Free-space nanoprinting beyond optical limits to create 4D functional structures

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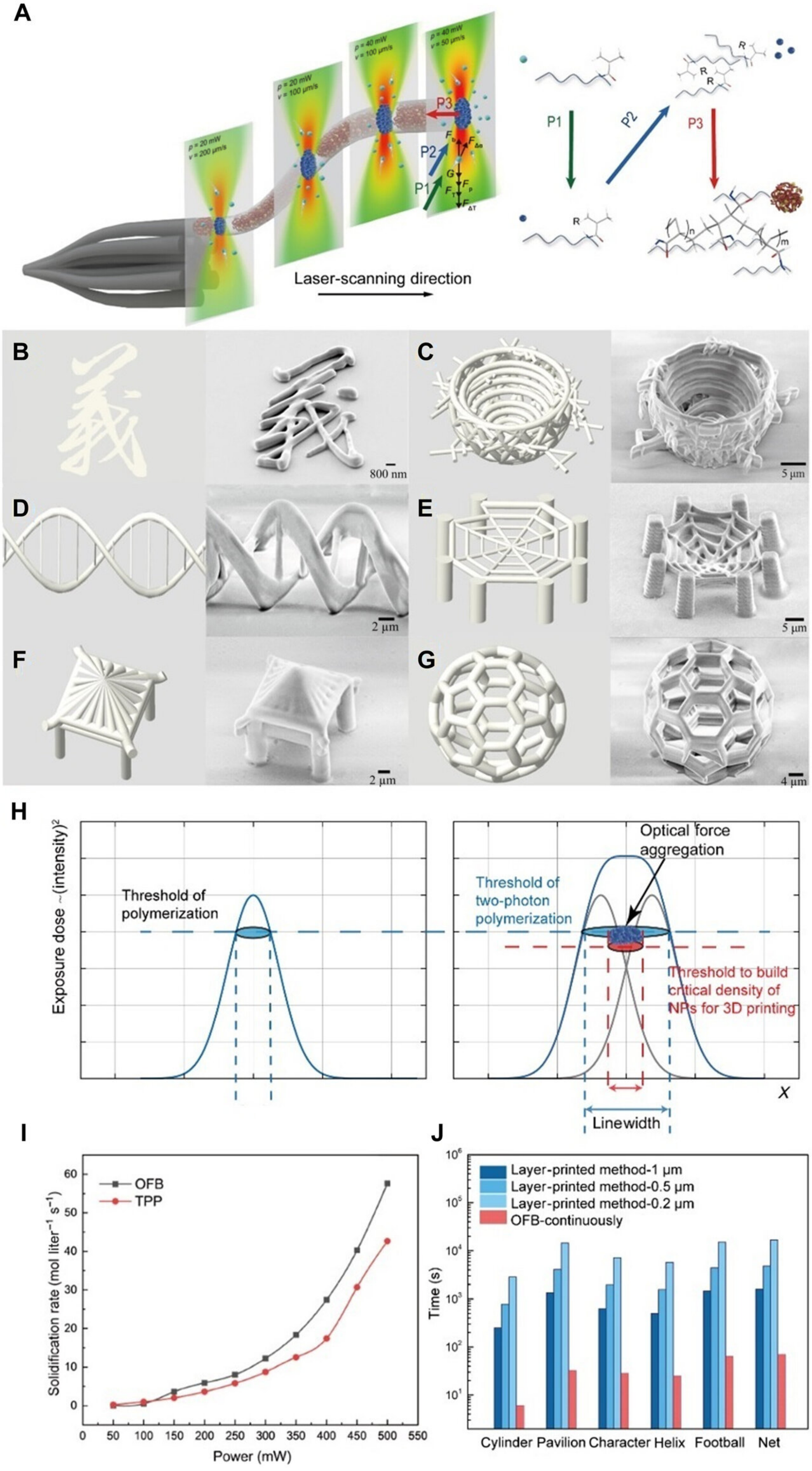

