

AFRL-RX-WP-TR-2019-0209

HOLOGRAPHIC ASSEMBLY OF RECONFIGURABLE NANOSCALE PLASMONIC AND PHOTONIC ELEMENTS

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30 JULY 2019 Final Report

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Form Approved OMB No. 0704-0188

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1.	REPORT DA	TE (DD-MM-YY)		2. REPORT TYPE		3.	DATES COVERED (From - To)			
		30 July 201	9	Fina	1		26 June 2015 – 30 June 2019			
4.	TITLE AND S	SUBTITLE				1	5a. CONTRACT NUMBER			
Holographic assembly of reconfigura				ble nanoscale plasmonic and			FA8650-15-C-7546			
photonic elements						ŀ	5b. GRANT NUMBER			
						ľ	5c. PROGRAM ELEMENT NUMBER			
							65502F			
6.	AUTHOR(S)						5d. PROJECT NUMBER			
	Paul Bo	hn					DARPA			
						Ī	5e. TASK NUMBER			
							5f. WORK UNIT NUMBER			
							X101			
7.	PERFORMIN	G ORGANIZATI	ON NAME(S) AN	D ADDRESS(ES)			8. PERFORMING ORGANIZATION REPORT			
	T T · · ·						NUMBER			
	040 Groop	United Date	ne DU LAC							
940 Glace Hall Notro Dome, IN 46556 5602										
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9. SPONSORING/MONITORING AGENCY NAM				E(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY ACRONYM(S)			
	Air Force Research Laboratory			Defense Advanced Research		h	AFRL/RXAP			
Materials and Manufacturing Directorate			Projects Agency 3701 North Fairfax Drive Arlington VA 22203-1714		ŀ	11. SPONSORING/MONITORING AGENCY				
WPAFB OH 45433-7750						REPORT NUMBER(S)				
Air Force Materiel Command United States Air Force						AFRL-RX-WP-TR-2019-0209				
12			TY STATEMEN	r						
	DISTRIB	UTION STATI	EMENT A. Ap	proved for public re	lease; distribu	itior	i is unlimited.			
13	B. SUPPLEME	NTARY NOTES								
	Report co	ntains color.								
14	. ABSTRACT	(Maximum 200	words)							
	This report	t was develope	d under a DAR	PA contract for topic	Atoms to pr	odu	cts. Two primary goals were addressed in this			
	project. In	Focus Area 1 ((Assembly Dev	elopment) the goal w	vas to assemb	le a	10 µm microelement consisting of an			
anisotropic lattice of ~5000 (~100 nm) dielectric nanoparticles (NPs) embedded in a polymer electrolyte. Successful										
completion of the objectives of this goal required that NPs be spatially located with nm-scale precision in a polymer matrix at										
scales up to $\sim 10 \mu\text{m}$ (total). In Focus Area 2 (Functionality Development) the goal was to establish the efficacy of reconfigurable microelements by demonstrating atomic junction formation/dissolution between core shall motal NPs in a										
polymer electrolyte on a model thin-film system. Work on this goal demonstrated that conductive channels can be formed and										
	dissolved between metal NPs. Additional work in Focus Area 2 demonstrated the controllable formation and dissolution of									
	self-limiting nanofilaments connecting multiple NPs (beads-on-a-string morphology) and demonstrated the formation of									
	nanofilaments in self-organized polyelectrolyte nanopores for the growth of Ag nanofilaments by conductive-AFM.									
	Conecuvery, work on the two focus area goals developed and demonstrated the technology needed for assembly and post- assembly reconfigurable wiring of nanoscale optical lattices									
15. SUBJECT TERMS										
DARPA report, Electrooptical and Optoelectronic Devices, Holography. Polymer Chemistry										
16	SECURITY	CLASSIFICATIO	N OF:	17. LIMITATION OF ABSTRACT:	18. NUMBER O PAGES	OF	19a. NAME OF RESPONSIBLE PERSON (Monitor)			
a.	REPORT	b. ABSTRACT	c. THIS PAGE				Carl Liebig			
ι	Inclassified	Unclassified	Unclassified	SAR	45		19b. TELEPHONE NUMBER (Include Area Code)			
							(937) 255-9649			

Standard Form 298 (Rev. 8-98) Prescribed by ANSI Std. Z39-18

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1. SUMMARY

The goal of this DARPA A2P Technical Area 1 (TA1) fundamental research project was to develop an assembly technology to advance the manufacture of a new class of reconfigurable optical materials. In this TA1 project, we developed optical microelements consisting of precisely arrayed nanoparticles (NPs) embedded in a polymer matrix. By manipulating the features of this NP array, including lattice structure and NP materials, we were able to imbue the microelements with deterministic heterogeneous optical properties. Working in collaboration with our TA2 partner (PARC), we laid the foundation for conformable 2D and 3D optical metamaterials - tiles - that harness the collective behavior of the nanoengineered elements to to manipulate the designed optical index profile. The core atomistic feature of these optical microelements was obtained from the formation and dissolution of atomic-scale conductive channels between metallic NPs embedded in a polymer electrolyte matrix. These conductive channels could be formed and dissolved 'on demand' to change the local index of refraction of the material, such that materials constructed from these microelements displayed adjustable optical properties depending on the application, environmental conditions, or external forces. The core assembly technology feature consisted of the three-dimensional (3D), parallel assembly of the NPs in a polymer matrix using holographic trapping, enabling high throughput assembly of thousands of NPs. In this research project, we assembled optical microelements, \sim 1-10 µm in size, to form the building blocks for larger scale optical materials. We will produce multiple generations of feedstocks for our TA2 partners, starting from "baseline" photonic microelements of dielectric NPs in a polymer matrix. Our research plan was organized along two concurrent tracks: Focus Area 1-Assembly and Focus Area 2-Functionality in order to address two challenges in production of state-of-the-art optical materials: (1) by using holographic assembly techniques, we established an assembly technology to rapidly produce feedstock materials with precisely controlled heterogeneous optical properties; and (2) by developing the building blocks for a new class of optical materials with reconfigurable properties, we addressed the need for new materials with non-classical optical response functions, which could eventually be used in applications ranging from optical cloaking to wearable sensors.

2. INTRODUCTION

The over-arching goal of our work was to develop a new manufacturing paradigm combining massively parallel alignment with atomic-scale registration of nanomaterials enabling emergent plasmonic and photonic materials with reconfigurable properties. We envisioned that successfully realizing this goal would enable wholly new products, such as <u>tiles</u> with atomistic features that could be reconfigured to change their plasmonic and photonic properties depending on the application, environmental conditions, or external forces. These tiles could then be assembled to create conformable surfaces for applications such as optical cloaking, thermal management, wearable sensors, *etc*.

Metamaterials are engineered materials consisting of rationally designed (nano)structures yielding composites that exhibit entirely new, anisotropic plasmonic and photonic properties. Previously, such materials had been slow to mature, because making the required graded index profiles in three-dimensional (3D) materials is extremely challenging. Thus, metamaterials offer

a compelling example of a case in which a manufacturing bottleneck blocks implementation of a potentially transformative war-fighting technology. To address this bottleneck, we identified the need for new manufacturing processes that could assemble nm-scale materials with precise, atomic-scale control through multiple, hierarchically-organized levels, ultimately yielding macro (mm-scale) products. Thus, the principal goal of this TA1 research project was to establish the manufacturing principles to support purposeful, hierarchical construction across 5 logs of size – 0.1 nm to 10 μ m – to produce μ m-scale building blocks for macroscale optical materials (which could then be assembled by our TA2 partner, PARC). In doing so, we developed a *new class of reconfigurable optical materials* with designer functionality by controlling the formation and dissolution of atomic-scale (0.1-1 nm) contacts between molecularly-engineered nanowires and nanoparticle-based (1-100 nm) nodes assembled in a lattice (1-10 μ m) imprinted into a polymer electrolyte.

The key atomic-scale element which enabled the unique optical response properties of the microelements exploited conductive AFM to fabricate self-terminating atomic-scale nanowires - either stand-alone or between NP nodal elements. To create these nanowires we built upon the directed electrodeposition and electromigration developed previously by PI Bohn to form conductive junctions with well-defined quantum conductance ($G < 10G_0$) states. As shown in **Figure 1**, NPs and NP lattices were fabricated by selective formation/dissolution of conductive channels (*on* vs. *off* state), locally altering the plasmonic and photonic properties of the feedstock. Both the individual optical microelements and their mesoscale assemblies could be reconfigured by applying appropriate spatiotemporally-organized voltage programs and in so doing produce carefully engineered nanoscale properties, thereby accessing emergent metamaterial properties on the µm-mm scale through self-organized connectivity at the atomic-scale.

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Figure 1. Manufacturing concept for reconfigurable optical microelements.

Note: Nanoparticles are assembled holographically using the gradient forces associated with focused optical or electron beams into 3D lattices; addition of polymer electrolyte provides mechanical structure and a matrix for electrical connectivity. This process is repeated to build 1-10 μm microelements whose plasmonic and photonic properties are reconfigured by (on/off) conductive channels formed/dissolved through electrochemical filaments between individual NPs. Anisotropy can be introduced through multi-metallic and/or heterogeneous NP arrays, generating gradients in the properties of the polymer electrolyte, or lattice heterogeneity during holographic assembly.

The key assembly strategy employed in our work exploits a manufacturing concept in which massively parallel assembly of NPs into 3D lattices is realized using holographic optical traps (HOTs). Assembling and organizing matter at the atomic scale is inherently difficult, and serial mechanical methods such as atomic force microscopy are too slow to rapidly assemble nanoscale features into \Box m-scale structures. Instead, we built upon decades of experience in using lasers to assemble and organize matter. Co-PI Timp called upon his extensive experience using optical traps for positioning atoms and bacteria in 2D and 3D arrays in order to build HOTs for the creation of an "optical lattice" of NPs as shown in Figure 2. Multiple optical traps were used to organize tens to thousands of NPs constituting each of the layers in a multilayer system. Thus, NPs are simultaneously organized into an aggregate assembly according to a specific lattice design, after which they are immobilized in a polymer electrolyte scaffold to provide mechanical structure and electrical conductivity for the NP interconnections described above.



Figure 2. Schematic diagram of time-shared holographic optical trapping apparatus and microfluidic conveyer.

Note: NPs are manipulated using optical traps formed with infrared laser (red) and detected by scattering from another laser (blue) through a microscope. Inset: images of (a) 3x3x3 array, (b) 4x4 array of 210 nm particles, and (c) 16x16 array of 500 nm NPs.

3. METHODS, ASSUMPTIONS, AND PROCEDURES

3.1 Focus Area 1 (Assembly Development).

In this effort, a nascent manufacturing method was developed that works just like modular construction—but on a nanometer-scale—to produce nanosystems. It used light gradient forces to assemble pre-fabricated monodispersed nanoparticles (NPs) into regular three-dimensional (3D) arrays on a hydrogel scaffold, which was then vitrified. The NPs were all synthesized to specifications by 'bottom-up' methods with high yield using approaches like vapor-phase (pyrolysis and inert gas condensation) and liquid-phase synthesis (precipitation, hydro-thermal synthesis, sol-gel fabrication or micro-emulsions), which made them more economical and green (environmentally friendly).

