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Electrophotographic Nano-Patterning in Solution

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Abstract

Micro- and nanopatterning confers functionality to molecular and nanoscale structures, underpinning devices ranging from electronic circuits¹ to photonic components² and biotechnological platforms^{3–4}. Conventional patterning approaches, however, are constrained by limited scalability, high cost, and incompatibility with fragile materials. Here we introduce an optically-induced electrical nano-painting technique that yields patterned features over centimetre-scale areas and a spatial precision of 140 nm. The process exploits an unexpected surface-charging phenomenon that persists after the initiating illumination is removed and in the absence of external fields. Patterning is based on electrostatic interactions and proceeds at low light intensities, is parallel and thus scalable, and is compatible with a broad palette of functional inks—including live bacteria, polymeric and inorganic nanoparticles, nanowires, two-dimensional materials, biomolecules and inorganic compounds. We demonstrate rapid generation of complex photorealistic images from these materials after merely a few short light exposures. We further demonstrate printing heterogeneous structures and the transfer of patterns. Crucially, the method operates in buffers spanning biologically relevant ionic strengths as well as in pure water, underscoring its versatility for a diverse range of applications.

1. Introduction

Material patterning is a foundational technology that underlies the device fabrication of various engineering fields, including electronics, photonics, sensing, bioassays, and multiomics.¹⁻⁴ Common to almost all applications is the need to attain high resolution, fast printing speeds and ideally an ability to organize and position a wide range of materials. The latter, for instance, is essential when realizing electronic devices and sensing chips including microarray technologies. In comparison with serial processing, parallel methods are especially promising when large-area patterning is of importance.⁵ Considerable effort has been invested to address the need for high resolution using top-down lithography-based approaches, including photolithography,⁶ electron-beam lithography,⁷ and nanoimprint lithography.⁸ These techniques provide excellent pattern fidelity and precision, which have been widely combined with standard deposition and lift-off processes, surface functionalization, or templated trapping for placing nanoparticles and molecules. However, they typically require multi-step processing, material-specific chemicals, and in the case of imprint, and electron-beam lithography, a cleanroom infrastructure and sophisticated instrumentation. Another major limitation is the multi-step nature of these processes. In particular, the chemical treatments necessary for polymer processing make it difficult to directly pattern live or biological materials. Beyond conventional lithography,^{9,10} other methods have also been adapted for patterning purposes. While atomic force microscopy enabled techniques, such as dip-pen nanolithography and related scanning probe methods, allow nanometer-scale placement of molecules and nanoparticles with exceptional precision. The mostly serial processing complicates scaling to larger print sizes.¹¹⁻¹³ While lithography fabricated tip arrays can improve throughput, achieving uniform patterning and delivering multiple distinct inks remain challenging.¹⁴ Photochemical and photoactivated approaches employ light to locally trigger chemical reactions, binding, or crosslinking, enabling maskless patterning.^{15,16} While highly attractive due to their scalability, these methods are often restricted by specific photochemistries, limited ink diversity, and trade-offs between resolution and throughput. Given the constraints, there is a need for a parallel patterning method that affords high spatial resolution and broad material compatibility.

In this work, we introduce an optically-induced electrical nano-patterning method that enables parallel assembly of a diverse range of materials over centimeter scales (**Fig. 1A**). The method relies on light-induced electrical activation of a surface, which in turn triggers the localized charge reversal, enabling the electrostatic patterning of a broad range of materials and functional inks. Furthermore, combining controlled electrical bursts and adding polyelectrolyte coatings, we achieve both prescribed etching and multi-layer patterning (**Fig. 1B**). Modest light intensities are used to activate the substrate onto which organic and inorganic nanoparticles (metals, polymers,

and 2D materials), biomolecules (DNA, proteins, and cancer biomarkers), and even living bacterial cells can then be deposited. The particle size spans four orders of magnitude, from micrometers for bacteria down to a few nanometers for proteins (**Fig. 1C**).

The method allows us to readily create photorealistic nanopaintings by applying kilohertz (kHz)-range AC electric (*E*-) fields of controlled bursts (each 200 ms) to a photosensitive hydrogenated amorphous silicon (a-Si) surface within an electrochemical cell (**Fig. 1A**). Following the *E*-field application, the target ink or material, dispersed in the same aqueous ionic support electrolyte, is readily deposited in the shape of the projected light images. The light-activation utilizes a digital light projector (DLP). Depending on the polyelectrolyte functionalization of the a-Si, the surface charge can be controlled, where PDDA (poly-diallyldimethylammonium chloride) yields positively charged surfaces, while PDDA/PSS (poly-sodium 4-styrenesulfonate) produces a negatively charged counterpart.^{17,18} Surprisingly, only ink constituents carrying the same charge polarity as the initial polyelectrolyte-functionalized surface are selectively deposited in light-defined regions. For instance, negatively charged particles assemble on PSS-terminated surfaces under light in the *E*-field. The effect has been found consistently across different particles and charge polarities. Alternately, it is also possible to use the method for light-directed removal (etching) of deposited materials. The combined deposition and etching yields features at a precision of 140 ± 40 nm using a standard optical microscope.

The reported technique can readily be used to form centimeter-scale patterns with sub-micrometer precision, for a broad range of materials. We show direct printing to form electrical connections, patterning of heterogenous protein assemblies and particle arrays, and selective pattern transfer (**Fig. 1D**). Our method does not require physical masks, specialized biochemicals, ultraviolet illumination, or vacuum processing—constraints that commonly limit existing nanopatterning methods (**Table S1**).

2. Working Mechanism, Characterization, and Optimization

To elucidate the working mechanism, we systematically examine and characterize the effects of key components in the system (**Fig. 2**): (1) The photoconducting a-Si layer, where the illumination pattern spatially controls the application of *E*-fields; (2) the polyelectrolyte layer, which exhibits charge reversal in response to the applied *E*-field onto which the material is deposited; (3) the solution, whose conductivity is determined by the salt concentration; and (4) the applied *E*-field itself, which governs the efficiency of material deposition in the printing process. As will be discussed below, the surprising like-charge patterning results from a combined effect of the entire system.

Upon E -field application during light illumination, particles (nanoparticles, molecules, and even bacteria) inside the solution gradually deposit onto the surface. Here, we use the density of the deposited particles (DDP) as a measure for the amount deposited, which critically depends on the amount of charges accumulated in and near the polyelectrolyte layer that drives the assembly, where clear patterns arise as soon as the E -field has been applied.

