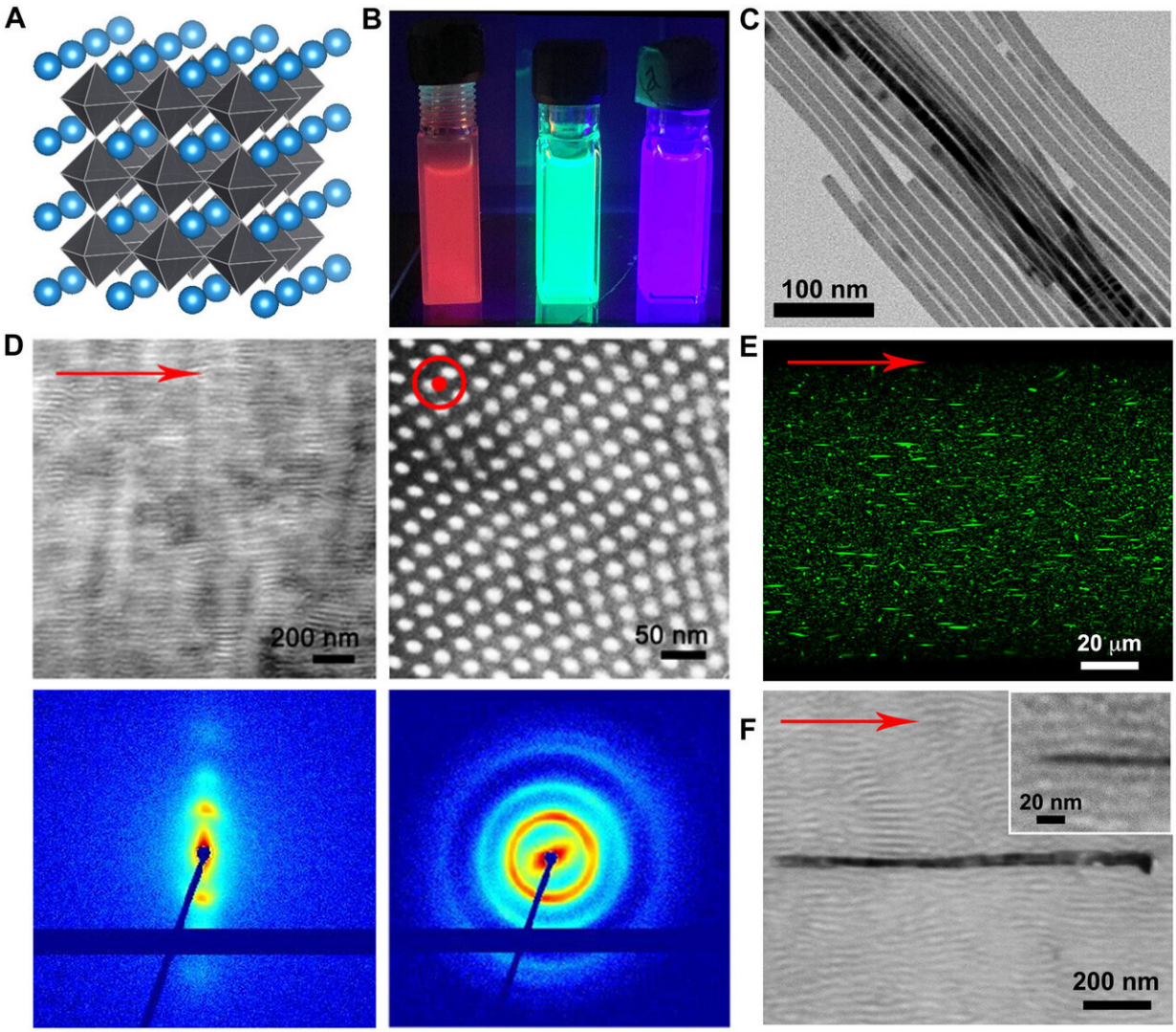
Digitally programmable perovskite nanowire-block copolymer composites

