

Supporting Information for:

Customizable and stretchable fibre-shaped electroluminescent devices via multicore-shell direct ink writing

Experimental Section

1. Fabrication of multicore-shell printheads

Printheads used for this multicore-shell 3D printing method was designed by a CAD software and was fabricated by digital light processing (DLP) 3D printers (NanoArch P140 and S140, Wuxi BMF Precision Technology Co., Ltd., China). The printheads had four channels, corresponding to the four layers of the fibre.

2. Preparation of printable inks

2.1 Phosphor layer ZnS/dragon skin (DS) ink.

ZnS phosphor powder (D512C Green, D502B Blue and D611S Orange, Shanghai Keyan Phosphor Technology Co., Ltd., China) was used as received without any further modification. The green, blue, and orange light-emitting ZnS phosphor material were named after ZnS: Cu (G), ZnS: Cu (B), and ZnS: Cu, Mn, respectively. ZnS: Cu (G) powder was used in all experiments and measurements. ZnS: Cu (B) and ZnS: Cu, Mn powders were only used to print demonstrations of different light-emitting colors. A series of ZnS: Cu (G)-based composite inks were prepared by mixing the ZnS: Cu (G) phosphor powder with silicone elastomer DS (Dragon skin 00-10, Smooth-On, USA) at different ZnS contents of 40, 50, and 60 wt%. Then the mixture was stirred to a homogeneous ink using a planetary mixer (ARE-310, Thinky Mixer, USA) at 2000 rpm for 2 min.

DS was made from silicone elastomer Part A, Part B, silicone thickener (Thi-Vex, Smooth-On, USA) and platinum silicone cure retarder (Slo-Jo, Smooth-On, USA) with a weight ratio of 100:100:2:1. Thickener was used to modify the rheological properties to be suitable for printing, and the cure retarder was added to enhance its printable time.

2.2 Inner electrode layer Ag/TPU ink.

Ag/thermoplastic polyurethane (TPU) ink was prepared based on a previous report.^{S1} Specifically, 1.6 g of TPU was firstly dissolved in N, N-dimethylformamide (DMF, General-Reagent, China), and subsequently 16.7 g of silver flakes with an average size of 3–5 μm were added into the solution.

2.3 Outer electrode layer PVA/PEO/LiCl ionic gel ink.

12 g of Poly (vinyl alcohol) (PVA, average molecular weight of 205,000, Aladdin, China) and 0.96 g of poly (ethylene oxide) (PEO, powder, average molecular weight of 100,000, Shanghai Kaiyuan Chemical Industry Technology Co., Ltd., China) were swollen and dissolved together in 35 g of deionized (DI) water at 95 °C for 12 h to form a homogeneous solution. 4 g of lithium chloride (LiCl, Aladdin, China) was dissolved

in 6 g of DI water to prepare a separate LiCl solution, which was added slowly to the polymer solution. The mixture solution was stirred at 95 °C for another 20 min to form a homogenous ionic gel ink.

2.4 Encapsulation layer DS ink.

Pure DS was used as the encapsulation material as described above.

3. 3D Printing of the ACEL fibre-shaped devices

A custom-made 3D printer was used to print ACEL devices in 1D, 2D, and 3D configurations. Three-axis motion of x, y and z-stages was independently controlled by a custom-designed computer program. Arbitrary shapes could be realized by deploying appropriate G-code commands. Printing details are as follows.

Four inks were hosted in four separate syringes (3 cc, Nordson, USA), and were degassed by centrifugation at 4000 rpm for 10 min. Two pieces of conductive aluminium adhesive were adhered onto cleaned glass slides, used as electrical connections. An air-powered fluid dispenser and a high-pressure adapter were used to pressurize the syringes and to control the ink flow rate. The typical pressure values of Ag/TPU, ZnS/DS, ionic gel and pure DS inks required for printing were 126, 140, 126 and 140 psi, respectively, with a printing speed of 140 mm·min⁻¹. Appropriate commands were registered to make the inner and outer electrode connecting to the external measurement electrodes. The fibres were solidified at room temperature for ~10 h.