2.1. The a-Si layer

The DDP increases linearly as a function of the applied light intensity (E -field: 12 Vpp, 1.5 kHz, 200 ms, 1 pulse, waiting time after E -field application: 30 min+, electrolyte 0.75M Na₂SO₄), as seen in **Fig. 2A**. This agrees with the dependence of the photocurrent (i_p) on the photon rate (N_0):¹⁹

$$i_p = eN_0(1 - R)[1 - \exp(-\alpha d)]\eta\tau/t_t$$

Where e , R , α , d , η , τ , and t_t are the charge carried by an electron, surface reflection, surface absorption coefficient and depth, electron-hole pair generation efficiency, recombination lifetime, and carrier transit time, respectively. Negatively charged 200nm polystyrene nanospheres can be assembled as a monolayer on a PDDA/PSS functionalized a-Si surface with a saturation DPP of ~ 3 particles/ μm^2 (at ~ 650 mW/cm²). At the lower intensity of 250 mW/cm² we obtain a DDP of ~ 1 particle/ μm^2 which indicates the capability to tune the density (gray scale) through light intensity during printing. In the subsequent discussion we employ an intensity of 790 mW/cm², unless indicated otherwise.

2.2. The polyelectrolyte layer

The saturation DDP value increases with the number of polyelectrolyte bilayers made of PDDA/PSS, with ~ 3 , 9, and 14 particles / μm^2 corresponding to single, double, and triple layers, respectively (**Fig. 2B**). We note that after applying an E -field burst (E -field: 12 Vpp, 1.5 kHz, 200 ms, 1 pulse, and light intensity of 790 mW/cm²), the DDP gradually increases with time and plateaus at ~ 30 min for all conditions (**Fig. S1, Movie S1**). Considering the deposition rate and concentration of the particles in the solution, we can infer the effective particle transport speed as 0.017, 0.092, and 0.106 $\mu\text{m/s}$ for the single, double, and triple layer PDDA/PSS functionalized surfaces, respectively. These are within the range of random Brownian motion (**Supplementary text 1**), which suggests that the assembly mostly occurs due to attractive interactions when particles are close to the Si surface, instead of directional transport driven by an external E -field. Such an effect can be attributed to the high-ionic nature of the solution, which not only effectively screens possible long-range E -fields in solution but also substantially suppresses the thickness of the electric-double-layer (**Supplementary text 2**).²⁰

Interestingly, when we change the outermost functionalization layer to PDDA,²¹ a positively charged polyelectrolyte, only positively-charged particles (**Fig. S2A**) can be deposited onto the areas that are illuminated (**Fig. S2B**), with a similar increase in particle density over time (**Fig. S2C and D**). The strong dependance of DDP on both the relative charge polarity of particle-surface pair and the time of assembly after the field is switched off, indicates that the particle assembly mechanism is based on electrostatic interactions. The electrostatic nature is further confirmed when we reduce the zeta potential of the polymer nanospheres (200 nm), showing a correspondingly reduced deposition efficiency (**Fig. S3**). The effect is highly stable without the need of continuing application of either light or electric voltage, as shown by the consistent assembly speed through the 30-min process and well-maintained particle density afterward. To determine if the working mechanism is only limited to a-Si surfaces, we also performed the same study on metal surfaces, such as Au thin films (**Fig. S4**). The results clearly demonstrate the same particle assembly effect as that observed on a-Si. In addition to PDDA and PSS, the same finding is obtained from various charge functionalized surfaces, such as PAA (polyacrylic acid, positively charged) and DNA (deoxyribonucleic acid, negatively charged) (**Fig. S5**), pointing to a general working principle underlying the observed phenomena.

2.3. The applied *E*-field

To unravel the role of the applied *E*-field, we systematically sweep the *V*_{pp}, frequency, and the total voltage application time. DDP linearly increases with *V*_{pp} and reaches its saturation at ~10 *V*_{pp} (1.5 kHz, 200ms, 1 pulse, light intensity: 790 mW/cm², waiting time: 30min, 1-bilayer PDDA/PSS). No obvious deposition is observed for *V*_{pp} values lower than 6 *V*_{pp} (**Fig. 2C**). Similarly, DDP monotonically increases with the total time of the applied *E*-field (1.5 kHz, 12 *V*_{pp}, 1 pulse, light intensity: 790 mW/cm², waiting time: 30min). Particle deposition starts at only 2 ms (**Fig. 2D, inset**) and saturates at 1000-2000 ms (**Fig. 2D**). The experimental parameters of *V*_{pp}, *E*-field time, and light intensity positively correlate with the charge passing through the electrochemical cell up to a saturation point. This further supports that the nature of the particle deposition is related to charges. While the DDP decreases with increasing frequency (**Fig. 2E**), at frequencies higher than 10 kHz, deposition efficiency greatly decreases. The results agree with frequency-dependent response of ions in solution, in which ionic transport becomes increasingly ineffective as the applied AC field frequency increases above 10 kHz.²²

2.4. The electrolyte

Last, we probe the effect of the electrolyte, specifically the concentration of sodium sulfate (Na₂SO₄) ranging from a low 2.5 mM to a high 0.75 M, and its impact on the DDP (**Fig. 2F**). As long as particles are stably dispersed,²³ their assembly can be obtained reproducibly spanning all concentrations; the higher the electrolyte concentration the greater the density. The method can be

applied across a wide range of ionic environments, from simple electrolytes, such as potassium bromide (KBr) and sodium bromide (NaBr), to more complex solutions relevant for biological samples, such as phosphate-buffered saline (PBS). This is notably different from previous works on dielectrophoresis (DEP)-enabled manipulation and assembly, where particle manipulation mostly benefit from low ionic concentration, and where the effective E -fields applied to particles are notably reduced in high ionic strengths.^{24,25} This is in addition to the fact that this assembly technique enables steady and continuous particle deposition for 30 min when the E -field application is off. Even shorting the terminals after application of the electric field does not affect the deposition. While DEP assembly requires the continuous application of fields for maintaining pattern quality.²⁶ Both our theoretical understanding and experimental results thus indicate that the present method is distinct from DEP. The present effect of like-charges assembling even in the absence of any applied voltage suggests that the light-triggered electric effect results in a polarity reversal of the surface in the electrolyte and that the surface charge persists and drives the patterning process. The surface charge increases with the number of polyelectrolyte bilayers, the strength and duration of the applied E -field, and the ionic concentration. Charged polyelectrolyte layers can electrostatically associate with oppositely charged ions, providing a basis for ion uptake and retention.^{27,28} We therefore hypothesize that application of an AC field increases counterion uptake of the polyelectrolyte-coated Si electrodes, which may result in surface charge reversal. Meanwhile, the photoelectrically-controlled local increase of the ionic strength could further induce structural rearrangement and even dissolution of the polyelectrolyte layer,^{29–31} an effect especially stronger for the solution-interfacing layer (e.g., PSS), which would thereby expose the underlying layer (e.g., PDDA) and thus aid the observed surface charge reversal. Irrespective of the mechanism, we observe that particles sharing the same charge polarity as the original polyelectrolyte surface, assemble irrespective of the material or size on the light-exposed regions. Interestingly, these particles are repelled from the non-light-illuminated surrounding areas.