The use of light gradient forces to manipulate and organize nanometer-scale matter is a radically new strategy for manufacturing nanosystems. The basic forces derived from a focused laser beam acting on a small particle are well known. Although the force is weak (< 100 pN), nanometer-scale objects have a miniscule mass, so light gradients can be effective for manipulation with nanometer-scale precision over a wide field, depending on the topography of the light gradients, and on the size and dielectric properties of the NP and the surrounding medium. Light gradients have already been used to manipulate, not only dielectric NPs, but metallic nano- or micro-particles in liquid and in air. With the recent development of evanescent-wave and plasmonic tweezers, and holographic and time-shared arrays and multi-functional traps, light gradients can be used to exert a wide range of force and torque at many points in space and time with sub-nanometer and sub-millisecond precision to produce metamaterials.

The use of light gradients for assembling nanoparticles differs from "optical binding", which uses a uniform beam to form self-organized crystals through light-mediated inter-particle interactions, derived from the mutual Lorentz force that redistributes the momentum in the incident beam. Importantly, the time-averaged Lorentz force decreases with distance *r* like $1/r^4$ in the near-field and 1/r in the far-field. Thus, for a distance comparable to the wavelength, the mutual Lorentz force on 100 nm-radius gold NPs is about 1 pN in a uniform irradiance of 10 MW/cm². Although optical binding can be stronger apparently than the gradient force in an intense field, optical crystals formed this way are nevertheless constrained in size, shape and inter-particle spacing. On the other hand, the constraints on light gradient forces are associated mainly with distortions in the electromagnetic environment encountered during assembly, which restricts the packing density of NPs, that is set by the wavelength λ_0 of the laser to $\lambda_0/2$. To compensate for these distortions, one of the work-arounds that was exploited in this effort is a so-called "diffraction-free," self-reconstructing Bessel beam (*vide infra*).

In the work described in this report a new approach was taken in which light gradients were used to manipulate, with nanometer-scale precision, thousands of NPs simultaneously into complex heterogeneous lattices on a (hydrogel) scaffold to create a voxel, and then the process was repeated to stitch together voxels, registered to one another, to form nanosystems of any size, shape and constituency. The force exerted on a NP is ultimately due to conservation of the linear and angular momentum carried by the photons that the particle absorbs or scatters from the incident light field. To rigorously compute the force on the NP, the <u>G</u>eneralized <u>L</u>orentz-<u>M</u>ie scattering <u>T</u>heory (GLMT) has to be employed since the radius $a > \lambda/20$ so that the usual

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Rayleigh approximation is not valid. Following other work, the resulting (non-relativistic) force acting on a NP illuminated by a laser depends on both the laser and the NP according to:

$$\left\langle \vec{F} \right\rangle = \underbrace{\frac{1}{4} \varepsilon_{0} \varepsilon \alpha' \nabla(\overbrace{\vec{E}}^{2I(r)/n_{m} \varepsilon_{0} c})}_{gradient} + \underbrace{\frac{1}{2} \varepsilon_{0} \varepsilon \alpha'' \operatorname{Im}\left(\sum_{l} E_{l} * \nabla E_{l}\right)}_{scattering}$$

(1)

where the subscripts extend over l = x, y, z and *I* represents the beam intensity/irradiance. So, for example, for a Gaussian laser beam in cylindrical coordinates,

$$\vec{E}(r,z) = \vec{E}_0 \sqrt{\frac{2}{\pi}} \cdot \frac{1}{\sqrt{[1 + (z/z_0)^2]}} \cdot \exp\left[-\frac{r^2}{\varpi_0^2 [1 + (z/z_0)^2]}\right] \cdot \exp\left[i\frac{\beta \cdot r^2}{2\{z[1 + (z/z_0)^2]\}}\right] \cdot \exp\left[i\beta \cdot z - i\tan^{-1}(z/z_0)\right]$$
(2)

where $z_0 = \pi \overline{\sigma}_0^2 n / \lambda_0$, $\overline{\sigma}_0 = \lambda / \pi \cdot NA$, is the beam waist in the focal plane, λ_0 is the (free space) wavelength and $\beta = 2\pi n / \lambda_0$ as usual, so that the irradiance becomes:

where P is the beam power. Through substitution analytical expressions for the radial and zcomponents of the gradient and scattering forces can be derived, as shown in prior work.

$$I = \left(\frac{2P}{\pi \sigma_0^2}\right) \cdot \frac{1}{1 + (2z/z_0)^2} \cdot \exp\left[-\frac{2r^2}{\left[1 + (2z/z_0)^2\right]}\right]$$
(3)

Thus, the gradient force originates from the gradient of the intensity profile of the beam and is proportional to the real (dispersive) part of the polarizability, α' , while the scattering force is proportion to the dissipative part α'' and captures the momentum transfer from the laser to the NP and absorption. Generally, stable trapping should be possible so long as the gradient force exceeds the scattering force, and thus, the criterion for trapping depends on the material, size and shape of the NP as well as the topography of the laser beam and background medium. For example, if the laser wavelength is close to the metal plasmon resonance, then α'' predominates and the scattering force on a metal NP in a focused Gaussian beam could push it along the direction of light propagation out of the trap. On the other hand, illumination with a vanishing net momentum transfer, *e.g.* using a focused Gaussian standing wave optical trap (GSWOT) tuned off-(above) the plasmon resonance, can produce a stable trap.

3.2 Focus Area 2 (Functionality Development).

In order to study and understand how atomic scale junctions (ASJs) form and dissolve in polymer electrolyte matrices, a model system was developed that was intended to mimic the polyelectrolyte environment to be used in forming the microelements being produced in FA1. The model system consisted of thin-film polymer electrolytes, and a conductive atomic force microscope (C-AFM) probe was used as a movable, position-selectable top electrode to induce the formation of nanofilaments and ASJs through the thickness of the polyelectrolyte. Varying the polymer material and electrolyte properties (*e.g.*, salt concentration, film thickness) made it possible to study the basic process of nanofilament formation, and embedding NPs in the polyelectrolyte thin-film enabled their use as nanoscale bipolar electrodes to facilitate

nanofilament formation. The C-AFM simultaneously provided a convenient platform to electrically characterize the formation and dissolution of nanofilaments at the scale of, and under conditions similar to, those anticipated for the reconfigurable microelements.

3.2.1. Polymer Electrolyte Systems

Two different polymer electrolyte systems were studied. The first consisted of silver ions (Ag^+) dissolved in poly(ethylene oxide) (PEO), a system which was used as a baseline to study nanofilament formation due to the wide use of PEO. However, the optical trapping methods developed in FA1 involve crosslinking the polymer matrix to secure the NP lattice in place and form rigid microelements, and PEO cannot be crosslinked. Furthermore, other polymer systems, such as hydrogels, contain water, which is prone to electrolysis under the applied potentials required to create and destroy nanofilaments. Therefore, a three-component polyelectrolyte system - consisting of (*a*) Ag⁺, (*b*) the crosslinkable polymer poly(ethylene glycol) diacrylate (PEGDA), and (*c*) the ionic liquid (IL) 1-butyl-3-methylimidazolium nitrate -was studied as a polyelectrolyte platform in an attempt satisfy the technical requirements of FA1, while retaining the ability to form nanofilaments.

3.2.2. Polyelectrolyte Thin-Film Fabrication

For both systems, polyelectrolyte thin-films were fabricated on glass or silicon (Si) substrates coated with an ~100 nm Au film. Practically, this Au film acted as an anode in the C-AFM-based filament formation and dissolution processes.

3.2.2.1. PEO/Ag+ and PEO/Ag+-AgNP Thin Films

Glass slides were cleaned in piranha solution (3:1 sulfuric acid (95%) : hydrogen peroxide (30%)), rinsed with deionized (DI) water, and dried at 110°C. A 100-nm thick Au layer was deposited by electron-beam evaporation (UNIVEX 450B, Oerlikon) after deposition of a 10 nm Ti adhesion layer. Then, a 100 nm Ag layer was deposited on the same glass slide. In an argon-filled glovebox with oxygen and water concentrations controlled to less than 0.1 ppm, 10 mM and 20 mM solutions of AgNO₃ in anhydrous acetonitrile (ACN) were prepared; similarly, PEO was dissolved in ACN to make 0.5 wt%, 1 wt%, and 2 wt% PEO solutions. The AgNO₃ solution were added to the PEO solutions in a 1:9 volume ratio, yielding final solutions of AgNO₃ in ACN with concentrations of 1 mM, 2 mM, and 2 mM for PEO wt% of 0.5, 1, and 2 wt%, respectively (ether oxygen:Ag⁺ ratios of 180:1, 90:1, and 45:1). Each solution was then spin-coated at 4000 rpm for 30 s onto the Ag-coated glass slides inside the glovebox. Scanning electron microscope (SEM) imaging showed film thickness of 40 ± 5nm, 80 ± 5 nm, and 130 ± 10 nm for 0.5 wt%, 1 wt%, and 2 wt% PEO solutions, respectively.

In order to embed AgNPs in the polyelectrolyte film, An α,ω -dithiolpoly(ethylene glycol) (PDT) linker was used to secure the AgNPs above the Ag-coated substrate. After self-assembling PDT on the surface, AgNPs were attached to the PDT layer and 1 wt% PEO/Ag⁺ was applied by spin-coating to complete fabrication of the PEO thin film.

3.2.2.2. PEGDA/Ionic Liquid (IL)/Ag+ Thin Films.

Silicon wafers (University Wafer, P/Boron, $500 \pm 15 \,\mu$ m) were cleaned by sonication in acetone followed by a 2-propanol rinse and drying in nitrogen (N₂). 5/100 nm of Ti/Ag was deposited by electron-beam evaporation (Plassys, MEB 550s) at 5×10^{-7} mbar base pressure. The following steps were completed inside an argon-filled glovebox (Mbraun, MB-200B) where O₂ and H₂O < 1 ppm. AgPF₆, BMIMPF₆ (IL), and PEGDA were dissolved in ACN and combined to prepare a total of 9 samples with PEGDA/BMIMPF₆ compositions of 90/10, 70/30 and 50/50 wt.% at 0, 0.2, and 2 mM AgPF₆. In all 9 samples, the PEGDA concentration was 1 wt.% together with 0.02 wt.% of HMPP (photoinitiator). The polymer electrolytes were spin-coated on the Ag-coated silicon substrate at 4000 rpm for 30 s, and annealed at 80 °C for 2 mins to drive-off ACN. Samples were photo-crosslinked with a UV lamp (UVP Compact UV Lamp, $\lambda = 365$ nm, P = 1.3 mW/cm² at 3 inches) at a working distance of 1.25 cm for 1 h.