June 20 2019, by Thamarasee Jeewandara



Perovskite nanowire–block copolymer supramolecular nanocomposites. (A) Schematic diagram of the perovskite crystal structure. (B) PL of CsPbX3 (X = I, Br, and Cl) perovskite nanowires in toluene solution. Halide composition

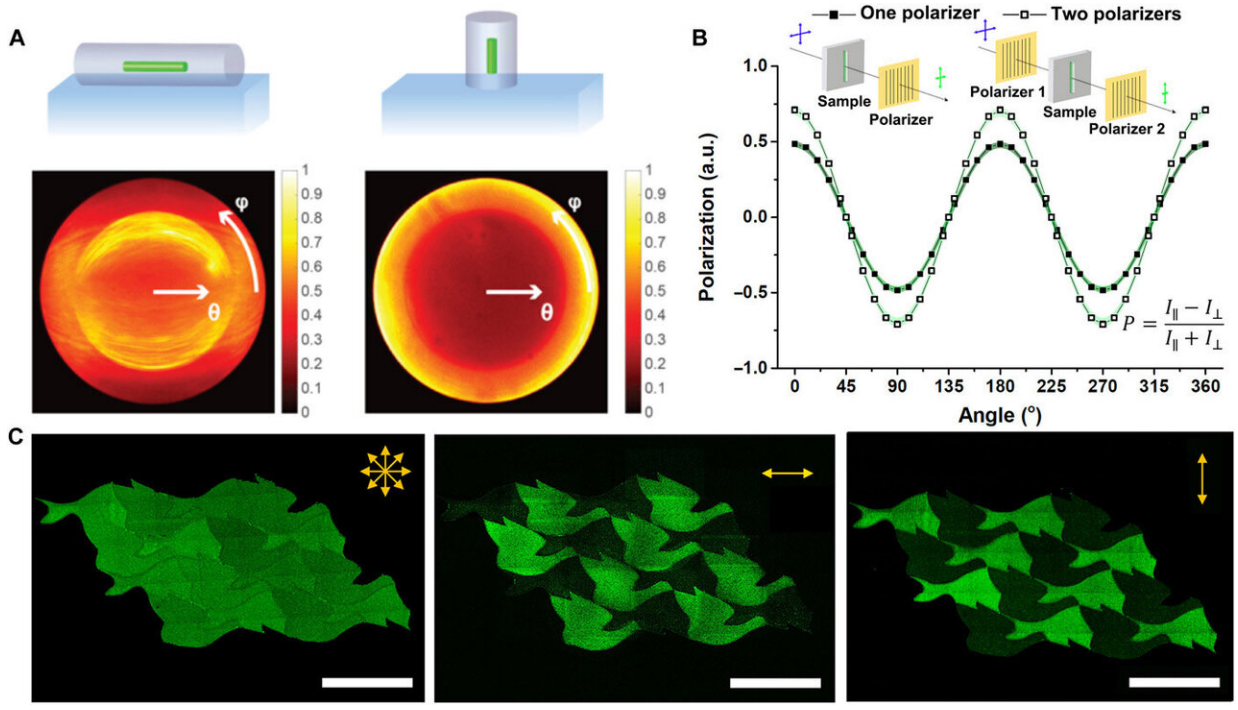
determines the material's bandgap and color of emitted light (λexcitation = 380 nm). (C) TEM images of naturally aligned bundles of CsPbBr3 perovskite nanowires (length, ~1 μm; diameter, ~10 nm). (D) TEM images (top) and SAXS measurements (bottom) of the pure SIS filaments without nanowires printed using 1-mm-diameter nozzle (left, horizontally printed sample; right, filament cross sections), demonstrating microphase separated SIS hexagonal domains with long-range order and anisotropy. Red arrow indicates printing and the micro-domain alignment direction. (E) A maximum intensity projection of z-stack fluorescence confocal image of the printed nanowire-block copolymer filament (diameter, 100 μm; λexcitation = 365 nm). (F) Representative TEM images of nanocomposite filaments printed using 1-mm-diameter nozzle showing perovskite nanowires oriented in parallel with the print direction and locally conform to the SIS block copolymer microdomains. A higher-magnification TEM image (inset) shows that nanowires primarily segregate to PI-rich domains. The TEM samples in (D) and (F) are sectioned using cryo-ultramicrotome and stained with OsO4, which selectively darkens the PI domains. Credit: Science Advances, doi: 10.1126/sciadv.aav8141