3. Versatile Nanopainting

3.1. 2D positive/negative patterning and particle reconfiguration

We show that the method can be used to deposit many different materials and to create intricate images. As shown in **Fig. 2G**, we paint a rose using 200-nm polystyrene nanoparticles and the Minerva logo of the Max Planck Society (**Fig. 2G, inset**). Here we notice that when applying multiple E -field bursts, a plateau is reached around 10-30 bursts, agreeing with the results in **Fig. 2D**. However, beyond 30 bursts, the assembled particles gradually start to desorb from the surface with the number of subsequent E -field bursts (**Fig. 2H**). This demonstrates that the technique not only can deposit but also can remove material and thus be used to etch patterns. Therefore, we also successfully create negative images of the same rose by first depositing a uniform layer of material

followed by light-controlled etching (**Fig. 2I, Movie S2**). Here, for double and triple PDDA/PSS bilayers, the nanoparticles maintain their adhesion even after 50+ bursts, likely due to the enhanced electrostatic binding from the additional polyelectrolyte layers. Notably, re-applying a polyelectrolyte layer after etching allows subsequent particle redeposition on targeted areas, enabling a versatile approach for reconfigurable, multi-cycle patterning based on deposition and etching (**Fig. 2J to L**). Last but not least, the technique is not restricted to monolayer 2D painting. By simply adding additional PDDA/PSS bilayers on the nanopatterns, we readily create the second, third, and fourth layers of patterns (**Fig. S6**), which suggests the potential for 2.5 or 3D assembly.

Resolution and optimization

As is the case of any printing technology, resolution is a key characteristic that determines the clarity and precision of the final pattern.³³ Here, we determine the resolution by printing an array of line patterns of varying widths and lengths (**Fig. 3A**). We note that a change of the *E*-field frequency also slightly impacts the output pattern size. When printing a square pattern with a target side length from the DLP device, the resulting output shows a linear decrease in the pattern's length with increasing frequency (**Fig. 3B**). We find that 3 kHz generates a close match to the intended target length, which we therefore use for the resolution characterization below. Projecting a DLP-generated pattern we can examine if the deposited material matches the intended optical pattern. The fitted curve demonstrates that each one-pixel increase in DLP pattern width corresponds to an additional 560 nm in deposition length (slope of the linear fit), with an initial offset of 110 nm (y-intercept), which could arise from conditions, such as light pattern dynamics, electric field distribution, and device configuration. (**Fig. 3C**). We anticipate that this resolution can be further improved by using a DLP with a higher areal density of mirrors and reduced mirror size. When combining both deposition and etching, we create line patterns at a precision (σ) of 140 ± 40 nm (**Fig. 3D and E, Fig. S7**).

Complex Photorealistic Nanopainting

The high-fidelity material deposition enables creating complex patterns with control of the deposition density that results in shading effects. This allows us to realize photorealistic paintings, such as an image of the “Girl with a Pearl Earring” (**Fig. 3F and G**) or an image depicting NASA's first landing on the Moon (**Fig. 3H and I**). The images are obtained only after 8 illuminations, where the corresponding binary images are derived from the original image's grayscale values (**Fig. S8A and B**). Each binary image is sequentially projected to generate localized surface charge densities corresponding to target grayscale levels. These variations modulate the local deposition density, which is controlled by the duration and number of applied *E*-field bursts. The entire painting process is shown in **Movie S3**.

3.2. Multiplex assembly

The technique is highly versatile and compatible with diverse inks. While a high ionic solution of Na_2SO_4 (0.75 M) is primarily used for PS sphere deposition for performance characterization, the technique can also be used to assemble particles dispersed in low-ionic solutions, such as deionized (DI) water. This is achieved by simply replacing the high-ionic Na_2SO_4 solution after the light-controlled *E*-field activation with a DI water suspension containing the particles (**Fig. S9-10, Supplementary text 3**). Particle deposition is significantly accelerated in DI water compared to that in high ionic solutions. High-density patterns form within 3 min as soon as the solution is exchanged. The obtained density in 3 min is practically the same as that obtained after 33 min in Na_2SO_4 (**Fig. S10**). The speed-up can be attributed to the greatly reduced ionic screening to both the charged surface and charged particles in DI water, which further supports that electrostatic attraction is the primary cause for the observed assembly. Further demonstrations include the direct deposition of μm -long *B. Subtilis* bacterial cells (**Fig. 4A**), silver nanowires (**Fig. 4B**), 100 nm (**Fig. 4C**) and 10 nm (**Fig. 4D**) Au particles, as well as graphene oxide nanosheets (**Fig. S11A**) and carbon nanotubes (**Fig. 4E, Fig. S12**). We also show that even salt (Na_2SO_4) dissolved in solution (**Fig. S13**) can precipitate owing to the locally enhanced ion concentration. The bacterial cells are directly observable via SEM, and viability tests confirm the technology's compatibility with biological matter (**Fig. S14**). Furthermore, 100 nm Au nanoparticles, graphene oxide nanosheets, are verified by using dark-field and Raman spectroscopy, respectively. In particular, the successful patterning of the graphene oxide is confirmed by the D and G bands in the Raman scattering^{34,35} (**Fig. S11B**) and Na_2SO_4 is confirmed by EDX measurements (**Fig. S13B**). We also successfully pattern DNA (**Fig. 4F**) and antibody proteins (**Fig. 4G and H**), showing potential high-throughput analysis of molecular interactions, gene expression, and biomarker detection in biomedical assays and diagnostics. Finally, nanocomposites made of Ag/SiO₂ were deposited (**Fig. S15**). High-magnification SEM images confirm dense nanoparticle accumulation within the prescribed patterns.