3.2.3. Conductive AFM Formation of Nanofilaments.

Nanofilaments were formed by using a C-AFM to make contact with the top surface of the polyelectrolyte thin film, while the Ag sublayer was electrically connected to the AFM chuck and acted as a counter electrode. Identical C-AFM systems were used in work performed at Notre Dame (PEO/Ag⁺) and Pittsburgh (PEGDA/I/Ag⁺). A Bruker Dimension Icon AFM was used in contact mode. Before each run, a force *vs.* distance calibration curve was taken to ensure that the engagement setpoint was not distorted by the reflectivity of the surface. A custom script was written to: (1) move the tip from point-to-point in a raster scan pattern at a preset point spacing; (2) apply the desired voltage; and (3) measure the current between the conductive AFM tip and the AFM chuck. The AFM tip was grounded and the voltage was applied to the chuck. PF-TUNA tips consisting of a Pt-Ir coating on a Si cantilever with spring constant of 0.4N/m, were used for all measurements. At each point, the chuck voltage was set to a formation voltage until the current increased above a set threshold value, after which the voltage was switched to the dissolution voltage until the current (now of the opposite sign) decreased in magnitude below a set threshold. Data were recorded both as a current *vs.* time trace and as measurements of the nanofilament formation and dissolution times at each spatial location.

For the PEO/Ag⁺ experiments, measurements were conducted at a 200 nm pitch, a formation voltage of +0.6 V, dissolution voltage of -1 V (limited by the compliance current of the instrument), and a rest voltage of 0 V relative to ground. Formation and dissolution thresholds were chosen as +450 nA and -25 nA, respectively. The instrument exhibits a compliance current of *ca*. 600 nA. The accuracy of the script was verified with an external oscilloscope, triggered by the voltage applied to the tip in single-run edge mode, and shown to exhibit a time resolution of ~ 1.5 ms. For the PEGDA/IL/Ag⁺ experiments, a formation voltage of +2 V, dissolution voltage of -2 V, and a rest voltage of 0 V relative to ground were used. Formation and dissolution current thresholds were chosen as +4 nA and -0.5 nA, respectively. The compliance current of the instrument was *ca*. 5 nA at a current sensitivity of 1 nA/V, which was selected by the user.

Additionally, for the PEGDA/IL/Ag⁺ system, PeakForce Quantitative Nanomechanical Mapping (PF-QNM) was used to map the Young's modulus. Different types of AFM probes were used for the measurement of 9 samples based on their working ranges selected based on the working

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range for modulus measurement: RTESP-150 (5 - 500 MPa); RTESP-300 (200 MPa- 2 GPa); RTESP-525 (2 - 20 GPa). All probes were calibrated for their deflection sensitivity, spring constant, and tip radius. The force applied to the electrolyte was then correlated with the surface indentation to give a quantitative measurement of its mechanical properties.

4. **RESULTS AND DISCUSSION**

4.1 Focus Area 1 (Assembly Development).

While the equations presented in Section 3.1 offer an approximate guide to stable trapping using a single focused beam GSWOT, the throughput is still quite limited. To improve throughput, one avenue pursued in this effort utilized a rapidly scanned SWOT to create multiple optical traps by time-multiplexing or time-sharing the beam. An estimate of the number of traps that a timesharing strategy like this can produce was obtained, assuming a GSWOT with a waist $\varpi_0 = 0.28$ μ m to stabilize the position of a number of NPs, N, with radius a = 100 nm. One constraint on the time-sharing approach is the propensity of the temporarily non-trapped NPs to wander. If the time-shared beam is temporarily servicing another site, the NP may diffuse out of the capture range for the trap while it is in the dark. For a spherical NP, the diffusion coefficient is D = $k_BT/6\pi\eta a$, where η is the viscosity of the medium. If the medium is water at room temperature, then $\eta = 1.025 \times 10^{-3}$ N·s/m². For a 100 nm-radius silica bead in water, $D = 2.2 \times 10^{-12}$ m²sec⁻¹. The mean square motion is given by the product of the diffusion coefficient and the dark time < $x^2 > (4 \times 0.280 \ \mu\text{m})^2 = 2 D \tau_{dark}$. Consequently, the dark time should be $\tau_{dark} = 6\pi\eta \ a \ (2w_0)^2/2k_BT$ < 280 ms. On the other hand, the dwell time required to restore the NP to its proper position will depend on the stiffness of the optical trap and the positional precision required. By balancing the optical force against Stoke's law, it was determined that: $F = 6\pi \eta av = \kappa x$, where $\kappa = -\partial (\hat{x} \cdot \vec{F}_{gr}) / \partial x$ denotes the lateral (weakest) stiffness, \vec{F}_{gr} is the gradient force, η is the viscosity and v is the velocity of the liquid. Thus, for a silica particle with a = 100 nm and P =1.5 W, $\kappa < 1$ pN/nm, typically, and so the minimum time required for restoring the NP to its position is $\tau_{light} = x/v = 6\pi\eta a/\kappa = 2 \mu s$.

From estimates like these, a prescription for the duty cycle for the modulation single-beam trap and the period can be obtained. The NP position must be refreshed at about 5-10 Hz with a duty cycle that depends on the ratio $\tau_{light} / \tau_{dark}$, which can easily be accomplished within the specifications of an acousto-optic deflector (AOD). The ratio of τ_{dark}/τ_{light} also gives an indication of the number of NPs that can be effectively trapped by scanning a single-beam:

$$N = \frac{\tau_{dark}}{\tau_{light}} = \frac{6\pi\eta a \cdot (2\varpi_0)^2 / 2k_B T}{6\pi\eta a / \kappa} = \frac{2\varpi_0^2 \kappa}{k_B T} = \frac{64P}{3k_B T \cdot \varpi_0^2 c} a^3 (n_p - n_m) \approx 10^5.$$
(4)

This expression elucidates how the number of NPs manipulated by a time-multiplexed trap depends on the irradiance (power), the beam waist, the index difference between the particle and the medium, and the particle size. All of these parameters combine to impose an upper bound on the number; *i.e.* typically, $\tau_{dark}/\tau_{light} < 1000$ silica NPs with a 100-nm radius can be assembled into an array in <10 s in water, with the throughput limited mainly by power, although the distance to the laminar flow and velocity of the shepherd beam are also factors. The irradiance required to stabilize a NP with a small radius grows geometrically (like a^3), but it is limited in practice by the optical coatings and absorption/reflection from the optics, generally, which inevitably affects the transmitted wave front.

So, following these prescriptions, to put light gradients to work, monodispersed NPs, synthesized with a coefficient of variation CV < 5%, were conveyed using multiple laminar flows in a multiport microfluidic device, within the field of view of an array of time-shared optical traps. Generally, multiple, time-multiplexed optical traps were generated using acousto-optic deflectors (AODs) in conjunction with a high numerical aperture (NA) objective. To form a two-dimensional (2D) array of optical traps, a Gaussian beam was rapidly scanned between 2D lattice sites using the AODs. Likewise, 3D arrays of optical traps were formed by rapidly scanning a regular one-dimensional (1D) string of optical traps, produced from either a Gaussian beam (GSWOT) or pseudo-Bessel beam (BSWOT) retro-reflected from a heat reflecting mirror (HRM), between 2D lattice sites, **Figure 3(a)**.

Since a SWOTs were usually stiff both longitudinally and traverse to the beam, and the scattering force was nullified in it, a focused Gaussian beam (optical tweezers with no reflection) presented the most rigorous test of trap stability. To test it, twenty five, nominally 125 nm-radius silica (*SiO*₂, $n_p = 1.45$) NPs were assembled in water ($n_m = 1.33$) with a focused time-multiplexed, P = 200 mW Gaussian beam at wavelength $\lambda_0 = 870$ nm scanned over a regular 2D 5×5 lattice, **Figure 3(b)**. The positions of the traps within the lattice were dynamic in the *xy*-focal plane with a lattice constant that ranged from 2 µm to 625 nm, **Figure 3(b)**; top to bottom. Likewise, a regular 2D 5×5 lattice of high index, 130 nm-radius titania (*TiO*₂, $n_p = 2.5$) NPs were assembled this way using the same conditions, **Figure 3(c)**, as was a 5×5 array of 125 nm-radius gold (*Au*, n = 0.167, k = 5.48) NPs, **Figure 3(d**). Below the closest approach of 625 nm, the lattices all collapsed regardless of the material, however, and so the NP density was restricted to about 2.6 µm⁻². This density was likely affected by the repulsion between NPs in phosphate <u>b</u>uffered <u>s</u>aline (PBS) at pH7 and by the spatial definition of the Gaussian beam.

Stringent control of the lattice spacing like this is likely to be important in the manufacture of photonic metamaterials (PMs), which was a stretch goal in this effort. For example, by exercising control of the electric field and especially evanescent-waves, surface plasmons might be harnessed to produce a negative refractive index and extraordinary transmission or index near zero this way. Moreover, any lattice symmetry with a variety of unit cell sizes can be accommodated. For example, a 10×10 square lattice with a 2 µm constant, **Figure 3(b)**; top, was subsequently transformed into at hexagonal array, **Figure 3(e)**; middle, and then contracted into a 32×32 lattice with a 1 µm lattice constant drawn using $\lambda_0 = 850$ nm light and an irradiance of *P* = 0.5 W per trap, **Figure 3(e)**; bottom. Finally, the particle positions within the lattice were entirely discretionary, depending on which traps were loaded, and so it was possible to produce irregular structures. For example, using a shepherd beam to load traps in the array, point defects could be introduced into a lattice, **Figure 3(f)**; top, middle, that could be used as cavities or merged to form waveguides, **Figure 3(g)**.

Whereas light gradients can be used to create complex modular structures of NPs, the light still has to be held in place to maintain the lattice. So, to fix the position of the NPs without light, a scaffold made from a photopolymerizable hydrogel was used to encapsulate the lattice, at least temporarily. Once the array was formed, typically, the pre-polymer constituted from 400 Da polyethylene glycol diacrylate (PEGDA) and a photoinitiator was photopolymerized by exposure to near UV laser light to form a "voxel". Subsequently, the voxels were stitched, or tiled, together one-at-a-time to create super-lattices by stepping to an adjacent location in any direction

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using a computerized stage, while maintaining registration to a fiducial mark, and then repeating the process, **Figure 3**(h).

Using the same step-and-repeat strategy, but with a basis set consisting of different NP constituencies, heterogeneous lattices of fluorescent NPs were constructed in two different ways. The first method stitched together heterogeneous voxels consisting of two different NPs, **Figure 3(i)**; top, whereas the second stitched together homogeneous voxels of two different types, **Figure 3(j)**; top. This was accomplished by shepherding NPs into a voxel using a combination of multiple, independent computer-controlled optical traps to pluck them from separate laminar flows in the microfluidic device, and then loading them into optical traps to produce a heterogeneous compilation. Subsequently, fluorescence microscopy was used to interrogate the heterogeneous lattices illustrated by lattices consisting of nominally (red fluorescent) 100 nm-and (green fluorescent) 175 nm- and (red fluorescent) 500-nm-radius NPs, **Figures 3(i)** and (**j**); center. The size and positions of the NPs were inferred from fluorescence confocal microscopy after iterative de-convolution.