A
p = 20 mW
v = 200 µm/s
p = 20 mW
v = 100 µm/s
p = 40 mW
v = 100 µm/s
p = 40 mW
v = 50 µm/s
P3
P2
P1
F_b
$F_{\Delta\alpha}$
G
F_p
F_T
$F_{\Delta T}$
Laser-scanning direction
P1
P2
P3
R
R
R
R
n
m
B
800 nm
C
5 µm
D
2 µm
E
5 µm
F
2 µm
G
4 µm
H
Exposure dose ~(intensity)^2
Threshold of
polymerization
Optical force
aggregation
Threshold of
two-photon
polymerization
Threshold to build
critical density of
NPs for 3D printing
X
Linewidth
I
Solidification rate (mol liter^{-1} s^{-1})
Power (mW)
OFB
TPP
0
10
20
30
40
50
60
0
50
100
150
200
250
300
350
400
450
500
550
J
Time (s)
10^1
10^2
10^3
10^4
10^5
10^6
Layer-printed method-1 µm
Layer-printed method-0.5 µm
Layer-printed method-0.2 µm
OFB-continuously
Cylinder
Pavilion
Character
Helix
Football
Net

Process scheme, demonstration, and mechanism of OFB. (A) Process diagram of OFB free-space painting. (B) Scanning electron microscopy (SEM) images of calligraphy (follow the strokes of Chinese characters). The SEM images of 3D structures, which are bird's nest (C), DNA (D), spider web (E), pavilion (F), and C60 (G). (H) Linewidths and required solidification thresholds for different principles. NPs, nanoparticles. (I) Relationship between solidification rate and laser power. (J) Processing time of the layered printing method and OFB. TPP, two-photon polymerization. Credit: *Science Advances*, DOI: 10.1126/sciadv.adg0300

Two-photon polymerization is a potential method for nanofabrication to integrate nanomaterials based on femtosecond laser-based methods. Challenges in the field of 3D nanoprinting include slow layer-by-layer printing and limited material options as a result of laser-matter interactions.

In a new report now on *Science Advances*, Chenqi Yi and a team of scientists in Technology Sciences, Medicine, and Industrial Engineering at the Wuhan University China and the Purdue University U.S., showed a new 3D nanoprinting approach known as free-space nanoprinting by using an optical force brush.

This concept allowed them to develop precise and spatial writing paths beyond optical limits to form 4D functional structures. The method facilitated the rapid aggregation and solidification of radicals to facilitate polymerization with increased sensitivity to laser energy, to provide high accuracy, free-space painting much like Chinese brush painting on paper.

