Three-dimensional (3-D) printing or additive manufacture (AM) is a popular technique that has presently attracted tremendous attention as a promising method to revolutionize design and manufacture. Researchers
have expanded its applications from rapid prototyping to tissue engineering, electronic devices, soft robotics and high-performance metamaterials, but most 3-D printing techniques only use a single material to print parts or form components using multiple discrete properties with complex mechanical gradients that cannot be cohesively controlled.

Comparatively, most natural structures such as fish scales and tendon-to-bone are made of a variety of materials with markedly different properties that function together. As an alternative, functionally graded materials (FGM) have drawn substantial recent research interest to improve the mechanical robustness and flow tolerance of substrates. This allows for FGM 3-D printing with widely tunable printing properties in a single process, which has increasing importance in materials science.

In a recent study, now published in Science Advances, Xiao Kuang and colleagues at the interdisciplinary departments of Mechanical Engineering, Nanobiomechanics and Advanced Structure Technology in China and Canada presented a single-vat grayscale digital processing (gDLP) 3-D printing method. In the work, they used grayscale light patterns and a two-stage curing ink to obtain functionally graded materials (FGMs) with high resolution and mechanical gradients up to three orders of magnitude. To demonstrate the method, they developed complex 2-D and 3-D lattices with controlled buckling and deformation sequences, metamaterials with a negative Poisson's ratio, presurgical models with varying stiffness, composites for 4-D printing and a method to anti-counterfeit 3-D printing.

3-D printing techniques at a glance

For advanced 3-D printing applications, researchers had demonstrated the PolyJet method with multiple inkjet printheads to simultaneously deposit different materials on the printing bed. However, the method had
some notable drawbacks including high equipment cost, rigorous resin requirements, limited material choices and a relatively low resolution multimaterial printing mode.

![Diagram of g-DLP 3D printing of FGM via two-stage curing](https://www.physorg.com/science-news/)

g-DLP 3D printing of FGM via two-stage curing. (A) Schematics showing the g-DLP printing of graded material via a two-stage curing process. A hybrid ink was used for DLP 3D printing first followed by thermal curing the printed part in a heating oven. (B) Predicted normalized conversion of cured material under different grayscale light with only one exposure (solid lines) and multiexposure (dashed lines) by the model using the exposure time of 20 s and curing thickness of 60 μm per layer. (C) Gel fraction of hybrid ink after the first- and second-stage curing. (D) Tensile stress-strain curves of printed materials using different grayscale during printing (sample size, >3). (E) Young’s modulus and glass
Researchers therefore pursued many other 3-D printing methods including fused filament fabrication and direct ink writing, although these techniques were not pursued further due to slow printing rates. When they used digital light processing (DLP) based on digital micromirror devices (DMDs) as a rapid, high-resolution AM approach, the polymer resins cured abruptly and were too fast in comparison. While methods in the past demonstrated limited capacity to practically manufacture functionally graded materials with tunable properties. In a more recent technique, scientists developed continuous liquid interface production (CLIP) as a true breakthrough to offer the fastest 3-D printing technology close to the production level; also relevant to the present work.

Introducing g-DLP (grayscale digital light printing) to develop digital materials

In the present work, Kuang et al. developed a new, two-stage curing hybrid ink system in a single-vat to achieve grayscale digital light processing (g-DLP) 3-D printing. They synthesized the hybrid ink using bisphenol A ethoxylate diacrylate (BPADA), glycidyl methacrylate (GMA), a diamine crosslinker, n-butyl acrylate (BA), photoinitiators and photoabsorbers. In the experimental setup, they used monochromatic light intensity settings to cure the resin layer-by-layer, analogous to the CLIP technique.
For this, they used an oxygen permeable membrane to separate the cured section from the window for faster printing. The scientists first sliced the designed structure into images corresponding to individual printing layers, followed by processing each image with a MATLAB code to generate the grayscale distribution containing the desired properties. They then passed the images of individual layers with grayscale patterns to the UV projector for printing.
FTIR spectra showing the two-stage curing for practical printing. (A) The hybrid ink using a G70 light for printing. (B) The enlarged area showing the double bond evolution during the two-stage curing. (C) The enlarged area showing the epoxide group evolution during the two-stage cure. The hybrid ink was cured forming a network by photopolymerization. The following thermal curing results in both the decrease of the double bond and epoxide group. The residual monomer and dangling functional groups, such as end-terminated double bond and dangling epoxide group, would be further reacted by the diamine crosslinker to form more linkages. Credit: Science Advances, doi: 10.1126/sciadv.aav5790.

During the experiments they induced radical-based photopolymerization to form the polymer network and printed structure, and showed that the crosslinking density and modulus of the material decreased with increased grayscale percentage. In the work, the GMA monomer and the diamine crosslinker played a critical role in the thermal curing process and determined the effects of grayscale photopolymerization of the hybrid ink.

Kuang et al. showed the method's nonlinear dependence on light intensity and developed reaction kinetics models to examine time-dependent light curation. The scientists prevented light leakage-based resolution reduction in the setup by adjusting the software using an optical system with smaller magnification, or via increased photoabsorber content to improve the resolution of printed materials.

They monitored the chemical structure evolution during photocuration with Fourier Transform Infrared Spectroscopy (FTIR) and tested the mechanical and thermomechanical properties of the materials. Kuang et al. included tests on the Young's modulus and glass transition temperature (Tg) as functions of the grayscale percentage to characterize the new material. Since the method offered the potential to create digital
materials by controlling the grayscale, the scientists followed the initial experiments by printing samples of simple geometry with graded properties.