Figure 3. Modular assembly of 2D lattices using light gradients in a Gaussian beam.

Note: (a) A schematic is shown of the time-shared holographic optical trapping apparatus and microfluidic conveyer. Nanoparticles (NPs) are manipulated using light gradients formed with a near-infrared (NIR) laser (red). The evolution of the trapping beam profile from a Gaussian to a pseudo-Bessel beam is delineated by the intensity maps located alongside the red NIR-laser track in the figure. The microscope optics can also be used for (fluorescent)

imaging (yellow path). (Upper left inset) A schematic of the time-shared optical trap used to assemble a photonic metamaterial (PM) is shown. In this case, a pseudo-Bessel beam standing wave optical traps (BSWOTs, red), formed by focusing a Ti:sap laser through an axicon lens onto a heat reflecting mirror (represented red), is used to create a regular array of NPs. The SWOTs are rastered from site-to-site in the xy-focal plane to assemble the threedimensional heterogeneous NP array on a hydrogel scaffold. (b) A 5x5 array of (nominally) 125 nm-radius silica (SiO2) NPs is shown assembled using a Gaussian beam at a wavelength of $\lambda_0 = 870$ nm with a 200 mW irradiance. The xy-lattice constant ranged from 2 μ m (i), through 1 µm (ii) to 625 nm (iii). (c) Like (b), but a 5x5 array of nominally 120 nm-radius titania (TiO_2) NPs is shown assembled using the same conditions. (d) Like (b), but a 5x5 array of nominally 125 nm-radius Au NPs is shown, which was assembled using the same conditions. (e; i) A fluorescent micrograph of a 10x10 lattice of nominally 100 nm-radius fluorescent PLGA NPs is shown, formed into a square lattice using a time-multiplexed Gaussian SWOT (GSWOT) with an irradiance of 500 mW at a wavelength of $\lambda = 900$ nm. (e; ii) Like (e; i), but assembled into a hexagonal lattice. (e; iii) Like (e; ii), but a 32x32 lattice of PLGA NPs. (f; i, ii) Optical micrographs of a two-dimensional (2D) voxel, consisting of a 5×5 array of 350 nm-diameter (fluorescent) polystyrene NPs, are shown. The arrays were assembled with a single vacancy using a focused time-shared, optical trap (OTs) at $\lambda_0 = 870$ nm with 200 mW in the beam. The image demonstrates that a vacancy can be positioned anywhere within a voxel. (g) Like (f), but showing a single voxel consisting of a 6×6 array of 350 nm-diameter polystyrene NPs with two vacancies in adjacent lattice sites. (h; i-iii). A time-sequence, stepped in 10 s intervals, is shown illustrating the step-and-repeat methodology used to create a 1×3 lattice of 3×3 voxels formed from 125 nm-radius Au NPs on a hydrogel scaffold. A time-multiplexed Gaussian beam with an irradiance of 150 mW at $\lambda_0 = 1064$ nm was used to create the voxels. (i) An optical (i), confocal fluorescence (ii) and de-convolved image (iii) of a lattice of four 2×2 heterogeneous voxels on a regular lattice is shown assembled using a time-multiplexed Gaussian beam in combination with step-andrepeat method. Each voxel consists of two types of fluorescent polystyrene NPs with nominally 175- (green) and 500 nm (red) radii. (j) Like (i), but the heterogeneous lattice was formed from homogeneous voxels consisting of either nominally 100 (red) or 175 nm (green) radii fluorescent polystyrene NPs.

Nonlinear iterative deconvolution can be used to recover a true representation of an image blurred by diffraction and aberrations or compromised by noise. The essential problem that has to be solved is that the lateral resolution of the confocal microscope is limited by diffraction to be: $\sigma_{xy} = 0.51\overline{\lambda} / NA = 212 \ nm$, where $\overline{\lambda} = \sqrt{2}\lambda_{ex}\lambda_{em} / \sqrt{\lambda_{ex}^2 + \lambda_{em}^2} = 499 \ nm$ with $\lambda_{ex} = 488 \ nm$ and $\lambda_{em} = 510 \ nm$ whereas the resolution along the optic axis is supposed to be limited to $\sigma_z = 0.88 \overline{\lambda} / (n_m - \sqrt{n_m^2 - NA}) = 580 \ nm$. However, the actual resolution was assessed using mono-dispersed 10 nm-radius fluorescent NPs to be worse: $\sigma_{xy} = 499 \pm 25 \ nm$ and $\sigma_z = 1,740 \pm 140 \ nm$. So, to recover a true representation of the image and improve the overall resolution, the confocal fluorescence micrographs were deconvoluted with a custom MATLAB algorithm, starting with an estimate of the point spread function (PSF) derived from a 10 nmradius fluorescent NP, and proceeding through successive iterations to obtain an image with optimal visibility, defined by the contrast in the fluorescence over the mean. In this manner, the

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actual sizes of the nominal 100, 175 and 500 nm-radii NPs were inferred (from the deconvoluted) images to be 105 ± 14 nm, 171 ± 18 nm, and 490 ± 20 nm, respectively, consistent with the nominal radii within the CVs. Correspondingly, the separations between NPs measured after de-convolution were $5,570 \pm 35$ nm, and $7,234 \pm 845$ nm, **Figure 3**(**j**), which were in-line with the designed lattice constants (5.5 and 7.25 µm).

Lattices were not constrained to planar 2D configurations either. For example, NPs were assembled by scanning a GSWOT across 2D lattice sites to create a super-lattice of 3D voxels. The construction of a standing wave has the effect of producing anti-nodes in the intensity along the optic *z*-axis, which were separated by $\Delta z_+ = \lambda_0/2n_m$. Corresponding to the increase in the intensity gradient, we expected a concomitant improvement in the stiffness along the optic axis so that, ostensibly, multiple NPs could be trapped along the *z*-axis simultaneously, with the proviso that the distortion or obstructions due to the NPs in a trap didn't adversely affect the neighbouring optical traps. To test these ideas, a GSWOT formed at $\lambda_0 = 870$ nm with P = 200 mW was used to assemble a super-lattice consisting $7 \times 7 \times (>8)$ voxels of nominally 175 nm-radius fluorescent polystyrene latex NPs, **Figure 4(a)**. Nominally 175 nm-radius NPs were chosen to form the lattice because the separation between optical traps along the *z*-axis was designed to be $\Delta z_+ = \lambda_0/2n_m = 326$ nm. With these choices for the radius and trap wavelength, the NPs were expected to abut one another along the *z*-axis, making this an exacting test of the closest approach between NPs and rigorous gauge of the maximum achievable packing density.

An image of the resulting lattice was recovered from confocal fluorescence microscopy, both raw, **Figure 4(b)**, and after iterative de-convolution, **Figure 4(c)**. (The fluorescence not attributed to the array, due to NPs inadvertently sticking to the HRM mirror, was expunged from the de-convolved image.) The de-convoluted images routinely revealed NPs stacked about eight to ten deep along the *z*-axis. Commensurate with the nominal 175 nm-radius and (2.5 µm) lattice spacing, the NP size (in the transverse *xy*-plane) inferred after de-convolution was 163 ± 15 nm with an average *xy*-distance between particles of $2,636 \pm 40$ nm. Importantly, the separation between successive fluorescent intensity maxima along the *z*-axis, was measured to be $\Delta z = 360 \pm 75$ nm, **Figure 4(d)**, indicating that the NPs must have abutted each other since $\Delta z_+ = 326$ nm. Beside the positional errors along the *z*-axis, stacking faults were also evident in the deconvoluted images starting just off the mirror (*z* = 0) and even in the transverse, *xy*-image since multiple NPs were frequently visible at some lattice sites, but not all, **Figure 4(b)**. Finally, it is evident that the lattice structure extended about 3 µm along the *z*-axis, which was likely related to the confocal parameter of the Gaussian beam.



Figure 4. Modular assembly of 3D lattices of fluorescent NPs using time-shared standing wave optical traps (SWOTs) formed from retro-reflected Gaussian and pseudo-Bessel beams.

Note: (a) A top-down optical micrograph is shown of what is nominally a tetragonal lattice formed from two $3\times3\times15$ -3D voxels assembled from nominally 175 nm-radius NPs on a hydrogel scaffold using time-multiplexed, Gaussian standing wave using an irradiance of 200 mW at $\lambda_0 = 870$ nm. (b) A confocal fluorescent micrograph acquired from the lattice shown in (a) *xy*- (left), *xz*- (bottom) and *yz*- (right)-views of the same lattice are shown. Fluorescence not attributable to the array, due to NPs inadvertently sticking to the HRM mirror, was expunged. (c) Images reconstructed from the confocal data in (b) are shown after iterative de-convolutions starting with a PSF derived from a 10 nm-radius NP. (d) A magnified view of the de-convolved *x*-*z* cross-section highlighted in red in (c). (e) Like (a), but the NPs were assembled with a time-shared, pseudo-Bessel beam SWOT (BSWOT) using an irradiance of 200 mW at $\lambda_0 = 850$ nm. (f) Like (b), but acquired from the lattice

shown in (e) that was assembled with a BSWOT. (g) Like (c), but reconstructed after iterative de-convolution from the lattice shown in (f) assembled with a BSWOT. (h) A magnified view of the de-convolved x-z cross-sections highlighted in red in (g).

A tightly focused monochromatic Gaussian beam diverges rapidly as it propagates away from focus due to diffraction, which should affect the extent of the *z*-axis order. The depth-of-focus (confocal parameter) of an ideal Gaussian beam is defined by the Rayleigh range to be: $z_{\text{max}} = 2z_R = 2\pi \overline{\varpi}_0^2 / \lambda = 2\pi n \overline{\varpi}_0^2 / \lambda_0$, which was estimated from the beam waist (with $\overline{\varpi}_0 = \lambda / \pi \cdot NA = 160 \ nm$) to be $z_{\text{max}} = 250 \ nm$. (The measured number was about twice this size, however. The well-known formulas offered by Pillar and Born & Wolf, may be flawed. Based on wave-optics, a revised version of the depth-of-focus that was more in-line with empirical results is given by: $z_{\text{max}} = \lambda_0 / 4n(1 - \sqrt{1 - (NA/n)^2} = 505 \ nm$.) So, comparing the extent of the *z*-axis stacking to the confocal parameter, it was concluded that the lattice structure ranged over multiple Rayleigh lengths.