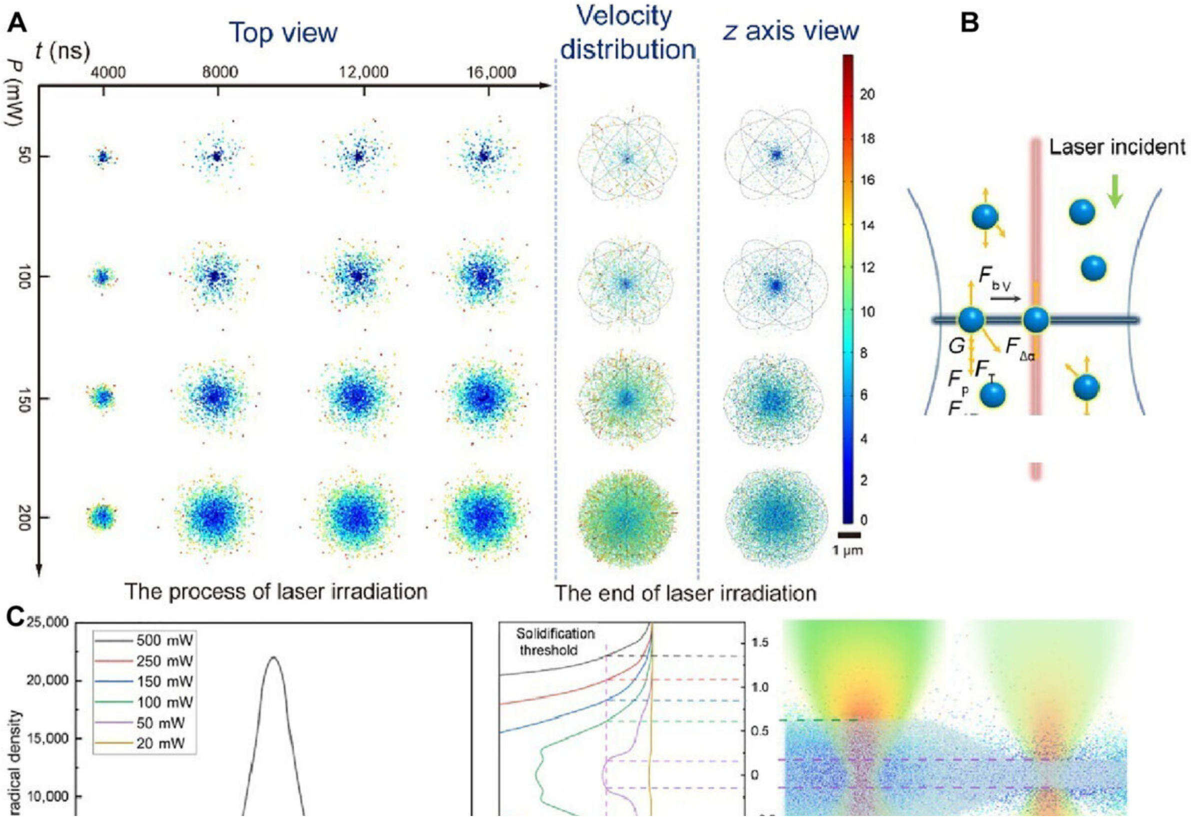
Using the method, they increased the printing speed to successfully print a variety of bionic muscle models derived from 4D nanostructures with tunable mechanical properties in response to electrical signals with excellent biocompatibility.

Device engineering

Nanodevices and nanostructures can be engineered at high resolution and speed to form next-generation products. The semiconductor industry can use lithography, deposition and etching to create 3D structures from a variety of materials, although the high processing cost and limited selection of materials can affect flexible fabrication of 3D structures of functional materials.

Materials scientists have used two-photon polymerization-based femtosecond laser direct writing to create complex 3D nanostructures using micro/nanopolymers to form photonic quasicrystals, metamaterials, and nanoarchitectures.

However, this method is still limited by a slow speed of printing, stairwise surface textures and limited photocurable materials. In this work, Yi et al. examined free-space laser writing to analyze how it yields photochemical forces to accomplish optical force brush-based nanopainting.



Process modeling, principles, and parametric study of OFB. (A) Complete process of laser irradiation with free radicals in solution by simulation, particle distribution state (left) at laser power and time, respectively, at 50, 100, 150, and 200 mW and 4000, 8000, 12,000, and 16,000 ns; velocity distribution (middle) at the end of laser irradiation; and particle distribution state (right) in z-axis at the end of laser irradiation. (B) Forces on free radicals at the laser beam waist radius. (C) Relation between free radical density and relative distance and different power versus linewidth at solidification threshold. (D) Simulation results and SEM images of an OFB process at a scan speed of 10 μm/s and varying laser intensities for a rod with continuous varying diameters from 120 to 400 nm and continuous beads with abrupt varying diameters from 200 to 600 nm. The relation between particle number and time (E), power (F), and the TPA cross-section (G). (H) Theoretical values of the finest linewidths that can be achieved with different particle sizes. (I) Difference of free radical density between TPP and OFB. The relation between width and height and power (J), speed (K), and defocusing distance around the substrate (L). Credit: *Science Advances*, DOI: 10.1126/sciadv.adg0300