3.3. Demonstrations – centimeter-scale printing, pattern transfer, electric connection, and protein microarrays

Finally, we present four demonstrations that showcase the ability to create large-scale patterns, transfer printed designs, build electric connections, and make dense heterogeneous protein and particle arrays. First, we demonstrate the scalability of the deposition method by showing centimeter-scale particle patterning with a feature size of $< 100\ \mu\text{m}$. The large-scale pattern is made using a single pattern as a “stamp”, while moving the stage and applying an *E*-field burst at each step. Alternatively, the *E*-field can be applied continuously, while patterns are created only in areas under light exposure, comparable to direct inkjet printing. For the former, we demonstrate a

1 cm x 0.5 cm wide “Bevo” pattern, (**Fig. 5A**) each created from a plethora of “Bevo” stamps (**Fig. 5A, inset**). For the latter, we print Richard Feynman’s prose poem, ‘An Atom in the Universe’ in a 1cm x 0.3 cm space (**Fig. 5B**) using fluorescent PS spheres (**Fig. S16**). Next, we show the efficient transfer of deposited multiplex particle patterns to gel substrates. First, PS spheres are assembled into a line, followed by silver nanowire dot patterning (**Fig. 5D, left**). A customized hydrogel (see Materials and Methods) is then applied to achieve high-fidelity pattern transfer (**Fig. 5D, right**), as confirmed by both fluorescent and dark-field microscopy (**Fig. S17**). The gel transfer is selective, *e.g.* can be implemented such that it is selective for one type of particle but not another by adjusting the optoelectric patterning process (**Fig. S18-19, Supplementary text 4**). Furthermore, we deposit silver nanowires as a bridge between two electrode pads separated by 45 μm (**Fig. 5C, inset, Fig. S20**). Electrical I-V measurements show that the nanoparticle bridge is conducting (5.13 k Ω , **Fig. 5C, Supplementary text 5**). We expect that the conductivity of the interconnect can be further improved by a thicker coating and sintering. Finally, the technique also is used to generate multiplex protein array patterns from suspension. We show patterns made of P53 and IL-6 antibodies (**Fig. 5E**), and achieve a feature density of 5.70×10^5 spots/cm² (**Fig. 5F**). The results suggest a new fabrication method to obtain biomolecule arrays, including, protein and DNA assays, which are important for biomarker screening, disease diagnostics and multiomics applications.

Conclusions

In this work, we report a novel solution-based method that permits the scalable, precision patterning of molecules, nano-, and microparticles. The deposition pattern is defined by projecting visible light onto a photoconductive silicon surface functionalized with polyelectrolyte. Application of an AC *E*-field reverses the surface charge polarity, and, remarkably, draws particles of the same polarity as that of the initial polyelectrolyte from solution. The density of particles deposited can be precisely controlled by modulating the applied electric voltage, frequency, and duration, light intensity, and salt concentration. We show that the printing precision reaches 140 ± 40 nm. A variety of functional materials with distinct chemistries, size and shape can readily be deposited. Demonstrated examples include cells, metallic nanoparticles and nanowires, DNA, proteins, and salt, showing promising capabilities (**SI Table**). We further demonstrate that the technique is highly scalable, achieving cm-scale particle patterning, capable of creating electrical connections, easily transferable via hydrogels, and enabling heterogeneous patterns of both inorganic particles and proteins. The technique can also be implemented in buffers with biologically-meaningful ionic strengths or even in DI water, and achieve high density patterns that are useful in microwell-based array technologies.^{36,37} We anticipate that this technology will be used in a wide range of applications.

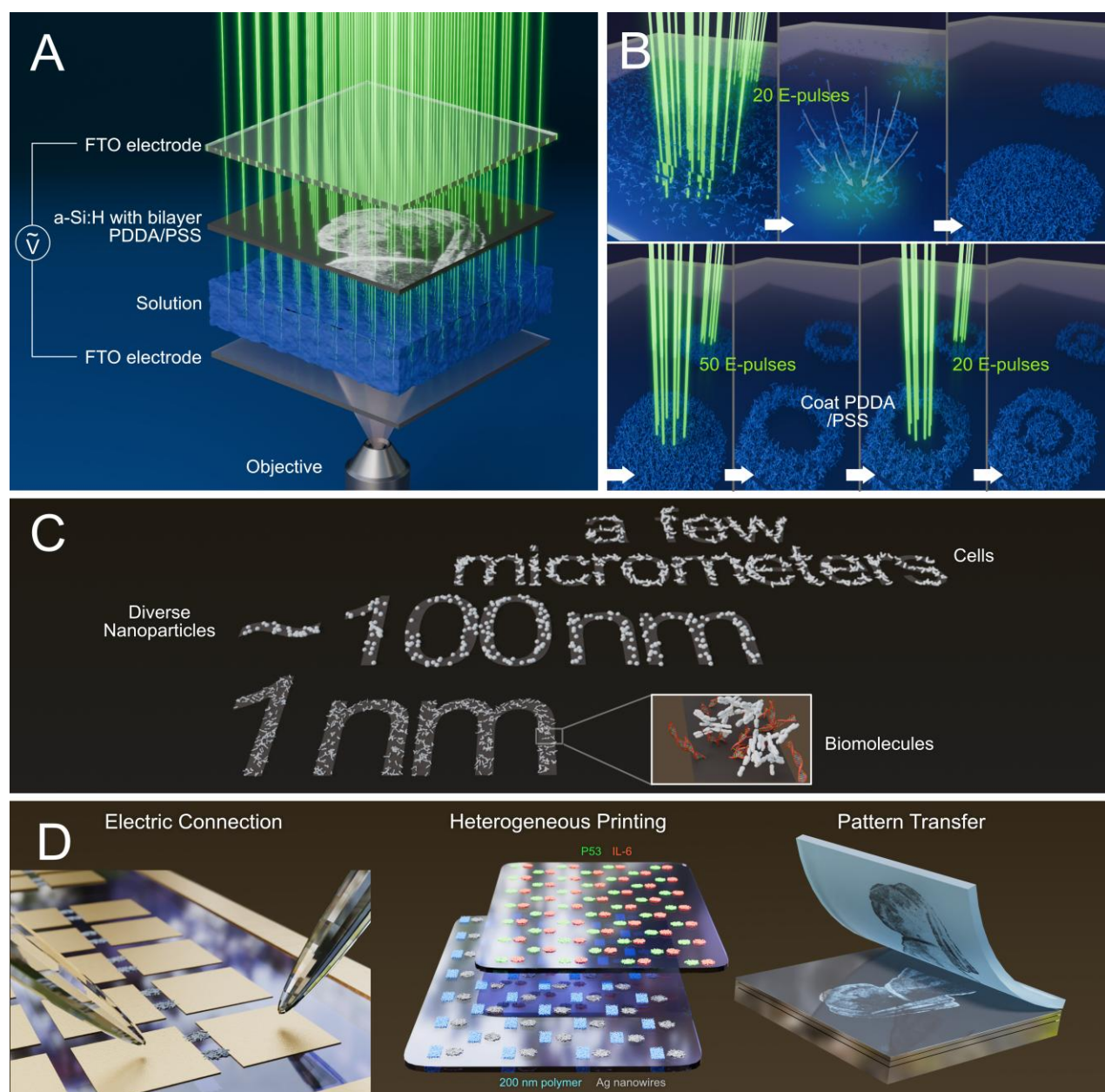


Figure 1. Schematic of experimental setup and overview. (A) A single 532 nm laser is expanded to illuminate the entire DLP mirror array, which dynamically projects light patterns. (B) Following the application of the light pattern and a pulsed AC E-field particles deposit from solution onto the surface of the functionalized photoconducting substrate (hydrogenated amorphous silicon). Controlled E-field bursts not only deposit but can also be used to etch. Adding polyelectrolyte allow for additional patterned depositions. (C) Molecules, nanoparticles, and even biological cells can be easily printed from suspension. The size of printable materials thereby spans 4-orders of magnitude from 1 nm to a few micrometers. (D) From left to right: Printing of Ag nanowire network for electrical connections, heterogenous patterning of both antibodies (e.g., P53 and IL-6) and nanoparticles (e.g., polymer spheres and Ag nanowires), and versatile, selective pattern transfer.