One-dimensional nanomaterials with highly anisotropic optoelectronic properties can be used within energy harvesting applications, flexible electronics and biomedical imaging devices. In materials science and nanotechnology, 3-D patterning methods can be used to precisely assemble nanowires with locally controlled composition and orientation to allow new optoelectronic device designs. In a recent report, Nanjia Zhou and an interdisciplinary research team at the Harvard University, Wyss Institute of Biologically Inspired Engineering, Lawrence Berkeley National Laboratory and the Kavli Energy Nanoscience Institute developed and 3-D printed nanocomposite inks composed of brightly emitting colloidal cesium lead halide perovskite ($CsPbX_3$, where X= Cl, Br, or I) nanowires.

They suspended the bright nanowires in a polystyrene-polyisoprene-polystyrene block copolymer matrix and defined the nanowire alignment

using a programmed print path. The scientist produced optical nanocomposites that exhibited highly polarized absorption and emission properties. To highlight the versatility of the technique they produced several devices, including optical storage, encryption, sensing and full color displays. The work is now published on *Science Advances*.

The unique anisotropic optoelectronic properties of semiconducting nanowires arise from quantum and dielectric effects for broad ranging applications in electronics and photonics. New paths can be opened to assemble optoelectronic devices by precisely patterning 1-D nanomaterials into planar and 3-D structures. Compared to many types of semiconducting wires reported so far, cesium lead halide nanowires ($CsPbX_3$) with a perovskite crystal structure have offered several advantages for optoelectronic applications. The lead halide perovskite nanocrystals are ultra-bright and exhibit near-unity quantum yield without an encapsulating shell—in contrast to conventional, colloidal semiconducting nanocrystals with a core-shell structure.

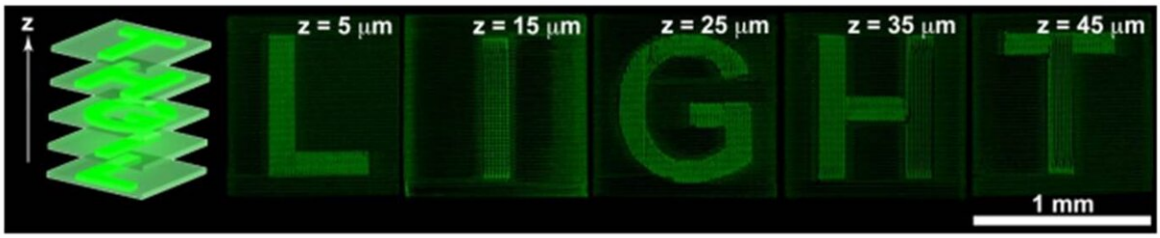


Polarized emission from printed perovskite nanocomposites. (A) Fourier images showing the angular emission from a nanowire bundle in the printed filament. Polar angle (θ) is plotted radially from 0° (center) to 70° (outer edge). Azimuthal angle (φ) is plotted around the circle starting at the right-hand side. Fourier image of a horizontal (left) and a vertical (right) filament on glass slide (cartoons, top). Angular emission pattern shows alignment of nanowires along filament axis. (B) Polarized emission of printed nanowire composites, measured using one linear polarizer installed in the emission path and two linear polarizers installed in both the excitation and emission paths. a.u., arbitrary units. (C) Artistic example of printed composites using their polarized emission (adapted from M. C. Escher, Sky and Water I art). Different parts are revealed for (left) no polarization, (middle) horizontal polarization, and (right) vertical polarization. Scale bars, 1 mm. Credit: Science Advances, doi: 10.1126/sciadv.aav8141