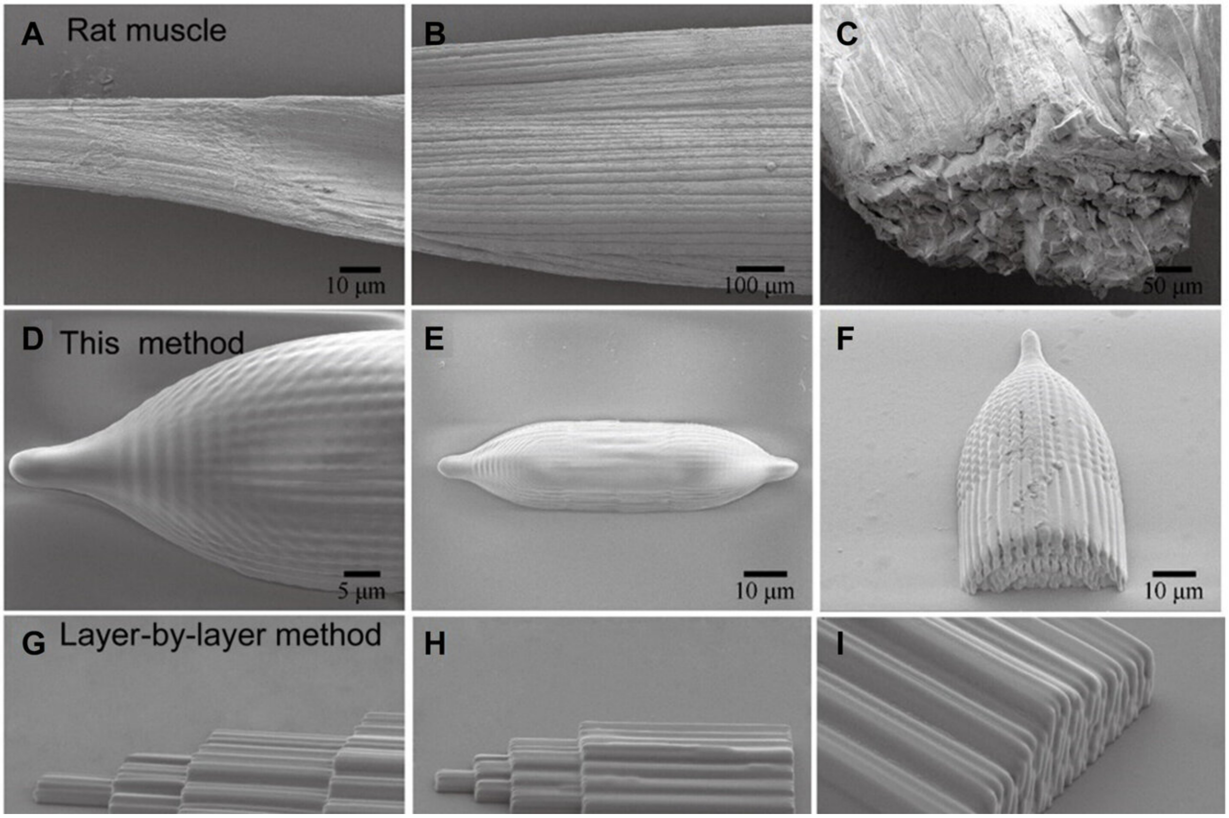
Free-space painting with a femtosecond laser

When timescales reach the femtosecond, molecules can absorb the photon for excitation into an electronically higher state with a repulsive potential energy surface, to generate free radicals.

Scientists can use multiphoton absorption mechanisms to absorb ultrashort pulse photon energy in molecules and activate electron transition between the ground and excited state. Yi and colleagues irradiated active radicals with a femtosecond laser for the optical forces to rapidly aggregate them and synthesize into macromolecules to quickly complete solidification without post-processing, while minimizing thermal motion of the solvent molecules.

The researchers developed a hydrogel-based ink as a photoswitch activated upon femtosecond laser writing through two-photon absorption, where radicals in the gel absorbed photon energy from the femtosecond laser. While free radicals formed binding energy in the molecules, the team connected the long-chain molecules to different functional groups for a variety of applications.

The printable hydrogel-based ink offered highly biocompatible, elastic, and flexible conditions for multiple applications of free-space printable nanostructures in biomedicine.