Multiple NPs have been trapped in a single, linear SWOT before, with small (\pm 36 nm) transverse fluctuations in the position, but not at this density and with such regularity. Since the gradient force pulls NPs toward the anti-nodes in the SWOT, close-packed optically bound clusters might form there. The defective stacking along the z-axis lattice could be attributed to multiple NPs occupying the same trap. For example, dimer, trimer and tetramer clusters of NPs have been observed in a tightly focused Gaussian beam before when more than one particle was introduced into the trap. Alternatively, defective stacking might be due to crowding affected by the NP size, aggregation, and distortions or occlusions in the GSWOT caused when a NP occupies a neighboring trap. However, 3D-lattices formed using the same conditions, but with smaller, (nominally) 100-nm-radius NPs alongside 175 nm-radius NPs produced similar defects suggesting that the size of the NP is irrelevant. Furthermore, to minimize the chances for multiple NPs occupying the same trap, the concentration of NPs was usually diluted from the original stock (concentration 2 mM) to a concentration of 20 µM using PBS solution, which guaranteed negatively charged NPs that should repel each other to avoid aggregation. Thus, it was reasoned that the GSWOTs were likely distorted during assembly by partial occlusions or optical binding.

Unlike a Gaussian beam, a true Bessel beam is ostensibly non-diffractive—it propagates, but does not spread out, which makes it especially useful for optical trapping because a tight focus can be maintained along the optic axis for an extended depth. One way to produce a pseudo-Bessel beam is to use an axicon lens. If a Gaussian beam is incident on a (thin) axicon lens, then the optical irradiance behind the axicon becomes:

$$I(\vec{r}) = \frac{I_0 \cdot \pi \cdot \beta \cdot \overline{\sigma}_0}{2} \cdot \left\{ \left[(F_1(\rho / \overline{\sigma}_0) + F_2(\rho / \overline{\sigma}_0) J_0(\beta \rho))^2 + \left[(F_1(\rho / \overline{\sigma}_0) - F_2(\rho / \overline{\sigma}_0) J_1(\beta \rho))^2 \right] \right\}$$
(5)

where J_0 and J_1 are respectively the zeroth-order and first-order Bessel functions of the first kind, and $\beta = 2\pi (n_a - 1)\theta / \lambda$, where n_a is the refractive index of the axicon and θ is the base angle. The functions F_1 and F_2 are given by:

$$F_{1}(\rho / \sigma) = \sqrt{z_{0} + \rho / \sigma} \cdot \exp[-(\xi_{0} + \rho / \sigma)^{2}]$$

$$F_{2}(\rho / \sigma) = \sqrt{z_{0} - \rho / \sigma} \cdot \exp[-(\xi_{0} - \rho / \sigma)^{2}] \cdot H(z_{0} - \rho / \sigma)$$
(6)

where $\xi_0 = (n_a - 1)\theta \cdot z / \varpi_0$ and $H(\cdot)$ denotes the Heaviside step function. The depth of focus of a (pseudo-)Bessel beam is defined as: $z_{\text{max}} = \overline{\varpi}_0 / (n_a - 1)\theta$. The central maximum propagates for several Rayleigh ranges without appreciable divergence, and thus approximates a rod of light.

Importantly, when it is obstructed, the outer rings of the Bessel beam act to replenish the central maximum and prevent it from spreading. If a beam has a NP of radius *a* placed at its center, then it will cast a shadow of length $l_s = a\beta / \beta_r = a/(n_a - 1)\theta$, where β_r is the radial wave-vector of the beam, with $\beta = \sqrt{\beta_r^2 + \beta_z^2}$. After this "self-healing" distance, the amplitude and phase re-forms, and the beam propagates without diffraction. (Actually, although an ideal Bessel beam has a large amplitude and maintains the same radial profile over a large propagation distance, it follows the formal laws of diffraction nevertheless. Moreover, a Gaussian beam also has a "self-healing" distance albeit longer.)

So, to improve the extent and stacking order along the *z*-axis over that produced by a GSWOT, a pseudo-Bessel beam was implemented using a conical-shaped axicon lens (with $n_a = 1.45$). Actually, this implementation, **Figure 3**(**a**), created an imperfect vortex beam that was then spatially filtered, passing a single ring, to produce a nearly perfect vortex that was subsequently deflected with AODs and Fourier transformed (using a lens) to create a 3D array of focused, time-shared (pseudo-)Bessel-SWOTs (BSWOT). The beam produced this way gave a close approximation to a Bessel beam over the characteristic propagation distance.

This time-shared BSWOT, formed at $\lambda_0 = 850$ nm with P = 200 mW using an axicon base angle of $\theta = 10^\circ$, in combination with a step-and-repeat method, was used to create a super-lattice from two voxels consisting of $3 \times 3 \times > 20$ arrays of the same (nominally) 175 nm-radius (CV = 5 %) fluorescent NPs on a hydrogel scaffold, **Figure 4(e)**. The fluorescent images of these voxels, **Figure 4(f)**, were iteratively de-convoluted to reveal fluorescent intensity maxima that were interpreted as NPs with an average radius (in the transverse *xy*-plane) of 165 ± 35 nm, separated by 2,280 ± 150 nm, which were in close correspondence with the nominal radius and the designed lattice constant (2.3 µm).

The de-convoluted images also revealed NPs stacked about twelve to sixteen deep along the *z*-axis, although not all the lattice sites were occupied, **Figure 4**(**g**). Importantly, the separation between successive fluorescent intensity maxima along the *z*-axis was measured to be $\Delta z = 366 \pm 44$ nm, **Figure 4**(**h**), indicating that the NPs must have been in contact with each other since $\Delta z_+ = 320$ nm. Thus, compared to the GSWOT, the BSWOT produced a lattice structure extending about twice as far (a distance of 5 µm), commensurate with the longer confocal parameter of the Bessel beam, i.e. $z_{max} = \varpi_0 / (n_a - 1)\theta = 632$ nm. However, positional errors and stacking faults were still evident in the de-convoluted images along the *z*-axis, although less so close to the mirror (*z* = 0), **Figure 4(h**). The faults were mainly attributed to the relatively long "self-healing"

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distance estimated to be about: $l_s = a\beta / \beta_r = a/(n_a - 1)\theta = 2,230 \ nm$. Thus, the extent of the zaxis stacking produced when a lattice of polystyrene NPs was assembled with a Bessel-beam, along with the modest improvement in the stacking order, supports the idea that a nondiffracting, self-reconstructing beam maintains trap fidelity over a wider depth-of-focus, perhaps due to the extended l_s . If the z-axis stacking faults were due to shadows cast by NPs in neighboring traps, then the trap fidelity should improve by shortening l_s . This could be accomplished either by shrinking the NP radius, a, or broadening the angle θ of the axicon lens. Thus, arrays of any size, shape and constituency can be assembled in 3D with light gradients using a step-and-repeat methodology and a BSWOT. This is analogous to the 2D lithography schemes used in semiconductor manufacturing to expose a large silicon wafer with a small image field. However, the variant used here is more akin to modular construction in the sense that low temperature, chemical solution methods, which offered economical and scalable synthesis, were used to first create monodispersed dielectric and metal NPs with built-in functionality. Finally, to punctuate the argument, a 10×10 lattice of voxels, each consisting of a $3\times3\times(>10)$ array of nominally 175 nm-radius polystyrene latex NPs was created using a time-multiplexed pseudo-Bessel SWOT at $\lambda_0 = 850$ nm using P = 200 mW, Figures 5(a) and (b).



Figure 5. Modular assembly of macroscopic 3D primitive tetragonal NP lattices.

Note: (a) An optical micrograph is shown that was acquired from a 10×10 super-lattice of voxels consisting of $3 \times 3 \times (>10)$ nominally 175 nm-radius fluorescent polystyrene NPs, assembled with a focused time-shared, 200 mW BSWOT formed at $\lambda_0 = 850$ nm, in combination with a step-and-repeat method using a voxel with a 3.5 µm lattice constant and a 10.0 µm step in the *x*- and *y*- directions between voxels. (b) Confocal fluorescent micrographs acquired from the super-array shown in (a). The *xy*- (left), *xz*- (bottom) and *yz*- (right)-views of the same lattice are shown

4.1.1. Vitrification of NP Arrays.

Parenthetically, the cross-linked PEGDA scaffold was only a stopgap used provisionally to maintain the registration between NPs. Generally, it was too pliable for practical handling—the modulus was calculated to be *ca*. $E_{PEG} = 110 \pm 2$ kPa, estimated by nano-indentation using an atomic force microscopy (AFM), with a mesh size of $\zeta < 4$ nm. Judging from the mesh size, the scaffold was judged to be porous to small molecules, and so to stiffen it, the scaffold was infiltrated with tetraethyl orthosilicate (*TEOS*) to form silica glass. Based on nano-indentation, the resulting modulus of a voxel improved to $E_{TEOS} > 94 \pm 2$ MPa, which was comparable to the rigidity of glass ($E_{glass} = 67 \pm 3$ MPa), representing about a thousand-fold increase in stiffness over the PEGDA hydrogel. Despite the gross change in modulus, however, fluorescent confocal micrographs acquired before and after vitrification

proved that the scaffold remained transparent and that the registration between NPs in the voxel was essentially preserved, **Figure 6**.



Figure 6. Vitrification of 3D lattices of fluorescent NPs assembled with standing waves optical traps (SWOTs). (a; i, ii)

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4.1.2. SiO2@Au Core-Shell Nanoparticles with Tunable Gold Surface Density.

The modular construction scheme using light gradients relies on the economical and scalable synthesis of NPs with built-in functionality. Calculations performed using Mie scattering theory to estimate the effective permittivity and permeability indicated that electric and magnetic dipole scattering resonances associated with core-shell NPs could produce a negative refractive index suitable for PMs. So, as part of the effort, methods were established to prepare SiO₂@Au core-shell nanoparticles (NPs) with a tunable gold surface density, **Figure 7**.



Figure 7. Synthesis of SiO2@Au core-shell NPs with a "patchy" gold shell of tunable surface density.

Note: TEM micrographs show (left to right) SiO2@Au core-shell NPs prepared using a volumetric ratio of SiO2 core NPs and Au seed NPs of 1:1, 1:10, 1:20, and 1:100 prior to plating. The surface density, or area fraction, of Au NPs SiO2 core NPs was measured from TEM micrographs by two different stereological methods – area segmentation and point counting – which exhibited excellent agreement and demonstrated that the area fraction was able to be tuned from approximately 20 to 60% surface coverage under these conditions.

The surface density (or "patchiness") of the Au shell on SiO₂ NPs was tuned by controlling the volumetric ratio of SiO₂ core NPs and Au seed NPs prior to plating additional Au. The surface density, or area fraction, of Au NP surface coverage on SiO₂ core NPs was measured from TEM micrographs and revealed that the surface coverage could be tuned from *ca*. 20 to 60%, **Figure** 7. The functionality of the tunable gold surface density was further investigated by measuring catalytic activity for ethylene oxide reduction by NaBH₄, which was correlated to the surface density of Au particles. The catalysis rate measured by UV-vis spectroscopy increased two-fold between SiO₂@Au NPS with 20 to 60% surface coverage. The significance of this finding is in the design of the NPs, which can enable the desired functionalities of tunable plasmonic/photonic properties and electrochemically-directed metal junction formation in HOT (*e.g.* BSWOT) assembled NP arrays.