Materials scientists can modify the halide composition and bandgap of perovskites to form bright and tunable emissions across the entire visible spectral range. As a result of the unique material properties and high quantum yields, perovskite nanowires have potential applications in optoelectronics, as active layers in liquid crystal display (LCD) backlighting, spectrum splitting, polarized photodetectors and optically pumped lasers. Researchers have explored several planar and 3-D patterning methods, including extrusion-based 3-D printing via direct ink writing (DIW) to form shape-morphing architectures composed of cellulose fibrils and aligned in a hydrogel matrix. However, general applications of DIW to pattern functional architectures in photonic devices still remain to be explored.

In the present work, Zhou et al. designed, printed and characterized polarized optical architectures composed of perovskite nanowire-filled block copolymer matrices. For this, they developed a nanocomposite ink with the perovskite nanowire bundles embedded in a cylindrical,

microphase polystyrene-polyisoprene-polystyrene (SIS) block copolymer matrix. Using the proposed method, Zhou et al. expect other anisotropic materials including metals, semiconductors and block copolymers, and dielectric nanowires to be similarly programmably patterned.

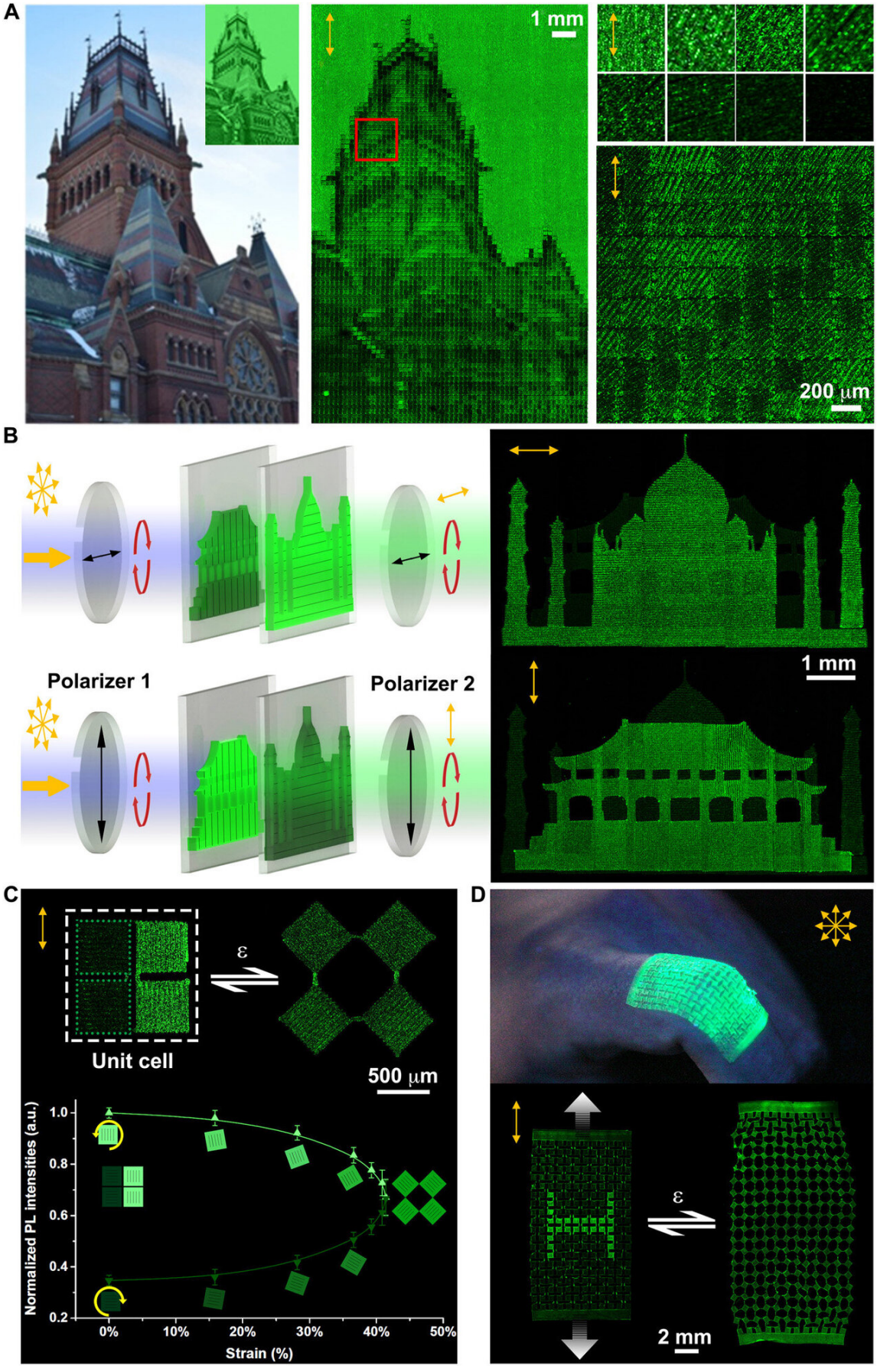


Five-layer photonic device showing "L-I-G-H-T" pattern imaged using polarized fluorescence microscopy along the z direction. The five letters are printed parallel to the polarization direction. Credit: Science Advances, doi: 10.1126/sciadv.aav8141

The scientists formed different inks composed of nanowires by varying the SIS concentration to develop shear-thinning behavior and viscoelastic response required for DIW (direct ink writing). Using transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) measurements, they revealed the ordered hexagonal micro-domains of the SIS block copolymer filaments and revealed the printed SIS-$CsPbBr_3$ nanocomposites to be highly aligned along the print direction. This patterning method allowed for programmable nanowire orientation in the printed optical composites to influence their polarized and angular emission.

During direct ink writing, Zhou et al. generated print paths using G-code generated via MatLab, Slic3r and CIMCO and used glass nozzles to form

nanocomposite architectures on glass coverslips. To demonstrate applications of digitally programmed polarization anisotropy in 3-D printed nanocomposites; Zhou et al. first engineered a 3-bit grayscale image of square shaped pixels (200 x 200 μm). Using the technique, the scientists achieved advanced patterned architectures to serve as optical memories for write once-read many (WORM) times devices of data storage.