Printing nested muscles and studying their mechanical properties. (A to C) SEM images of the muscle belly and tendons at the rat leg. (D to F) SEM images of the expansile and shrinkable striated muscle written by a femtosecond pulse laser. (G to I) SEM images of the expansile and shrinkable striated muscle printed by layer-by-layer method. (J) Relationship between concentration and Young's modulus/hardness. (M1, M2, M3, and M4 represent the concentration of 10, 20, 30, and 40%, respectively, using OFB. LM3 represents the concentration of 30% using layer-by-layer method.) (K) Results of nanoindentation experiment. (L) Stress distribution of the muscle fabricated by OFB and layer printing. (M) Simulation of stress-strain curves for muscle fabricated by OFB and layer printing. (N) Stress distribution of the single overhanging beams fabricated by two different methods. Credit: *Science Advances*, DOI: 10.1126/sciadv.adg0300

Mechanism-of-action

The laser beam moved freely in solution much like a pen in space and involved three steps: activation, aggregation, and solidification of free radicals. The scientists cultured the polymerization rates for two photon polymerization and optical force brush separately with a multiphysics model.

The approach greatly improved the efficiency of the writing structure through a layer-by-layer, line-by-line printing method, where the number of layers directly correlated with the thickness resolution. The method also facilitated greatly improved 3D nanostructure writing efficiency and accuracy. They refined the experimental results to show how the optical force applied to the free radicals were directly related to the number of pulses, the intensity of the laser-field and its absorption coefficient.

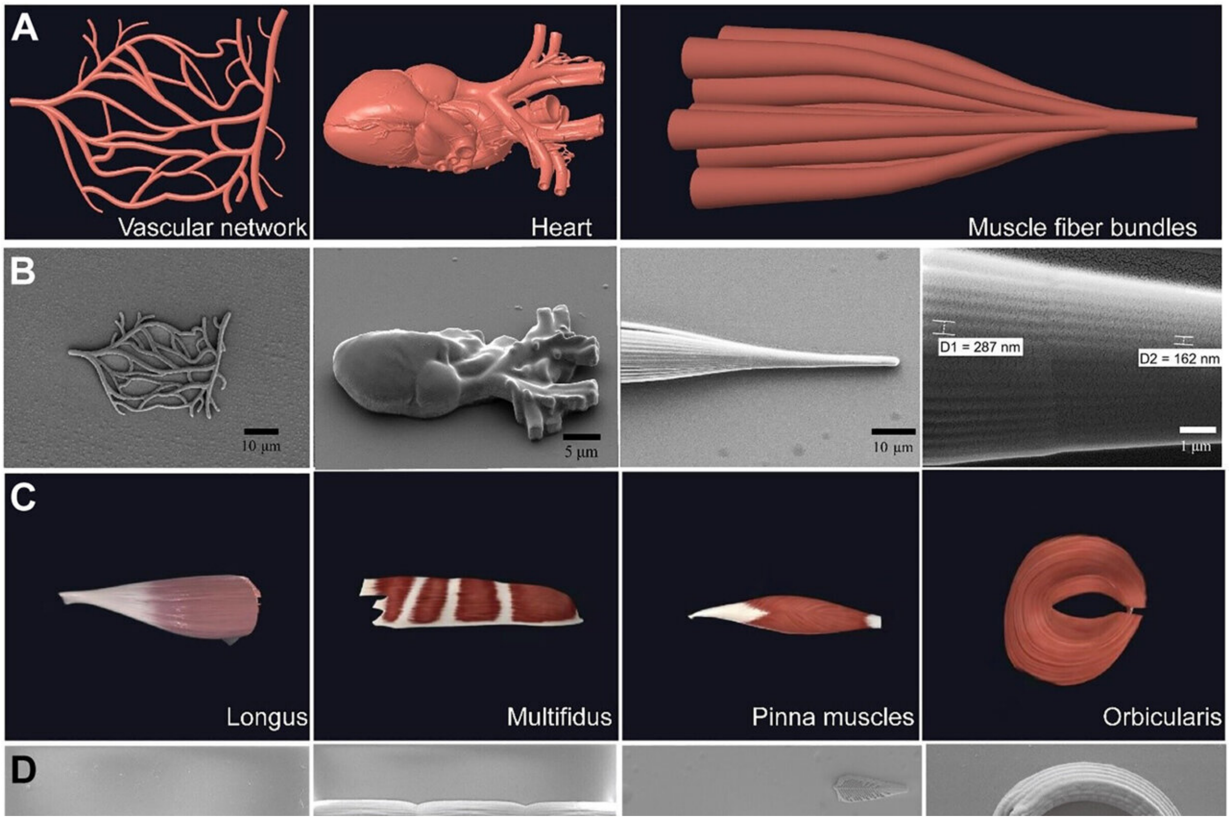
As the femtosecond laser irradiated the material, the kinetic energy from the photons were exchanged with the active free radicals to move by the optical force, eventually resulting in sharp and high-resolution 3D nanoprinting. The team studied the fundamental mechanisms underlying these processes through numerical simulations via multiphysics simulations to examine the motion and composite process of the radicals.