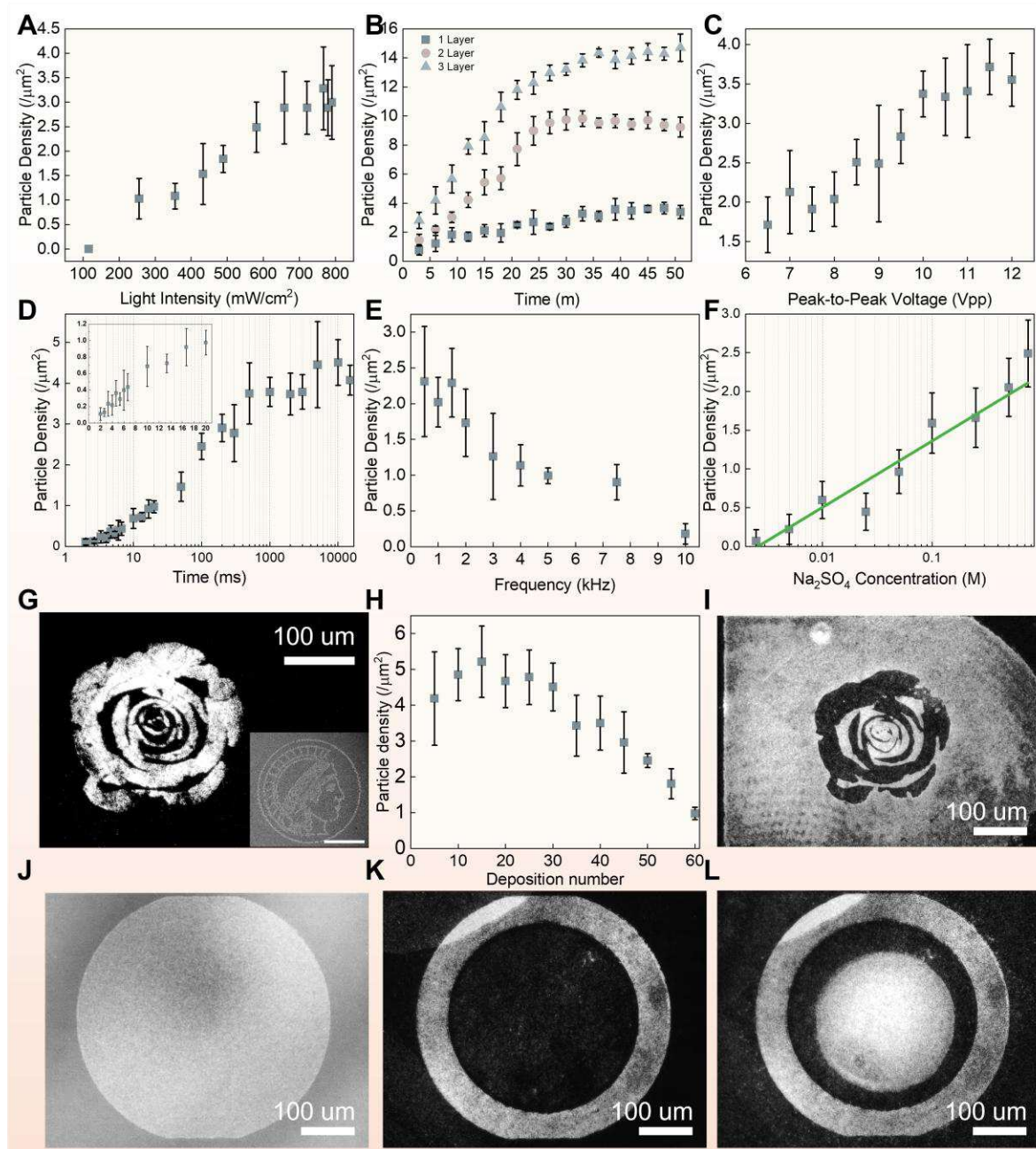


Figure 2. Characterization of Photoelectric Nano-Patterning in Solution. Density of deposited particles plotted versus (A) light intensity, (B) waiting time after E-field application, (C) AC V_{pp} , (D) applied E-field time, (E) AC frequency and (F) salt concentration. (G) Demonstration of positive particle patterning. (H) Change of particle density versus number of applied E-field bursts. (I) Negative particle patterning achieved by controlling the number of applied E-field bursts. (J) Deposition, (K) removal, and (L) additional deposition of particles after applying a new PDDA/PSS bilayer, showing reconfigurable patterning feasibility.