4. Structure and performance characterization

The morphology of the ZnS powder and ZnS/DS composite film were characterized by scanning electron microscopy (SEM, Gemini500, Zeiss, Germany). Rheological properties of the various inks were measured by a rheometer (DHR-3, TA Instruments, USA). Tensile properties were measured by a universal mechanical testing equipment (CTM 6000, Xieqiang Instrument Manufacturing Shanghai Co., Ltd., China). Tensile sample used in the experiment was a standard dogbone-shaped tensile test sample (ISO 527-5A) with its length, height, and maximum width of 75, 2, and 12.5 mm, respectively. The transmittances of ionic gel and DS films with thickness of 200 µm were measured by an ultraviolet-visible spectrophotometer (UV-2700, Shimadzu, Japan). The luminance and spectrum were carried out by a luminance meter (OHSP-350Z, HongPu Optoelectronics Technology Co., Ltd., China) under an AC electric field by using a high voltage AC/DC generator (Model 615-3, Trek, USA). The electrical resistance under stretching was measured by the AC/DC generator mentioned above and a home-made stretching setup. Electrochemical impedance spectra were measured with frequencies decreased from 1 MHz to 0.01 Hz. via an electrochemical workstation (Zennium pro, Zahner, Germany) and a conductance electrode (REX DJS-1, Shanghai INESA Scientific Instrument Co., Ltd., China). The conductivity was calculated based on the equation $\sigma = l/(A \times R)$, where σ is the ionic conductivity, and R is the resistance of the ionic gel, A and l is the area and distance of the two platinum electrodes,

respectively.

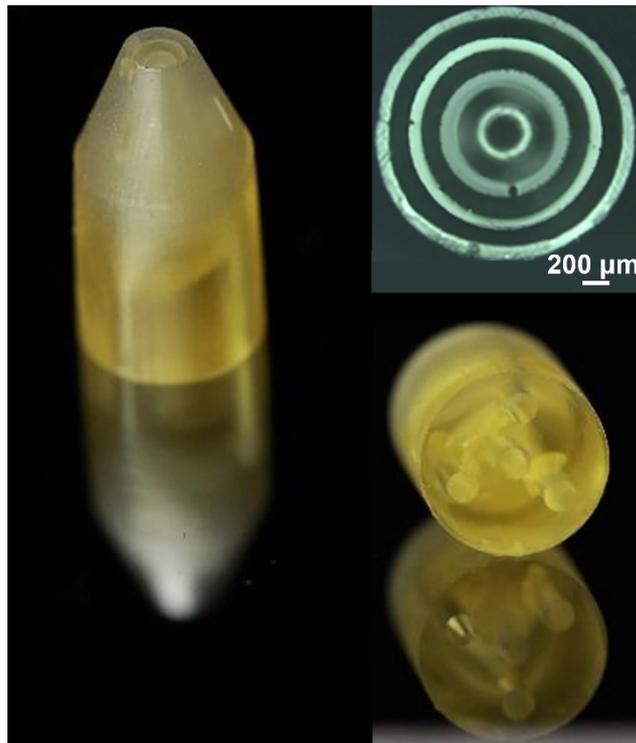


Fig. S1 Optical images of the DLP-printed multicore-shell printheads.

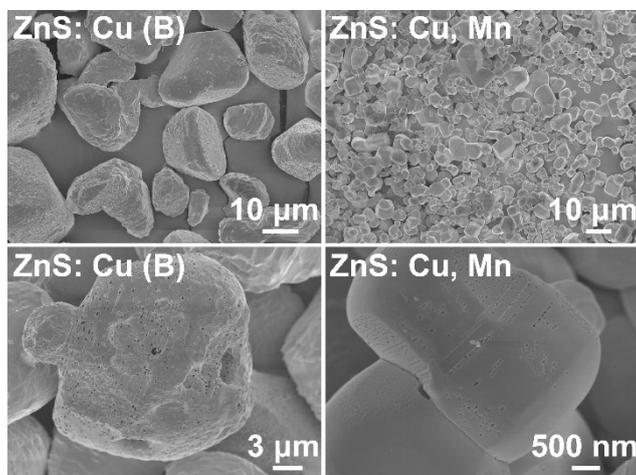


Fig. S2 SEM images of ZnS: Cu (B) and ZnS: Cu, Mn phosphor microparticles.

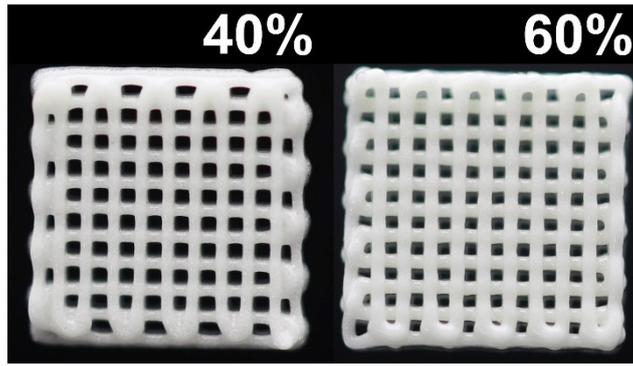


Fig. S3 Optical images of the printed woodpile structures using ZnS:Cu(G)/DS composite inks with different phosphor microparticle content.