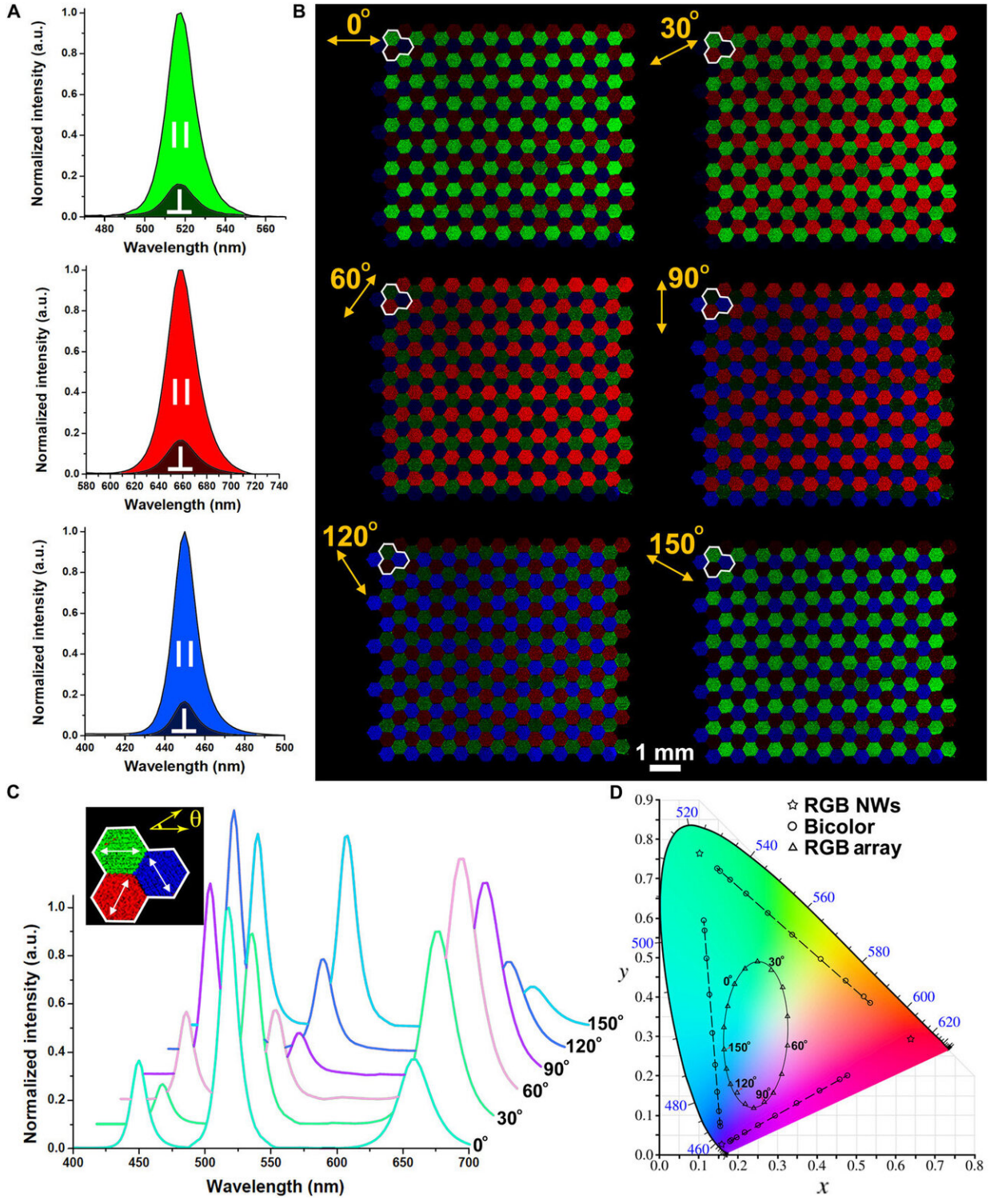

A
1 mm
200 μm
B
Polarizer 1
Polarizer 2
1 mm
C
ε
Unit cell
500 μm
Normalized PL intensities (a.u.)
1.0
0.8
0.6
0.4
0.2
0%
10%
20%
30%
40%
50%
Strain (%)
D
ε
2 mm

Polarized perovskite nanocomposites via 3D printing. (A) A photo (left) is downsized to a 3-bit grayscale image consisting of 60 (w) × 90 (h) square-shaped pixels (left, inset). Taking advantage of the polarization angle–dependent emission intensities, we convert the grayscale intensities to eight different printing directions (top right) and print the image (middle). (B) Polarization holograms. When viewed using a pair of linear polarizers, the two-layer device projects an image of Taj Mahal (horizontally printed, horizontal polarization) and Forbidden City (vertically printed, vertical polarization). (C and D) A mechano-optical metamaterial based on an auxetic structure. (C) The unit cell (top) consists of four rotating squares, which can rotate up to 45°. The polarization-dependent emission results in a strain-intensity relationship (bottom). (D) This structure is flexible and can adhere to a finger (top). Undergoing reversible stretching motions, the digitally patterned H letter (printed in vertical direction and in parallel with the polarizers) is displayed (left) or encrypted (right). Credit: Science Advances, doi: 10.1126/sciadv.aav8141