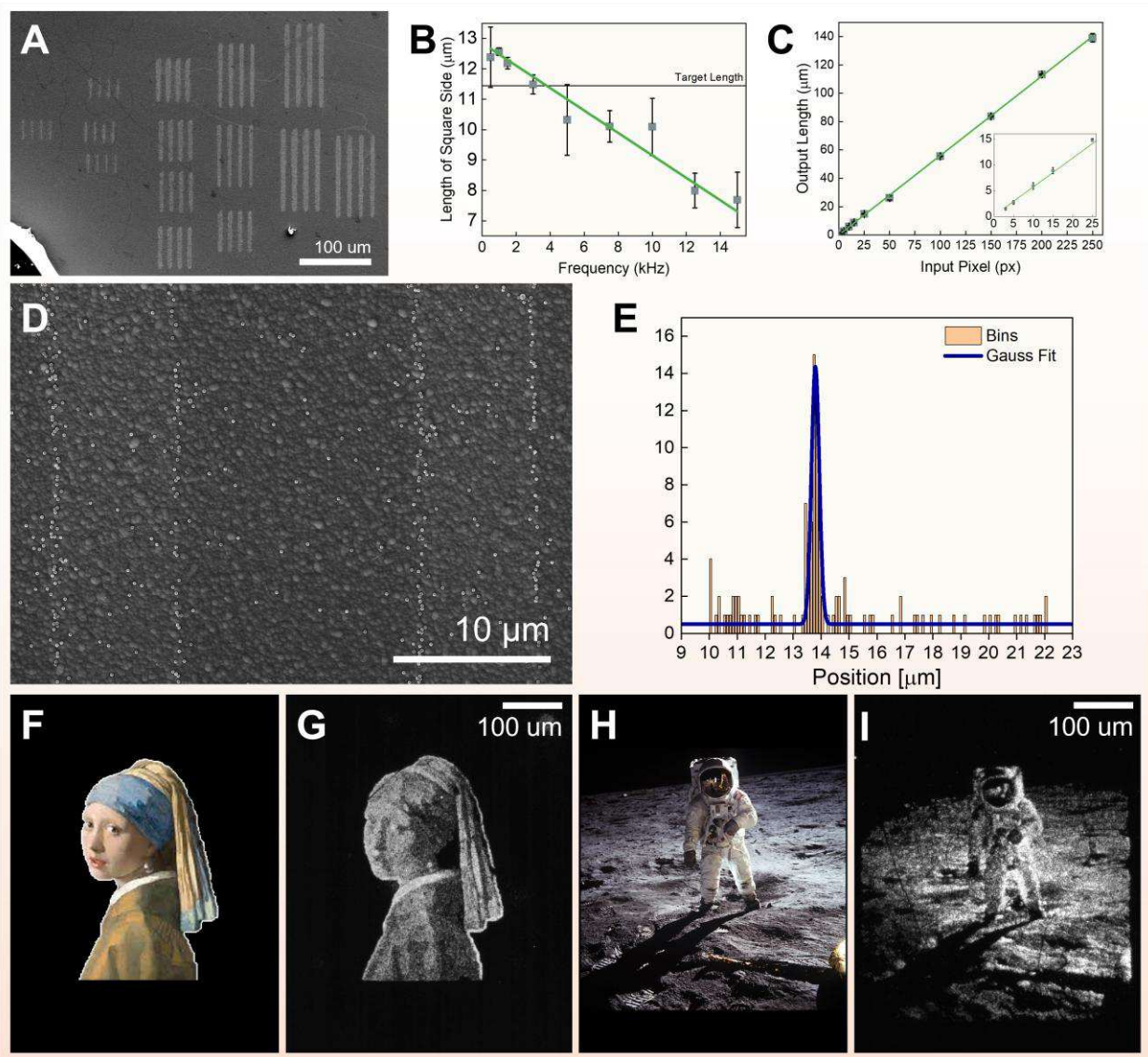


Figure 3. Printing accuracy of photorealistic nanopaintings. (A) Particles were deposited within controlled dimensions. (B) Frequency of the E-field is used to tune the deposition accuracy. (C) Characterization of deposition dimension versus projected pixel number at the optimized frequency (3 kHz). The stepwise dimensional change determined by the slope is 560 nm with an intercept at 110nm. (D) Lines obtained through combined deposition and etching, and (E) Precision analysis. The precision reaches a value of 139.2 ± 38.9 nm (standard mean). **Shaded image depositions through control of time and number of deposition cycles.** (F) Original and (G) particle-made image of Girl with Pearl Earring. (H) original and (I) particle-created picture of Apollo 13 Moon landing. These images are in the public domain.

