Nanoscale 4-D printing technique may speed development of new therapeutics

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The above Lady Liberty image illustrates the capabilities of polymer brush hypersurface photolithography. Fluorescent polymer brushes were printed from initiators on the surface, and variations in color densities correspond to differences in polymer heights, which can be controlled independently at each pixel in the image. Credit: Advanced Science Research Center

Researchers at the Advanced Science Research Center at The Graduate Center, CUNY (CUNY ASRC) and Northwestern University have created a 4-D printer capable of constructing patterned surfaces that recreate the complexity of cell surfaces. The technology, detailed in a newly published paper in *Nature Communications*, allows scientists to combine organic chemistry, surface science, and nanolithography to construct precisely designed nanopatterned surfaces that are decorated with delicate organic or biological molecules. The surfaces will have a wide variety of uses, including in drug research, biosensor development, and advanced optics. Importantly, this technology can create surfaces with different materials, and these materials can be patterned across the surface without the use of expensive photomasks or tedious clean room processes.

"I am often asked if I've used this instrument to print a specific chemical or prepare a particular system," said the study's primary investigator Adam Braunschweig, a faculty member with the CUNY ASRC Nanoscience Initiative and The Graduate Center and Hunter College Chemistry Departments. "My response is that we've created a new tool for performing organic chemistry on surfaces, and its usage and application are only limited by the imagination of the user and their knowledge of organic chemistry."

The printing method, called Polymer Brush Hypersurface Photolithography, combines microfluidics, organic photochemistry, and advanced nanolithography to create a mask-free printer capable of preparing multiplexed arrays of delicate organic and biological matter. The novel system overcomes a number of limitations present in other biomaterial printing techniques, allowing researchers to create 4-D objects with precisely structured matter and tailored chemical composition at each voxel—a capability the authors refer to as "hypersurface lithography".

"Researchers have been working toward using lithographic techniques to pattern surfaces with biomolecules, but to date we haven't developed a system sophisticated enough to construct something as complicated as a cell surface," said Daniel Valles, a Graduate Center, CUNY doctoral student in Braunschweig's lab. "We envision using this system to assemble synthetic cells that allow researchers to replicate and understand the interactions that occur on living cells, which will lead to the rapid development of medicines and other bioinspired technologies."

As proof-of-concept, the researchers printed polymer brush patterns using precise doses of light to control the polymer height at each pixel. As illustrated by the Lady Liberty image, coordination between the microfluidics and the light source control the chemical composition at each pixel.

"Polymer chemistry provides such a powerful set of tools, and innovations in polymer chemistry have been major drivers of technology throughout the last century," said the paper's co-author Nathan Gianneschi, who is the Jacob & Rosaline Cohn Professor of Chemistry, Materials Science & Engineering, and Biomedical Engineering at Northwestern University. "This work extends this innovation to the interfaces where arbitrary structures can be made in a highly controlled way, and in a way that allows us to characterize what we have made and to generalize it to other polymers."

"This paper is a tour-de force demonstration of what can be done with massively parallel lithography tools," said Chad Mirkin, George B. Rathmann, Professor of Chemistry and the director of the International Institute for Nanotechnology at Northwestern University's Weinberg College of Arts and Sciences, who is not a coauthor of the study. "The co-authors have created a powerful set of capabilities that should be heavily utilized across the chemistry, material science, and biological communities."

The researchers plan to continue development of this novel printing platform to increase system speed, reduce pixel dimensions, and develop new chemistries for increasing the scope of materials that can be patterned. Currently, they are using the patterns created by this platform to understand the subtle interactions that dictate recognition in biological systems.

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