4.2 Focus Area 2 (Functionality Development).

4.2.1. Nanofilament Formation in PEO/Ag+ Thin Films.

PEO/Ag⁺ systems were initially studied to demonstrate that Ag nanofilaments could be electrochemically formed and dissolved through a polyelectrolyte thin film at a scale similar to that of the microelements discussed in **Section 4.1**. In these experiments, the C-AFM tip was

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used as an addressable, direct-write working electrode.

Figure 8(A) illustrates the formation and dissolution of a single filament, and Figures 8(B) and (C) show characteristic electrical signals corresponding to this process. Starting in the OFF state, when a positive bias is applied to the substrate, Ag⁺ ions are reduced at the negative AFM tip *via* $Ag^+ + e^- \rightarrow Ag(s)$, while oxidation occurs at the sacrificial Ag electrode via $Ag(s) \rightarrow Ag^+ + e^-$. After a sufficient amount of material has been deposited, the filament contacts the Ag-coated substrate, completing a conductive path from the C-AFM tip to the substrate, causing an abrupt increase in the current measured through the tip (ON State). Subsequently, the filament can be dissolved by reversing the applied potential, which, after a delay, resets the filament to a nonconducting state. Filaments remain stable for substantial time periods under both steady and increasing bias and even under small reverse bias. If the formation bias remains applied substantially longer than the time needed for filament formation, τ_f , nanoclusters can form on the surface, which are evidence of filament overgrowth. Resistance measurements of 30 filaments show that the average resistance is ~ 200-400 k Ω .



Figure 8. Formation and dissolution of nanofilaments in PEO/Ag+.

Note: (A) Schematic representation of the four phases of filament behavior; initial nucleation at C-AFM tip with a positive substrate bias (i), leading to filament growth (ii), which contacts the surface at time $\Delta \Box f$ (iii). Under reverse, i.e. negative, substrate bias, dissolution occurs (iv). (B) An I-V characteristic of a single filament, starting at a substrate bias of -1 V (1. OFF state) and sweeping to +1 V (2. Formation), showing no measurable current until the filament is formed (3. ON state). The filament remains stable under a small negative bias

before resetting to a non-conductive state (4. Dissolution). Curve acquired at 0.6 V s-1, with a maximum readable current of \pm 600 nA. (C) Current vs. time trace showing the time difference ($\Delta \Box f$) between application of a formation voltage and the resulting increase in current corresponding to filament formation. The junction is stable under an applied positive bias to the substrate, which is stepped down in -200 mV increments to -1 V, at which the filament remains conductive until dissolution occurs.

In order to understand the repeatability and variability in nanofilament formation and dissolution, the C-AFM was used to form and dissolve 870 individual filaments on each sample, in a rectangular array with a pitch of 200 nm. Three samples were prepared with 0.5, 1, and 2 wt% PEO in acetonitrile/AgNO₃ solutions, corresponding to ether oxygen:Ag⁺ ratios of 180, 90 and 45:1. Spin-coating the electrolyte layer produced films of *ca*. 40 nm, 80 nm, and 130 nm, respectively. These films were tested with a +0.6 V substrate voltage for formation and -1.0 V for dissolution. Formation, τ_{f} , and dissolution, τ_{d} , time histograms are shown in **Figures 9(A)** and 9(B), respectively. It is evident that while τ_f follows a normal distribution for all three samples, the τ_d distributions of dissolution times are lognormal. This is clear evidence of inherent mechanistic differences between the two processes. Figure 9(A) shows a marked increase in τ_f with increasing film thickness, and **Figure 9(B)** shows a similar shift for τ_d distributions. While the ion concentration also affects the formation/dissolution times, the ionic conductivity of PEO is relatively insensitive to AgNO₃ concentration in the concentration range studied here. Therefore, the shift to longer formation/dissolution times in Figures 9(A) and 9(B) can be explained by the increasing film thickness from 40 to 80 to 130 nm. To test the effect of dissolution voltage, the 80 nm sample was tested with +0.6 V formation bias followed by a -0.6 V dissolution bias - compared to -1.0 V dissolution bias in Figure 9(B). The resulting histograms, **Figures 9(C)** and **9(D)**, show a small, but statistically-significant, decrease in τ_f but a markedly longer average dissolution time, approaching that of the 130 nm sample. The displacement to longer τ_d values at smaller dissolution voltage is consistent with a kinetically limited process in which the effective barrier height (for Ag atom displacement near the quantum point contact) is surmounted more easily at larger dissolution biases. The combination of different distributions for τ_f and τ_d and the thickness dependence of both processes demonstrates that formation and dissolution kinetics can be controlled independently.



Figure 9. Formation/dissolution time distributions for simple filaments.

Note: (A) Formation (τf) and (B) dissolution time (τd) distributions for simple filaments in 0.5 wt% (40 nm thickness, green), 1 wt% (80 nm thickness, blue) and 2 wt% (130 nm thickness, red) films of PEO with formation bias Vsubstrate – Vtip = +0.6 V, and dissolution bias of - 1.0 V. The solid lines are skewnormal on standard time (formation) and log time (dissolution) curve fits. (C) Formation (τf) and (D) dissolution (τd) time distributions for simple filaments in a 1 wt% (80 nm) PEO film with a formation bias of +0.6 V and a dissolution bias of -0.6 V. Insets to (B) and (D): The dissolution time distributions are clearly lognormal when plotted directly vs. time

4.2.2. Embedded Nanoparticles as Bipolar Electrodes in PEO/Ag+-AgNP Thin Films

The ultimate aim for the microelements is to embed them with a lattice of precisely placed NPs that serve as connectivity points for nanofilaments, allowing for purposely-designed electrical paths to modulate optical properties. Therefore, experiments were conducted to understand how embedded Ag NPs affect nanofilament formation. In this study, it was initially challenging to uniformly disperse Ag NPs in the polyelectrolyte film without aggregation. Therefore, to address this issue, a thiol linker was used to tether the NPs to the Ag-coated substrate, effectively creating a 'layer' of NPs in the polyelectrolyte (see **Section 3.2.2 - Methods**).

Notably, both the formation time τ_f and dissolution time τ_d distributions when using embedded

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NPs, **Figures 10**(**C**) and **10**(**D**), differ markedly from those obtained for simple polyelectrolyte thin films, **Figures 9**(**C**) and **9**(**D**). Both τ_f and τ_d distributions for the embedded NPs can be resolved into three components. The τ_f histogram in **Figure 10**(**C**) can be fit with an unresolvable short component and two normal distributions in the 0.1-2.5 s range. The shorter of these latter two matches the single distribution observed for the simple polyelectrolyte film. It is likely that the multicomponent nature of the τ_f and τ_d distributions arise from the imprecise placement of NPs in the polyelectrolyte thin film leading to the misalignment of the C-AFM tip above the NP. However, the slowest formation time distribution identified in **Figure 10**(**C**) likely corresponds to the NP being directly inline with the C-AFM tip such that filament formation requires the formation of two separate filaments (below and above the AgNP) to achieve a conductive pathway.



Figure 10. AgNP-functionalized sample after spin-coating 1 wt% PEO film.

Note: (A) Plan-view SEM image showing in-plane distribution of nanoparticles. (B) Crosssectional SEM image showing vertical placement of nanoparticles (white arrows overlaid) in

the PEO film. (C) Formation (τ f) and (D) dissolution (τ d) time distributions together with multi-peak fits (black line, overlay; individual peaks shown below.) Peaks are numbered corresponding to formation condition: (1) shorted nanoparticle against tip or substrate, (2) formation between tip and substrate in area away from AgNP, and (3) formation between tip and substrate through AgNP acting as a bipolar electrode.

4.2.3. Nanofilament Formation in PEGDA/IL/Ag+ Thin Films.

As noted earlier, PEO is not a compatible polymer for the HOT (*i.e.* GSWOT or BSWOT) processes developed in FA1. Therefore, nanofilament formation was studied in photopolymerized PEGDA/IL/Ag⁺ thin films. The IL is essential as a replacement for water in the HOT process (water can interfere with nanofilament formation by electrolyzing). The thin films prepared were *ca.* 50 nm thick; notably the thickness was independent of the IL concentration.

In order to determine if the IL affects the mechanical properties of the PEGDA, the modulus was measured using PF-QNM. Overall, the modulus decreases with increasing IL content. For example, increasing the IL composition by a factor of 3 (10 to 30 wt.%), decreases the average Young's modulus by about an order of magnitude. This trend is predictable, because the IL is a low viscosity liquid compared to the UV-crosslinked polymer. In contrast, adding Ag salt *increases* the modulus, which is most obvious for the electrolytes with the highest PEGDA concentration. For example, the modulus nearly doubles by adding 2 mM AgPF₆ to a sample with 90 wt.% PEGDA. These data show that the modulus of the polymer coating can be tuned more than 10-fold by relatively small adjustments in the PEGDA/IL ratio. In contrast, increasing the silver salt concentration by an order of magnitude (0.2 to 2.0 mM) increases modulus by at most a factor of two. Overall, depending on specific conditions, the modulus ranged from ~ 0.15 GPa to 7 GPa.

Similar to the study of PEO/Ag⁺, hundreds of nanofilaments were formed for PEGDA/IL/Ag⁺ thin films of varying composition as shown in **Figure 11**. Not unexpectedly, the formation time distributions are normal, **Figures 11(A)** and (**C**), while the dissolution events show a log normal distribution, **Figures 11(B)** and (**D**). Both the Ag salt and the IL strongly affect filament formation kinetics. The addition of up to 2 mM Ag salt in the 70/30 wt.% PEGDA/IL electrolyte decreases the formation time by as much as 42 %, **Figure 11(A)**, as expected from straightforward electrodeposition kinetics. The shift in formation times indicate that the kinetics of filament formation can be controlled by adjusting the Ag⁺ concentration without varying the electrical field strength. Decreasing the IL concentration from 50 to 10 wt.% increases the filament formation rate by ~ 6.5 times as shown in **Figure 11(C)**. Faster filament formation with decreasing IL content is unexpected, because the IL is conventionally thought to function as a plasticizer – enhancing polymer chain segmental motion and improving ionic conductivity.



Figure 11. Filament formation dynamics in PEGDA/IL.

Note: Formation (A) and dissolution (B) time distributions in electrolytes at 70/30 wt.% PEGDA/IL with 0, 0.2 and 2 mM AgPF6. Filament formation (C) and dissolution (D) time distributions for electrolytes with 2 mM AgPF6 at 90/10, 70/30 and 50/50 wt.% PEGDA/IL. The bin width is 1 s for all formation times and 0.4 Ln(ms) for all dissolution times. The data are fit by Gaussian distributions with adjustments in skewness to capture the asymmetric shape.