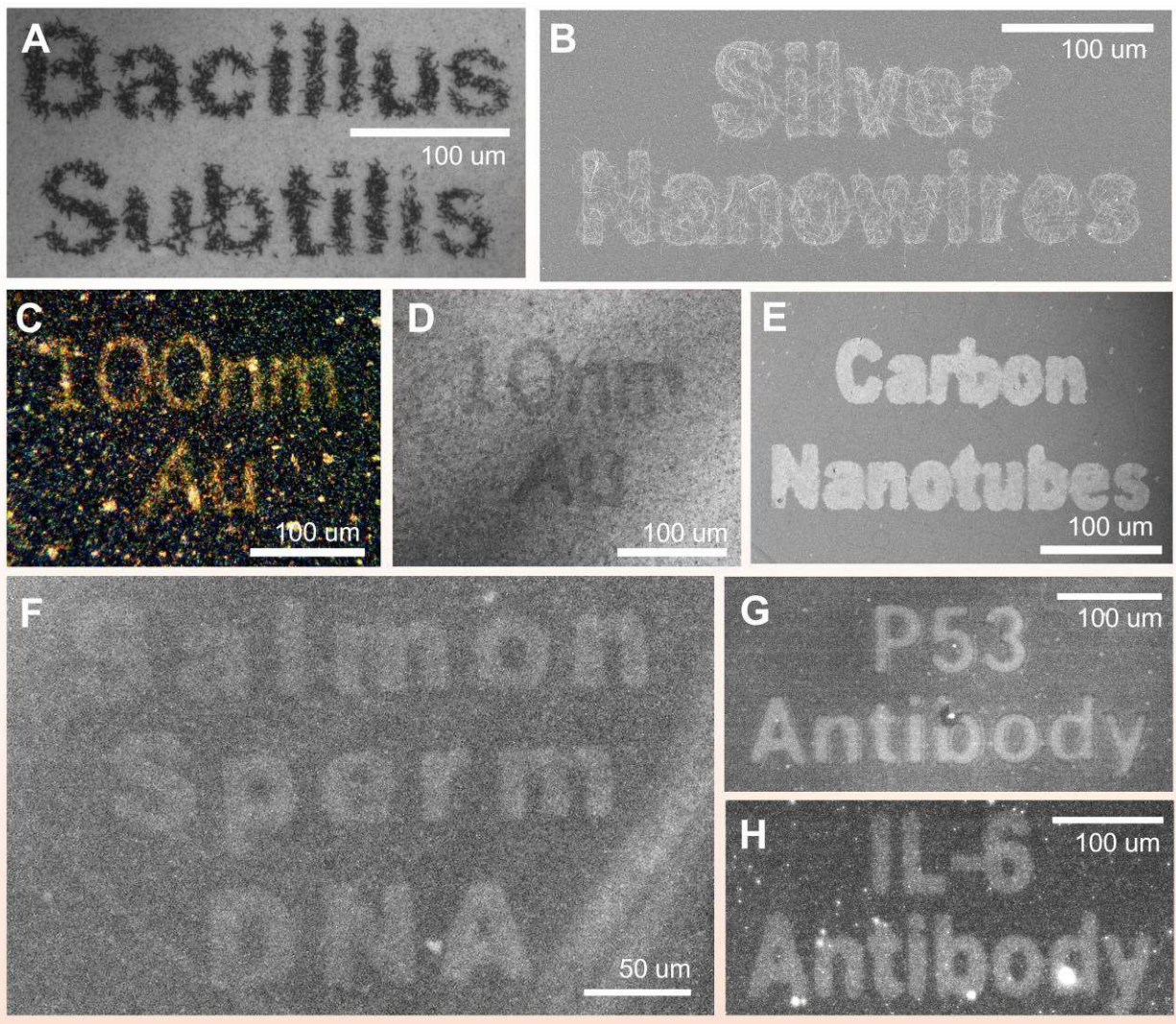


Figure 4. Deposition of inks made of diverse materials of distinct chemistry, shape, and size. Optical microscopy images of assembly of (A) *Bacillus Subtilis* cells and (B) silver nanowires. (C) Dark field image of 100 nm Au particles. (D) Optical image of 10 nm Au particles. SEM image of (E) carbon nanotubes. Fluorescent images of stained (F) salmon DNA (excitation/emission maximum wavelength: 535/617 nm), (G) P53 (excitation/emission maximum wavelength: 498/517nm) and (H) IL-6 antibody proteins (excitation/emission maximum wavelength: 565/576 nm).

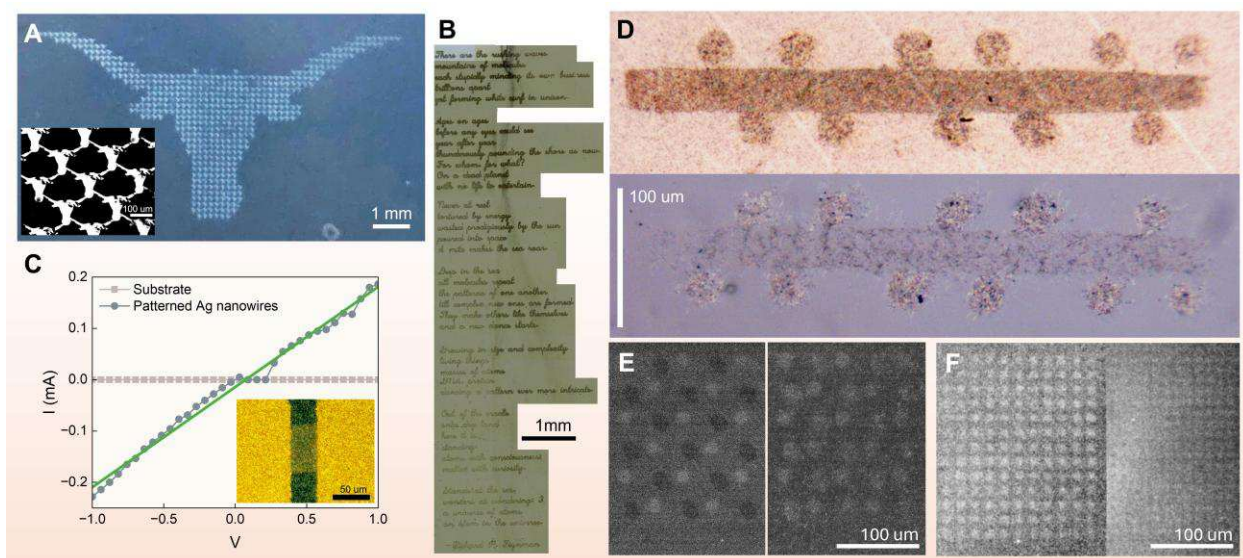


Figure 5. Performance demonstrations. Optical images of patterned structures (A, B, D) and fluorescent images of heterogeneous protein arrays (E and F). (A) cm-scale patterning of a Bevo consisting of (inset) smaller Bevo stamps (Bevo is UT-Austin's copyrighted logo), and (B) cm-scale writing of Richard Feynman's prose poem, 'An Atom in the Universe'. Ink: polystyrene nanospheres (200 nm), substrate: a-Si surface. (C) Measurement of the I-V curve and (inset) close-up image of Ag nanowires deposited between two gold pads. (D) Heterogeneous, spatially resolved particle patterning: a line made of PS spheres, with dots created on both sides made of Ag nanowires. The pattern made on a Si surface (upper panel) can be readily transferred to a gel (lower panel). (E) Multiplex protein arrays made of P53 (cancer biomarker, CoraLite 488) and IL-6 (cytokine, PE). (Left panel) P53 dots are fluorescent and IL-6 in dormant (500 nm shortpass excitation and 535/50 emission filter). (Right panel) both P53 and IL-6 are fluorescent (535/50 excitation and 610/75 emission filter). (F) High-density arrays of IL-6 to at least 5.70×10^5 spots/cm² (image on the right).

Methods

Materials

The following were purchased from Thermofisher Scientific: 200 nm carboxylate-terminated fluorescent PS spheres, with a surface charge of 0.3699 meq/g (technical data sheet), Sodium sulfate (anhydrous), glycerol, Salmon sperm DNA solution (UltrapureTM), IL-6 monoclonal antibody (MP5-20F3), and P53 monoclonal antibody (6C4B6). *Bacillus subtilis* (6051) was purchased from ATCC. Polydimethylsiloxane (Sylgard 184 silicone elastomer kit) was purchased from Dow Corning Corporation. Poly(diallyldimethylammonium chloride) (average Mw 200,000-350,000, 20 wt.% in H₂O) and Polyvinylpyrrolidone (average Mw 40,000) were purchased from Sigma Aldrich. Sodium chloride was purchased from Macron Chemicals. All chemicals were used without further purification. FTO (Fluorine-doped Tin Oxide) glass (0.7 mm thickness and 13 – 15 Ohm/Sq sheet resistance) used as the counter electrode were purchased from MSE Supplies (Product TEC 15). Sapphire glass–FTO glass–Hydrogen-terminated silicon substrates were fabricated at the University of Stuttgart on the FTO glass by depositing first SiN followed by a-Si:H using PEVCD. Total deposited film thickness was ~600nm.

Experimental setup, sample preparation and particle deposition

The sample was prepared by functionalizing the surface with PDDA or PDDA/PSS, with PDDA as the first layer coated on α -Si. The process followed standard layer-by-layer assembly protocols. In brief, the sample was first treated with UV/O₃ for 1 h to remove possible organic contaminants and to introduce surface hydroxyl groups. Next, the substrate was functionalized with charged polyelectrolyte layers made of alternating PDDA and PSS driven by charge overcompensation growth. The terminating layer was chosen based on the surface charge (negative or positive) of the particles that were to be deposited. Here, 4 wt% PDDA was applied for 3 m, washed with DI water and gently dried with N₂ gas, followed by 4 wt% PSS post-processed with the same washing and drying steps. Afterwards, a 100- μ m PDMS well (1.5 mm in diameter) was assembled on the substrate to define the working area and to serve as a container for Na₂SO₄ / nanoparticle solution and sealed by a second FTO substrate, which also works as the counter electrode.