Engineering a nested muscle system

This method allowed Yi and colleagues to print muscle, belly, and tendon tissues composed of multilayered nesting of fibers and fiber bundles that are difficult to print via traditional 3D printing methods. The team printed the muscle's internal and external shape, while activating its movement via electrical stimulation with a functional hydrogel-based ink. This results in the initial instance of simultaneously achieving both structural and functional bionic nanoprinting.

The scientists demonstrated the structure of rat hamstring's tendon and belly printed by optical force brush and layer-by-layer method. The methods showed the potential to print multilayer structures in 3D space, while the muscle fiber thickness turned thin to thick to impart a variety of functionalities.

The researchers showed the possibility of completely implanting the micro- and nanostructures into an organism to realize functional and structural biostructures at this scale. This free-space printing method through the optical force brush technique opens possibilities to apply multifunctional micro and nanostructures in biology.



Printing vascular network, heart, and muscle fiber bundles, and studying electrical-mechanical responses. (A) Schematic diagram of the vascular network, heart, and muscle fiber bundles. (B) Femtosecond laser–printed models of the vascular network, heart, and muscle fiber bundles. (C) Schematic diagram of the orbicularis, longus, multifidus, and pinna muscles. (D) Femtosecond laser–printed models of the rhomboid, longus, multifidus, and pinna muscles. The schematic diastolic contractile motion of a bionic long muscle printed differently scale (E), 3D vessel (F), and heart pumping model under electrical stimulation (G). Relation between voltage and swelling radio (H); the inset image shows the electroresponse experiment of GERM at 11 V, cycling stability (I), and response time (J). (K) CCK-8 experiment of 3t3 cells in nutrient solution and GERM solution. Credit: *Science Advances*, DOI: 10.1126/sciadv.adg0300

Outlook

In this way Chenqi Yi and colleagues used optical force brush as a method that integrated femtosecond laser paintbrush to print functional structures with true 3D freedom. The optical force brush has unique capabilities with an underlying process of optical force enabled nanopainting, to facilitate an ultrahigh solidification rate, low solidification threshold, and high sensitivity to laser to precisely regulate the printing process. The sensitivity allowed them to accurately regulate and create intricate structures with fine details.

This resulted in true 3D printing freedom for continuous printing and seamless transitions between different planes. The work further explored the mechanisms of optical forces for nanoprinting in free space during optical force brush use. This included interactions of the femtosecond laser with free radicals in the hydrogel ink photoswitch; a mechanism also explored through numerical simulations.

The research emphasized the capacity of the optical force brush to develop bionic functional structures and pave the way for additional studies in tissue engineering and regenerative medicine with breakthrough properties.

More information: Yi C. et al, Optical force brush enabled free-space

painting of 4D functional structures, *Science Advances* (2023). DOI: 10.1126/sciadv.adg0300

Ergin T. et al. Three-dimensional invisibility cloak at optical wavelengths, *Science* (2023). DOI: 10.1126/science.1186351

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