In addition, the magnitude of the formation time distribution is related to specific features in the time-dependent current data. Specifically, there are two different types of processes, denoted type-1 and type-2, in **Figures 12(A)** and (**B**), respectively. Type-1 formation involves an abrupt increase in current from zero to the compliance current over a narrow (few ms) time window, whereas type-2 formation involves current fluctuations over longer timescales (> 1 s) prior to reaching the compliance current. Systems with faster formation kinetics and the highest modulus have a higher percentage of type-1 formation events. For example, the 90/10/2 mM PEGDA/IL/Ag⁺ system with average formation time of 7 s has a 75 % type-1, while the slower 50/50/2 mM system, with average formation time of 45 s, exhibits only 5 % type-1 events.

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Although further studies are needed to confirm the origin of these two distinct types of formation dynamics, they may relate to the physical structure of the filament. For example, type-1 filaments that are more commonly formed in the high modulus electrolyte (90/10/2 mM) may have well-defined structure, whereas type-2 filaments that dominate in lower modulus electrolyte (50/50/2 mM) may be more dendritic, causing current fluctuations as they form and disconnect.



Figure 12. Current vs time data during filament formation.

Note: Formation at +2 V and dissolution at -2 V for (A) type-1 and (B) type-2 filament formation processes. Inset of (A) in the blue rectangular box is a magnified plot with expanded time axis.

Based on differential scanning calorimetry (DSC) measurements of the polymer crystallinity and the prevailing view that less crystal structure in polymer electrolytes correlates with faster ion mobility, we expected the 50/50 PEGDA/IL sample to exhibit the fastest filament formation/dissolution kinetics. In fact, we observed the opposite – the 50/50 PEGDA/IL electrolyte showed the slowest kinetics, Figure 11(C); the result suggesting that the local structure of the polymer - which can be evaluated by AFM - could be important for understanding the kinetics. Regions of highly crystalline (vs. amorphous) electrolyte can be differentiated by optical microscopy in the 90/10/2 mM electrolyte. Modulus measurements in Figure 13 show that regions that are primarily crystalline have an average modulus of 4.8 GPa, nearly an order of magnitude higher than the 0.6 GPa exhibited by regions exhibiting primarily amorphous morphology. The filament formation kinetics measured in these regions indeed show distinct distributions: the amorphous domain had a right-skewed Gaussian distribution with long formation times (21 % of the filaments formed within 5 s), while the predominantly crystalline region had a power-law distribution with a larger percentage of fast formation events (52 % of filaments formed within 5 s). Indeed, when compared to the kinetics of a 100/0 PEGDA/IL system, which is the most highly crystalline system by a wide margin, formation time distributions similar to the primarily crystalline 90/10/2 mM sample were obtained. In fact, a power-law distribution was observed in the formation kinetics is associated with large amounts of crystallinity, Figure 13(B). Moreover, regions of high crystallinity also have the highest

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percentage of type-1 formation events. Therefore, a picture emerges in which ion transport within primarily amorphous domains is mediated by polymer chain mobility and can be described by drift-diffusion that leads to poorly ordered filaments. In contrast, faster ion transport occurs in crystalline regions - likely by a hopping mechanism - that gives rise to a power law distribution and well-ordered filaments.



Figure 13. Formation times as a function of local crystallinity.

Note: (A) Formation time distributions in primarily crystalline (red) and amorphous (gray) regions of the 90/10 PEGDA/IL wt.% with 2mM AgPF6 sample using a 1 s bin width. Insets show modulus maps captured in each domain; (B) Log-log plot of formation time distributions vs. count percentages in primarily crystalline regions for 90/10 PEGDA/IL at 0, 0.2 and 2 mM of AgPF6. 120 s is the cutoff time for formation, bin width is 5 s.

The data show that some amount of IL is essential to achieve fast and reliable formation events. The electrolytes loaded with 10 wt.% IL further show that ion mobility is decoupled from PEGDA chain mobility, and suggest that different formation mechanisms operate in the two phases (amorphous and crystalline). While it is well understood that ion mobility in the amorphous phase is driven by chain mobility, there is also support for the notion that specific crystalline structures in PEO-based electrolytes can provide faster pathways for ion transport than their amorphous equivalents. Based on the results obtained here, a similar explanation can be used for the observation that primarily crystalline domains exhibit faster formation kinetics. Specifically, a balance is achieved at ~10 wt.% IL, where conduction through crystalline regions is favored over primarily amorphous regions. In contrast to the crystalline regions, the amorphous regions have strong electrostatic interactions that suppress polymer/ion transport and therefore filament kinetics.

4.2.4. Ordered Polyelectrolyte Systems for Sequential Nanofilament Formation.

All these results using different polyelectrolyte thin films have proven to be useful for studying basic nanofilament formation. However, imprecise placement of NPs using the thiol-linker rendered the results difficult to interpret mechanistically, so we pursued an alternative approach to studying nanofilament formation through AgNPs. Specifically, the challenge is to study the *sequential* formation of nanofilaments between 2 or more AgNPs. This problem more accurately reflects nanofilament formation through the lattice of NPs in the microelements or in a macroscopic material consisting of microelements. Addressing this problem required precise control over the placement of AgNPs in a vertical array. Therefore, a novel strategy for fabricating an ordered system of polyelectrolyte nanopillars with only 2-3 embedded NPs was developed.

The basis for this new fabrication strategy is a nanopore electrode array in which the nanopores are used to template the assembly of AgNPs. After assembly the multifunctional nanopores are used to photopolymerize the polyelectrolyte, thereby locking in the physical arrangement of AgNPs, by exploiting their zero-mode waveguides (ZMW) characteristics. Building upon the results with PEGDA/IL/Ag⁺ thin films, PEGDA/Ag⁺-AgNP systems were photopolymerized using the approach shown schematically in **Figure 14**. Implementing this strategy required having both optical access to the nanopore and a metallic back-plane for connection. Thus, instead of fabricating on an Ag-coated glass substrate, the nanopores themselves were fabricated to contain a recessed Ag ring electrode. Once photopolymerized, the array of nanopores essentially form Ag NP-containing PEGDA nanopillars as shown in **Figure 14**.



Figure 14. Schematic of fabrication process for AgNP-embedded in PEGDA/Ag+ nanopillars.

After testing various concentrations of PEGDA in the presence and absence of AgNPs, it was experimentally determined that (2.0 wt%) of PEGDA with 1 mM Ag⁺ salt is the optimal formulation for effective UV cross-linking to form polyelectrolyte nanopillars inside the nanopore arrays, **Figures 15**(**A**) and (**D**). Then, reactive ion etching (RIE) is used to remove a protective Cr layer to produce an array of polyelectrolyte nanopillars suitable for the controlled synthesis of nanofilaments. **Figures 15**(**B**) and (**E**) are top-down view SEM images of the nanopore array without and with AgNPs after removal of the Cr layer, and **Figures 15**(**C**) and (**F**) show cross-section SEM images of PEGDA nanopillars without and with embedded AgNPs in an array of nanopores.



Figure 15. Results of fabrication process for AgNP-embedded in PEGDA/Ag+ nanopillars

Note: (A) Cross-section SEM image of photopolymerized PEGDA in a recessed Ag ring electrode array without AgNPs. (B) SEM image of a nanopore array without AgNPs after RIE etching step. (C) Cross-section SEM image of photopolymerized PEGDA in nanopores without AgNPs. (D) Cross-section SEM image of photopolymerized PEGDA in nanopores with embedded AgNPs. (E) SEM image of nanopore array with AgNPs after RIE etching step. (F) Cross-section SEM image of photopolymerized PEGDA in nanopores with embedded AgNPs.

After optimizing the filling and photopolymerization procedures, we achieved near 100% efficiency in templated PEGDA-filled nanopores. Nanopore arrays with different depths and diameters were prepared by changing the parameters of the focused ion-beam (FIB) milling, establishing different geometries to act as zero-mode waveguides. To investigate pore size-dependent polymerization efficiency, nanopores were filled with PEGDA/Ag⁺-AgNPs and photo-polymerization was initiated by UV irradiation ($\lambda = 405$ nm). We found, as expected, that increasing the nanopore diameter allows deeper penetration of incident light for cross-linking the PEGDA. **Figure 16** shows arrays of nanopores and the trend for more efficient filling and polymerization with increasing pore size - an effect that is attributed to deeper light penetration. **Figures 16(c)** and (**f**), which have the biggest nanopores in the experimental set, exhibit 100% polymer-filled nanopores.



Figure 16. Effect of pore size on polymer filling.

Note: Plan-view SEM images showing more polymer formation in nanopore arrays with increasing pore size (from a to c) and corresponding enlarged images (d-f).

Using the above procedure to prepare the nanopores, we synthesized nanofilaments in the nanopore array in order to demonstrate nanofilament formation through multiple NPs, and we were able to directly image an as-grown nanofilament within a nanopore, as shown in **Figure 17**. Surprisingly, rather than observing a fractal- or dendritic-like structure, as anticipated, the nanofilament is more cylindrical, suggesting growth both along the primary axis (aligned with the dominant electric field) as well as radially.



Figure 17. Nanofilament formation from multiple AgNPs.

Note: SEM image showing a single nanofilament formed within a nanopore from multiple AgNPs.

To optimize the procedure further, templated nanopores, prepared by FIB milling, were treated with an O₂-plasma to generate hydroxyl groups on the interior pore walls, which were subsequently functionalized with 3-(trimethoxysilyl)propyl methacrylate (TMSPMA). The nanopores were filled with PEGDA/Ag⁺-AgNPs and photopolymerization was initiated by optically trapped (zero-mode waveguide) 440 nm UV irradiation. During the photopolymerization, TMSPMA acts as a linker to form covalent bonds with PEGDA, thus securing the polymerized PEGDA within the nanopores. **Figure 18** shows PEGDA polymer-filled nanopore arrays. After photopolymerization, all nanopores are uniformly filled with PEGDA polymers. It is noticeable from the tilt view at 35° in **Figure 18(a)** that the level of polymer filling is somewhat lower than the array plan surface. Next, using the same array, topological AFM images were obtained as shown in **Figure 18(c)** and (d).



Figure 18. SEM-AFM comparison of PEGDA-filled nanopores.

Note: SEM images after photo-polymerization within nanopores at 35° (a) and plan view (b). AFM images of portions of the same array at lower (c) and higher (d) magnification.