For a typical experiment, a digital light projector, paired with a 532 nm continuous laser, projected images onto a photoconductive α -Si substrate (**Fig. 1A**). A light pattern controlled by the DLP, along with an AC electric field, was applied to the α -Si surface (**Fig. 1B**). After the continuous deposition of particles for at least 30 min, the solution was removed and the surface was gently washed with DI water. A corresponding particle deposition was examined and characterized.

For relatively simple 2D images, the E -field was applied with conditions tuned to obtain the desired DDP. For complex shaded images, the original image was first dissected into 8 sub-images in grey scale based on the brightness values. The 8 images were sequentially projected via the DLP, while an E -field was only applied along with an image projection. Following each E -field burst, a 3 m waiting period allowed particles to deposit, yielding contrast through variations in local particle density, before beginning the next deposition.

Characterization

Unless specified otherwise, an $18\ \mu\text{m} \times 18\ \mu\text{m}$ square ($30\ \text{px} \times 30\ \text{px}$) laser pattern, a 0.75 M Na_2SO_4 solution in a $100\ \mu\text{m}$ PDMS well, with an $\sim 800\ \text{mW}/\text{cm}^2$ laser intensity and a pulse of 12 Vpp, 1.5 kHz AC *E*-field applied for 200 ms was used as the standard condition for the characterization of the deposition efficiency. The AC *E*-field time was controlled by the number of cycles in the function generator. The electrolyte solutions were prepared before use from a 1.0 M Na_2SO_4 stock solution and mixed with colloidal particles to get the desired particle and salt concentration.

Silver nanowire synthesis

For silver nanowire synthesis, two stock solutions were prepared: solution 1 consists of 1.25 g of PVP (Mw=40k) in 50 mL glycerol mixed under gentle stirring at $90\ ^\circ\text{C}$ until complete dissolution. Solution 2 was prepared by dissolving 37.5 mg of NaCl into 6.25 mL of glycerol and 0.3125 mL of DI water and adding 0.6375 g of AgNO_3 . Solution 2 was added to solution 1 under gentle stirring, followed with heating at $160\ ^\circ\text{C}$ for 16 h. After removing the solution from the flask, the resulting solution was mixed 1:1 with ethanol to decrease the viscosity. The solution was then washed 3 times at 2000 RPM, and one additional time at 1000 RPM with ethanol.

Multi-material deposition

For the deposition of graphene oxide (GO) nanosheets, 100 nm Au nanospheres, as well as salmon sperm DNA, P53 and IL-6 antibodies, the surface was first treated with 3x PDDA/PSS layers before applying *E*-field bursts. For GO nanosheets, 5 *E*-field bursts (1.5 kHz, 200 ms, 12 Vpp, every 30 s) were applied for the deposition process, in a 1 GO wt% - 0.5 M Na_2SO_4 solution. For *B. Subtilis* deposition, 5 bilayers of PDDA/PSS for surface functionalization and 10 *E*-field bursts (1.5 kHz, 200 ms, 12 Vpp, every 5 s) were applied with a concentrated bacterium (1.075×10^8 cells/mL) - 0.75 M Na_2SO_4 solution. For 100 nm and 10 nm Au nanoparticle deposition, 40 *E*-field bursts (3 kHz, 200ms, 10 Vpp, 30 s) were applied, with a 0.05 wt% - 0.5 M Na_2SO_4 solution. For salmon sperm DNA, P53, and IL-6 antibodies, 30 *E*-field bursts (1.5 kHz, 200ms, 10 Vpp, every 30 s) were applied. The original solutions were mixed with a 2x PBS solution 1:1 to create a 1x PBS solution before use. For silver nanowire and carbon nanotube deposition, solution exchange-based particle deposition methods were used, as depicted in **Fig. S9**. A 0.75 M Na_2SO_4 solution served for the ionic solution, 3x PDDA/PSS bilayers, and 10 *E*-field bursts (1.5 kHz, 200 ms, 10 Vpp, every 30 s) were applied.

Bacillus subtilis preparation and viability assessment

Bacillus subtilis cells were prepared and used according to standard handling procedures with some modifications. First, a nutrient broth was prepared by mixing broth powder at a ratio of 8 g:1000 mL of DI water, put in a glass vial, and autoclaved to ensure sterilization. A single tube of broth (5 to 6 mL) was prepared, and 0.5 to 1 mL of broth was first used to rehydrate a freeze-dried vial of *Bacillus subtilis* provided by ATCC. The aliquot was transferred back to the original tube and mixed well. Several drops of the suspension ($\sim 0.5\ \text{mL}$) were mixed with other broth tubes as needed and incubated at $30\ ^\circ\text{C}$ for 24 h, while shaking with a vortex mixer. The tubes were removed

and stored in a fridge for use, usually within a few days. The cells are used by first centrifugation with DI water 5 times, with 4000 RPM for 20 m.

Following deposition via the method above, *Bacillus subtilis* cells were stained with propidium iodide (5 $\mu\text{L}/\text{mL}$) for 15 m in the dark at room temperature. The sample was then rinsed with DI water and air-dried for fluorescence microscopy. Control experiments were also performed on dead cells that were treated with 70% ethanol for 5 m and stained with propidium iodide under identical conditions.

Fabrication of PDDA and PDDA/PSS coated PS spheres

For the fabrication of PDDA and PDDA/PSS coated PS spheres, we use a modified method based on reported work.²¹ Briefly, we prepare a 0.2 wt% PS sphere solution and a 20% PDDA wt% / 0.5 M NaCl solution. We mix the PS sphere solution with the PDDA/NaCl solution at a ratio of 3:1 and shake the mixture for 24 h. Afterwards, we collect the coated spheres via centrifugation and wash it with DI water for 3 times. The process is repeated for the coating of an additional PSS coating, using a 20% PSS wt% / 0.5 M NaCl solution.

Hydrogel fabrication used for pattern transfer

A gel precursor solution was formulated by dissolving 0.71 mL of [3-(methacryloylamino)propyl]trimethylammonium chloride solution, 5 mL of acrylic acid, 10 mg of N,N'-methylenebisacrylamide (BIS), and 0.02 g of the photoinitiator Irgacure 2959 in 5 mL of a solvent made of DI water and glycerol mixture. Upon complete homogenization, the solution was degassed by purging with nitrogen (N_2) gas for 60 m to remove dissolved oxygen and air bubbles. The precursor was then introduced into a polydimethylsiloxane (PDMS) mold separated by a 2 mm spacer. Photopolymerization was subsequently initiated via UV exposure at an intensity of 60 mW/cm^2 for 20 m.

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