They also used finite element modeling (FEM) simulations to predict the graded properties and deformation rates of the architectures to enable a continuous gradient pattern. This allowed Kuang et al. to manufacture a continuously graded material that bent with continuously changing curvature on application of a point load. The scientists showed that the experimental results agreed with the simulation on single-point bending behavior.

Compression of 2D lattice

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Compression of 2D lattice metamaterial. The movie play speed is 5X fast-forward. The FEM simulation predicts the experimental results well. Credit: Science Advances, doi: 10.1126/sciadv.aav5790.
Printing graded metamaterials with g-DLP (grayscale digital light printing) for multifunctional materials

The scientists then used g-DLP to explore the design and fabrication of lattice and cellular structures in the study. For this they first printed a 2-D lattice architecture matrix with a grayscale pattern of a triangular region and a blank space beneath it. During compression studies the deformation only occurred in the triangular region with soft material, where the space under the triangular band did not deform to provide a shield that protected any material under this region. The scientists showed that such controlled buckling could enhance the energy absorption capability – verified using the stable stress drop in the accompanying stress-strain curve. As before, the FEM simulation accurately predicted the experimental results.

Kuang et al. then designed a 3-D lattice architecture, where they assigned each layer with a different grayscale value to obtain a clean, printed lattice with high resolution. The architecture of the 3-D lattice showed sequential deformation behavior – with applications in energy absorption. The scientists can harness the graded material properties of the g-DLP printing technique to manufacture pre-surgical models.

For instance, using the method they printed tissue-like structures with bioinspired mimicry to create bone (with grayscale $G_0$), soft muscle ($G_{85}$) and skin ($G_{70}$) structures. They were also able to design a small-scale artificial limb structure with soft muscle ($G_{85}$) and hard bone ($G_0$), which was printed using the g-DLP method. Kuang et al. propose using the technique to engineer customized architectures with patient-specific physical properties to form presurgical models in tissue engineering for regenerative medicine.
LEFT: Applications of g-DLP–printed composites for sequential SMP components and 4D printing. (A) Design and print part of a helical SMP component with increasing grayscale level on the hinge from G20 to G80. (B) Snapshot showing the sequential shape recovery process of the helical SMP component with graded hinge materials in hot water (~60°C). (C) Design and print part of a sequential SMP as an artificial arm. (D and E) Snapshot showing sequential shape recovery of a single artificial arm (D) and artificial arms for soft robotics to lift a stick (E) by a heat gun. (F) Schematic of a shape-shifting film by cold drawing of printed lamina fiber-reinforced composites with asymmetric fiber distribution and recovery process. (G) Pictures of the printed strip with 0° of fiber orientation: original shape and bending shapes by applied stretching strain at room temperature. Scale bars, 1 cm. Photo credit: Xiao Kuang, Georgia Tech. RIGHT: Encryption via diffusion-assisted coloring for graded materials. (A) Two-stage cured films enabled by a continuous gradient grayscale pattern (inside G80 to outside G0) across the radius were immersed in fluorescein (B) or dye (C) solution followed by washing and drying to visualize the grayscale pattern by UV light and visible light, respectively. (D) Coloring kinetics of the film in (A) by analyzing the red value (RGB color) of the images. (E) Two-stage cured films using the design of staggered discrete gradient grayscale (G80 and G0) concentric circle pattern. The samples in (E) were colored using cyan dye solution and corresponding red value of image across the sample (F) as well as fluorescein solution and the green value of image across the section (G). (H) Design of a grayscale pattern for QR code and corresponding images of the colored pattern using fluorescein under UV light. (I) Design of a
4-D printing shape memory polymers (SMPs) and encryption assisted by diffusion

The g-DLP-printed material could be programmed or tuned across a temperature range ($T_g$) from $14^0$ C to $68^0$ C for use as a shape memory polymer (SMP), which exhibited actuation at different temperatures. To demonstrate this, they engineered a helical pattern, which when heated to $60^0$ C opened to form a straight line, followed by cooling in ice to reverse to the original conformation. However, if the helical structures were printed with the same grayscale (G20), all hinges recovered their shape simultaneously at the same speed, albeit without shape recovery to the original architecture. The scientists then investigated the applications of such SMPs by developing a robotic arm.

Since the graded materials had different moduli and $T_g$, this led to different diffusivity in the experimental system. The scientists were therefore able to view the diverse grayscale patterns with a variety of coloring dyes. Kuang et al. propose using fluorescein coloring for encryption and anti-counterfeiting applications. For instance, when the scientists included a QR (quick response) code into a film using grayscale patterning for printing, followed by fluorescein treatment, the pattern only became visible under UV light and invisible under visible light. Furthermore, when Kuang et al. printed a QR code as a grayscale pattern and scanned it using a smartphone, the scientists were able to directly link to the information or site encoded via the internet, preventing counterfeit 3-D products.
In this way, Kuang et al. developed a g-DLP 3-D printing technique via two-stage curing to achieve high-resolution digital manufacture with complex shapes and programmable functional gradients. The scientists aim to optimize constituents in the material for additional printing applications. They were able to directly develop complex 2-D/3-D lattices, metamaterials, 4-D printing with shape memory polymers and produce anticounterfeit techniques that were built-in to the 3-D material itself. The scientists aim to further improve the new g-DLP method to engineer materials for future applications, including 4-D printing metamaterials, biomimetic presurgical models, soft robotics and additive manufacture with ingrained cyber security.


Sean V Murphy et al. 3-D bioprinting of tissues and organs, *Nature Biotechnology* (2014). DOI: 10.1038/nbt.2958


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