The printed architectures can be used for security encryption in encryptable memories by printing multilayer architectures with different optical information stored in each layer. As a proof-of-principle, Zhou et al. patterned the letters "L-I-G-H-T' in a five-layer device in which they viewed each letter at different heights. They printed the letters "H' and "I' in random orientations and selectively viewed each letter in the transparent matrix by using a polarizer at the appropriate angle. Additionally, the scientists showed the possibility of encrypting an emission pattern—for instance, the letter H—by stretching the material. They envision the potential to create dynamic camouflage in skin-like material arrangements where different optical patterns emerge and disappear on mechanical stretching.

Thereafter, they extended the concept to mimic the RGB (red, green,

blue) quantum dots that are widely used in color mixing. For this, Zhou et al. used anion-exchange reactions to obtain halide perovskites composed of red-emitting and blue-emitting nanowires and created tunable, multiplexed color displays using multi-material 3-D printing. Although perovskite nanowires are not yet optimally suited as materials for display applications, the work highlighted the ability to exert programmable control on the nanowire composition and alignment offered via digital assembly. Zhou at al. presented the tunable spectral responses of the multiplexed RGB array and its corresponding color range in the CIE (commission on illumination) chromaticity diagram to show the remarkably simple design offered by the printed displays to achieve color tunability.



Polarizer tunable color multiplexing. (A) Polarized PL spectra of the printed nanocomposites incorporating CsPbBr3 (green), CsPb(Br0.2I0.8)3 (red), and CsPb(Br0.2Cl0.8)3 (blue) nanowires, taken with a pair of two linear polarizers

installed in both the excitation and emission paths. (B) Optical images of printed pixel arrays showing polarization-dependent emission multiplexing. Images are taken using a multiphoton microscope with a polarized excitation source and with a linear polarizer in the emission path. (C) Spectral emission profiles of the pixel array based on hexagonal tiles of red, green, and blue light-emitting perovskite nanocomposites printed along three directions oriented with a 60° difference upon rotating both polarizers. (D) Its corresponding colors on CIE 1931 chromaticity diagram (right). Two types of potential display operations are presented. The solid line and triangles represent colors using the multiplexed RGB pixel arrays in (B). NWs, nanowires. The dashed lines and circles represent the multiplexed RG, RB, and GB pixel arrays printed in two orthogonal directions. Credit: Science Advances, doi: 10.1126/sciadv.aav8141.

Unlike LCDs that rely on conventional quantum dot color filters, the printed films in the present work used direct polarization photon downshifters, also known as "active" color filters. Zhou et al. intend to improve both nanowire synthesis and printing to achieve higher efficiencies for display applications.

In this way, Nanjia Zhou and co-workers showed that direct writing nanocomposite inks composed of perovskite nanowire-filled block copolymer matrices could pattern optoelectronic devices in numerous designs. They programmed the nanowire composition and alignment to create optical nanocomposites for applications in information storage, encryption, mechano-optical sensing and optical displays. The new findings will provide a pathway to rapidly design and manufacture functional devices from anisotropic building blocks encapsulated in soft polymer matrices.

More information: Nanjia Zhou et al. Perovskite nanowire–block copolymer composites with digitally programmable polarization anisotropy, *Science Advances* (2019). DOI: 10.1126/sciadv.aav8141

Linyou Cao et al. Engineering light absorption in semiconductor nanowire devices, *Nature Materials* (2009). DOI: 10.1038/nmat2477

A. Sydney Gladman et al. Biomimetic 4-D printing, *Nature Materials* (2016). DOI: 10.1038/nmat4544

Ali Javey et al. Layer-by-Layer Assembly of Nanowires for Three-Dimensional, Multifunctional Electronics, *Nano Letters* (2007). DOI: 10.1021/nl063056l