Surprisingly, the AFM images in Figures 18(c) and (d) show PEGDA polymer bumps over the array surface, in contrast to the SEM image of the same array in Figures 18(a) and (b). The SEM images were taken under vacuum conditions, so that the polymers within the nanopores may have deformed upon evacuation. However, the AFM images were taken at ambient pressure in the presence of atmospheric moisture, resulting in polymer swelling out of the nanopore array. This is particularly beneficial for the study of the formation/dissolution kinetics on Ag nanofilaments, as the raised PEGDA bumps are more easily accessible for the C-AFM tip. In addition, the dichotomy between the AFM and SEM images suggests a fruitful follow-on experiment in which PEGDA is replaced with a more sensitive stimulus-responsive material (SRM), for example one displaying a sensitive lower critical solution temperature (LCST). One could imagine temperature-sensitive shrinking/swelling behavior being exploited to achieve junction formation and breaking using purely mechanical forces associated with the SRM. Figure 19 shows a current-voltage (I-V) traces obtained for the nanopores marked in the corresponding AFM image. We believe these represent formation, then stable operation, then dissolution/breaking of the filament followed by reformation of the Ag filament owing to Ag deposition at the substrate during the oxidation of Ag at the tip. Although we successfully obtained *I–V* characteristics through PEGDA-filled nanopores, unwanted side electrochemical

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reactions (*e.g.*, Ag₂O formation, water reduction/oxidation in the presence of a little moisture, unknown reactions at the Pt-Ir coated AFM tip) are a concern at the relatively high potentials applied during scans (\pm 10 V). In order to avoid these unwanted side reactions, we reduced the thickness of the SiN_x layer from 150 to 100 nm, in hopes that a lower bias voltage would suffice for Ag filament formation/dissolution. As illustrated in **Figure 19**, Ag nanofilaments were formed at potentials $|V_{appl}| \sim 2$ V in most cases and below 4 V in all cases. We believe that these fabrication and characterization experiments lay the groundwork for a new science of massively parallel arrays of nanofilaments that can readily be studied at the single filament level.



Figure 19. Point-and-shoot I-V characteristics of individual nanofilaments.

Note: (Upper left) AFM image of PEGDA-filled nanopores in a 100 nm SiN_x layer. (1-3) I-V characteristics of three individual polymer-filled nanopores illustrating the variation in formation and dissolution characteristics from pore-to-pore.

4.2.5. Fabricating Micrometer-sized PEGDA Particles for PARC.

In order to produce scaled microelements that could be assembled by our TA2 partner, PARC, we developed a fabrication strategy to mass-produce micrometer-sized polymer particles (50 x 50 x 10 μ m and 25 x 25 x 10 μ m) suitable for macroscale assembly.

Figure 20(a) shows the process flow for particle fabrication. A sacrificial layer of 900 nm polystyrene ($M_w = 50,000 \text{ g/mol}$) is deposited by spin-coating on a 1.5 x 1.5 cm Si wafer. PEGDA ($M_w = 2000 \text{ g/mol}$) is then spin-coated multiple times to the desired thickness (2 – 10 µm has been demonstrated). A maskless aligner (Heidelberg MLA 100) which generates a virtual mask while writing the features is used to write the squares into the PEGDA film by UV exposure. Toluene is a good solvent for the uncrosslinked PEGDA and the polystyrene, but not for the crosslinked PEGDA; therefore, lift-off is achieved by immersion in toluene. The solution is purified to remove uncrosslinked PEGDA and polystyrene by repeated centrifugation in toluene, where the particles migrate to the bottom of the vial and the supernatant is removed and replaced with fresh solution. The particles are stabilized with the surfactant, sulfosuccinate (GR-7M, Dow Chemical), and the toluene is replaced with Isopar - the oil required by PARC for assembly. To image the particles, a portion of the solution is drop-cast onto a glass side and an optical image is shown after washing with toluene, Figure 20(b), and after the solvent swap for Isopar, Figure 20(c). The solution can be lightly sonicated for a few seconds to redisperse the particles after sedimentation.



Figure 20. PEGDA particle fabrication for assembly by PARC.

Note: a) Process flow diagram where the PEGDA rectangles are directly written by UV exposure which crosslinks the PEGDA making it insoluble in toluene. Lift-off and purification is achieved by immersion in toluene and repeated centrifugation. Optical images of particles after drop casting from (b) toluene and (c) Isopoar. AOT is used as a surfactant.

5. CONCLUSIONS

The work executed under this DARPA-funded project has laid the groundwork for new manufacturing processes capable of assembling nm-scale materials with precise, atomic-scale control through multiple, hierarchically-organized levels, ultimately yielding macro (hundreds of μ m-scale) products. The goal of this TA1 research project was to establish a set of manufacturing principles that support purposeful, hierarchical construction across 5 orders of magnitude in size – 0.1 nm to 10 μ m – to produce micrometer-scale building blocks which are intended for applications as a *new class of reconfigurable optical materials* with on-demand functionality. The dynamic reconfiguration was achieved by controlling the formation and dissolution of atomic-scale (0.1-1 nm) contacts between molecularly-engineered, nanoparticle-based (1-100 nm) nodes assembled in 3D lattices (1-10 μ m) imprinted and/or templated into a polymer electrolyte.

5.1 Focus Area 1 (Assembly Development) - Conclusions.

The principal developments ensuing from work in FA1 span the range from theoretical design through implementation of sophisticated three-dimensionally precise optical systems to the development of new materials. To begin, it was important for our team to define the materials parameters necessary to achieve high fidelity two-dimensional nanoparticle assembly and to combine that with a robust strategy for manipulating the particles with electromagnetic radiation. These goals were achieved by a modular assembly strategy, in which 2D nanoparticles lettuces were assembled using hey variety of light gradient mechanisms exploiting either time-shared Gaussian beams or, in later work, pseudo-Bessel beams to avoid the optical aberrations inherent associated with Gaussian beam profiles. Next it was important to develop the tools to understand the fidelity with which the design patterns were imprinted into the nanoparticle lattices. Because direct measurements what happened by variety of optical artifacts we developed a nonlinear iterative deconvolution procedure that allowed us to recover the true three-dimensional spatial structure with nanometer-scale precision. After characterizing the spatial and temporal characteristics of the 2- and 3D voxels assembled in this manner, we developed a step-and-repeat strategy, based on well-understood circuit assembly principles developed in the semiconductor industry, in order to stitch together the individually constructed arrays into three-dimensional superlattice with true 3D registry.

These advances in our ability to achieve rapid, high fidelity assembly at the nanoscale were necessarily augmented by solutions to a number of materials an engineering problems. In order to ensure the temporal stability of particle assemblies, we developed a lock-in strategy in which the assembly was carried out in a low molecular weight pre-polymer, and after the desired 3D spatial structure had been achieved, the structure was locked into place by uv photopolymerization. Early lock-in experiments utilized a photopolymerizable form of PEGDA. However, the modulus of the materials produced was too low for effective handling. Therefore, we switched out the PEGDA for tetraethyl orthosilicate, which permitted us to vitrify the nanoparticle lattice-containing medium in a material with in order of magnitude larger modulus. The final materials problem that had to be addressed concerned the transition from easily manipulated, but ultimately uninteresting, dielectric particles to semi-metallic particles which could be manipulated using the tools developed in FA2. To accomplish this we developed synthesis strategies to prepare patchy core-shell SiO₂@Au with tunable Au coverage which

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could be connected into nanofilaments using the approaches developed in FA2 (vide infra).

5.2 Focus Area 2 (Functionality Development) - Conclusions.

The findings emanating from FA2 have many important implications. Critically, they demonstrated that it was possible to controllably form and dissolve Ag nanofilaments both through polyelectrolytes and polyelectrolytes with embedded AgNPs. These demonstrations set the physical basis for reconfigurable microelements based on the formation and determinate dissolution of nanofilaments between NPs. Beyond simple demonstration, the work with a more realistic formulation of PEGDA and IL revealed that nanofilament formation in crystalline and non-crystalline polyelectrolyte domains is fundamentally different, and any microelement system must account for this during SWOT synthesis. The modulus (stiffness) and nanofilament formation properties need to be balanced effectively, and our results suggest a 90%/10% PEGDA/IL ratio is close to optimal in this system.

Beyond revealing the impact of different thin film conditions on filament formation and dissolution, the fundamental studies in FA2 have two important implications for future research. First of all, this work illustrates the inherent variability in filament formation and filament properties. This is not unexpected as the length scales of these filaments are such that any variation in the film properties would affect ion transport and thus reduction and oxidation behavior. The PEGDA/IL system illustrates this effect most clearly. Because of this, there are two paths forward when considering the design of microelements that support nanofilament formation – either improving the material science to precisely control the polyelectrolye properties (long-range crystallinity, etc.) over the length scale of the microelement or designing the application to account for stochastic, rather than deterministic, nanofilament behavior. This latter approach perhaps represents an important new perspective on reconfigurable optical device design and future research to explore this in depth, specifically focusing on robust behavior in inherently stochastic systems, will be important. Recent developments in stochastic computing could provide a theoretical basis for such exploration.

The second important implication is that the C-AFM-patterned arrays that were used here to study the statistics of nanofilament formation could also be used to develop optical metasurfaces themselves. In fact, with a polyelectrolyte, these could be *flexible, conformal metasurfaces*, where varying periodic arrays of nanofilaments can be used to form mesoscopic architectures with well-conditioned and spatially-controlled optical permittivities. The array of nanofilaments could produce such strong anisotropy that the metasurface would be considered hyperbolic. Applications that could be developed from this conceptual basis include super-resolution imaging, filtering, and polarization control.

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In addition, there are several publications that the team anticipates submitting in the next few months that will also acknowledge support from DARPA FA8650-15-C-7546.

- [16] Timp, G.; Roeder, R.K., *et al.* Standing-Wave Optical Trap Construction of Three-Dimensional Nanoparticle Assemblies, *Nature Mater.*, in preparation.
- [17] Roeder, R.K., *et al.* Patchy Core-Shell SiO₂@Au Nanoparticles, *Chem. Mater.*, in preparation.
- [18] Bohn, P.W.; Go, D.; Fullerton-Shirey, S., Fabrication and Characterization of Arrays of Individual Nanopore-Templated Bead-on-a-String Nanofilaments, *Nanoscale*, in preparation.

LISTS OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

2D	2 dimensional
3D	3 dimensional
A2P	Atoms to Products
ACN	acetonitrile
AFM	atomic force microscope
AOD	acousto-optic deflector
ASJ	atomic scale junction
BSWOT	pseudo-Bessel
C-AFM	conductive atomic force microscope
CV	coefficient of variation
DARPA	Defense Advanced Research Projects Agency
DI	deionized
FA1	Focus area 1
FA2	Focus area 2
GLMT	Generalized Lorentz-Mie scattering Theory
GSWOT	Gaussian standing wave optical trap
HOT	holographic optical trap
IL	ionic liquid
LCST	lower critical solution temperature
NP	nanoparticle
PDT	dithiolpoly(ethylene glycol)
PEGDA	polyethylene glycol diacrylate
PEO	polyethylene oxide
PI	principle investigator
PM	photonic metamaterial
RIE	reactive ion etching
RXAP	Photonic Materials Branch, Functional Materials Division, Materials and
	Manufacturing Directorate of AFRL
SEM	scanning electron microscope
SRM	stimulus responsive material
TA1	Technical Area 1
TA2	Technical Area 2
TEM	transmission electron microscope
TEOS	tetraethyl orthosilicate
TMSPMA	3-(trimethoxysilyl)propyl methacrylate
UV	ultraviolet
WPAFB	Wright Patterson Air Force Base
ZMW	zero-mode waveguide