \frac{\pi}{3} \dot{G}^2 \dot{N} t^3 \right)} dt \quad (\text{eq S3.6.5})$$

Evaluating the integral in Mathematica:

$$A_{G} = \frac{1}{N_{Tot}} = \frac{A_{0}}{A_{0}N_{0} + 3^{1/6}\Gamma\left(\frac{2}{3}\right)e^{-\frac{2^{4}}{3^{4}\sqrt{3}}\left(\frac{\pi}{\Gamma\left(\frac{2}{3}\right)}A_{0}N_{0}\right)^{3}}}Bi\left(\frac{4}{3^{1/3}}\left(\frac{\pi}{\Gamma\left(-\frac{1}{3}\right)}A_{0}N_{0}\right)^{2}\right) - A_{0}N_{0}F_{q}^{p}\left[\left\{\frac{1}{2},1\right\},\left\{\frac{2}{3},\frac{4}{3}\right\},-\frac{2^{5}}{3^{4}\sqrt{3}}\left(\frac{\pi}{\Gamma\left(\frac{2}{3}\right)}A_{0}N_{0}\right)^{3}\right]}$$
(eq S3.6.6)

Where  $A_0 = A_G(N_0 = 0) = \frac{\left(\frac{\pi}{3}\right)^{\frac{1}{3}}}{\Gamma\left(\frac{4}{3}\right)} * \left(\frac{\dot{N}}{\dot{G}}\right)^{-\frac{2}{3}}$  is the crystalline grain size in the absence of prenucleation sites, Bi() is the Airy function of the second kind,  $F_q^p[]$  is the generalized hypergeometric series, and  $\Gamma()$  is the gamma function. Graphically, it is seen that even low concentrations of prenucleation sites can influence the final grain size (Figure S8).

This relationship between crystalline grain sizes may be used to estimate the prenucleation site density in the PAE films while accounting for nucleation concurrent with growth. First, the grain size  $A_G$  is estimated from the measured correlation length of the sample *L*:

$$A_G \sim L^2 \tag{eq S3.6.7}$$

Then the optically pre-processed sample has  $A_G \sim (450nm)^2 = 0.2 \ \mu m^2$  after thermal annealing, while the control sample has  $A_G^{ctrl} \sim (270nm)^2 = 0.07 \ \mu m^2$ . Assuming all pre-nucleation sites

were removed via optical processing  $(A_0 \sim 0.2 \mu m^2)$ , the pre-nucleation site density of the unprocessed sample may be determined from:

 $\frac{A_G^{ctrl}}{A_0} = 0.36 \rightarrow N_0 \sim \frac{2.4}{A_0} = 11.8 \,\mu m^{-2}$ 

(eq S3.6.8)



## 4 Image Processing and Data Analysis

## 4.1 Fourier Analysis of Helium Ion Images

For each sample processed at a given power and time, a helium ion microscope image was taken along the radius at intervals of 20  $\mu$ m in the x direction relative to the processing setup. Each image was taken with a 10  $\mu$ m FOV.



**Figure S9.** Typical helium ion images of optically processed samples (65mW for 3hrs shown here, inset at 260  $\mu$ m). At a 1000  $\mu$ m field of view (left, 100  $\mu$ m scale bar) the macroscopic hole may be observed, while at 10  $\mu$ m field of view (right, 1 $\mu$  scale bar) the individual nanoparticles may be observed. The 10  $\mu$ m field of view images were used to determine ordering along the hole radius, sampled every 20  $\mu$ m.

To analyze the ordering of the sample at each region, the 2D Fourier transform of each image was taken, and a 1D Fourier transform was generated from a radial average. The peak in the 1D Fourier transform was fit to a Gaussian peak with a linear and exponential background term. The inverse of the peak width was used to estimate the grain size, analogous to the Scherrer equation.<sup>6</sup> In this analysis, a high correlation length corresponds to large crystalline grains, while a low value indicates smaller grains or disordered PAE aggregates. It should be noted that correlation length can also be artificially lowered when various structural features not related to PAE arrays are present (*e.g.* bare regions of the substrate or silica particulates formed during the embedding process). Therefore, while high correlation lengths always correspond to high quality crystals, the origin of the disorder in samples with low correlation lengths was determined qualitatively from the microscopy images.



**Figure S10.** Typical Fourier transform helium ion images of optically processed samples (65mW for 3hrs shown here). The helium ion microscope image is used to generate a 2D Fourier transform, which is then radially averaged to generate a 1D Fourier transform. The peak is fit to a Gaussian profile with an exponential background term (red) and then isolated from the background (blue)

#### 4.2 Analysis of Ordering vs. Radial Distance

The width of the Gaussian peak as a function of radial distance was used to determine the location of maximum ordering for each sample, where the width corresponds to the inverse of the grain size, analogous to the Scherrer equation<sup>6</sup>. Near the center of the processed sample, the particles have been removed, resulting in a sparse nanoparticle film with low correlation length. Near the region of maximum ordering, the crystalline domains coalesce, forming a crystalline film. Farther from the center, the film continuously loses ordering, returning to a morphology comparable to the unprocessed sample.



**Figure S11.** Typical plot of order peak height vs. radial distance from center (65mW for 3hrs shown here). The helium ion microscope images (insets at 2.5 µm field of view) confirm that the order peak height corresponds to PAE ordering in the analyzed region.

## **5** Additional Kinetic Data

## 5.1 Correlation Length vs. Optical Processing Time and Power

The correlation length at the region of maximum ordering was computed as a function of both time and processing power. Above threshold power, the film dewets appreciably, and the resulting particle aggregates obfuscate the imaging and analysis of the underlying film. Processing at 65mW, 79mW, 95mW, and 104mW showed consistent trends of increasing correlation length with increasing time, despite the obfuscating debris.



**Figure S12.** Correlation length for samples processed at varying power and time. At low power, ordering increases with time, as illustrated in figure 4. At higher power, the film dewets, which obfuscates measurement of the ordering in the sample via image processing.

#### 5.2 Correlation Length vs. Optical Processing Time and Thermal Annealing Temperature

The correlation length at the region of maximum ordering was computed as a function of both optical processing time and subsequent thermal annealing temperature. For sufficiently short optical processing times (1s), no microscale hole formation was observed. Near 500ms, the measured correlation length is observed to drop slightly relative to the unprocessed control. This is attributed to either statistical variation between samples, or a transition from a partially paracrystalline initial state to a more amorphous glassy state due to particle heating and subsequent rapid cooling. Prior to this time, the particles likely failed to heat into a fluid phase, and therefore the correlation length remains comparable to the control. After this time, the particles may rearrange as the generated heat dissipates, so the correlation length increases.



**Figure S13.** Correlation length for samples optically processed at 65mW for varying lengths of time, and then thermally annealed at multiple powers. The correlation length is observed to decrease with short optical processing as the film transitions to a glassy state, which results in larger crystalline domains after thermal processing.

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