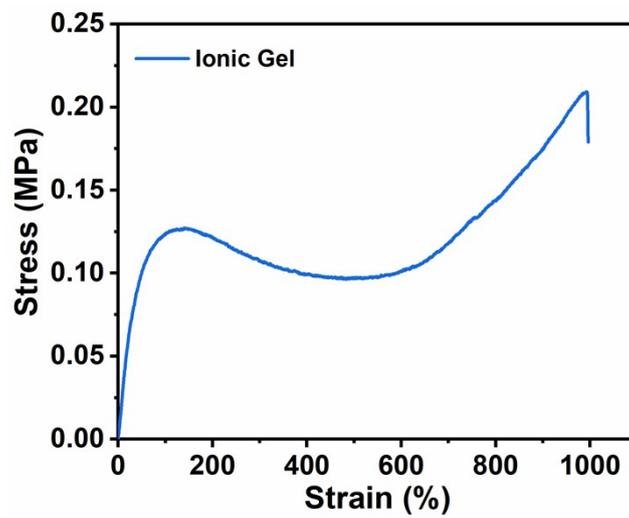


Fig. S4 Stress-strain curve of the ionic gel ink under tensile test.

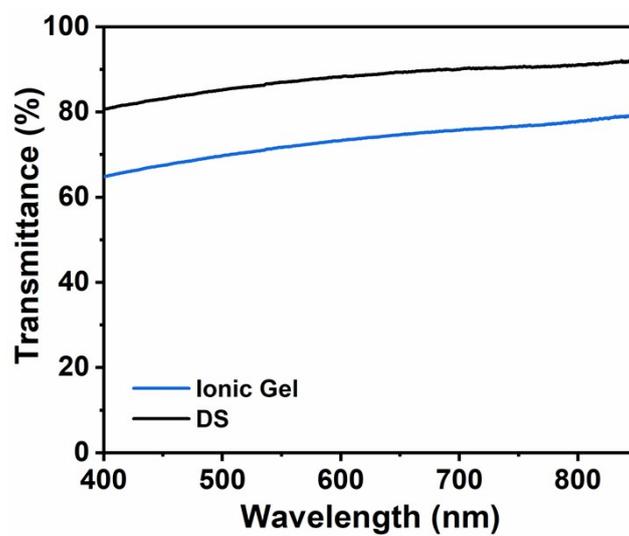


Fig. S5 Transmittances of the ionic gel and DS films with a thickness of $\sim 100 \mu\text{m}$.



Fig. S6 Photographs of “WASTLAKE” pattern under different voltages at the same frequency of 3 kHz.

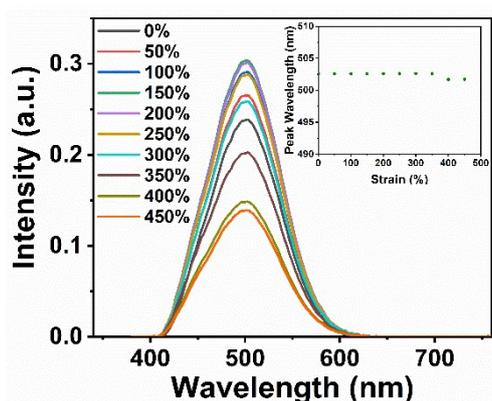


Fig. S7 The EL spectra of ACEL devices under different tensile states from 0% to 450% and the corresponding peak wavelength-strain curve (inserted).

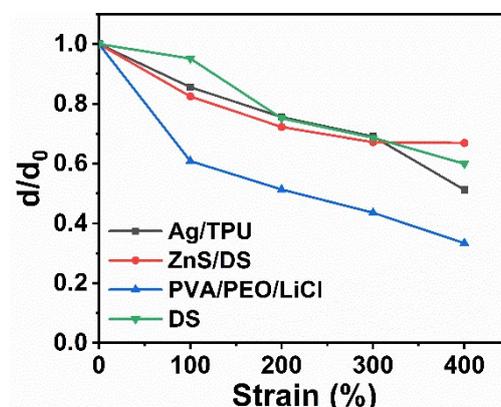


Fig. S8 The relative thickness change (d/d_0) of the four layers in coaxial ACEL devices under different tensile states from 100% to 400%.

The samples used to test the relative thickness change were prepared through fixing coaxial ACEL devices with different tensile states on a home-made clamp followed by DS cast. The thickness change was recorded from the cross-sectional images.

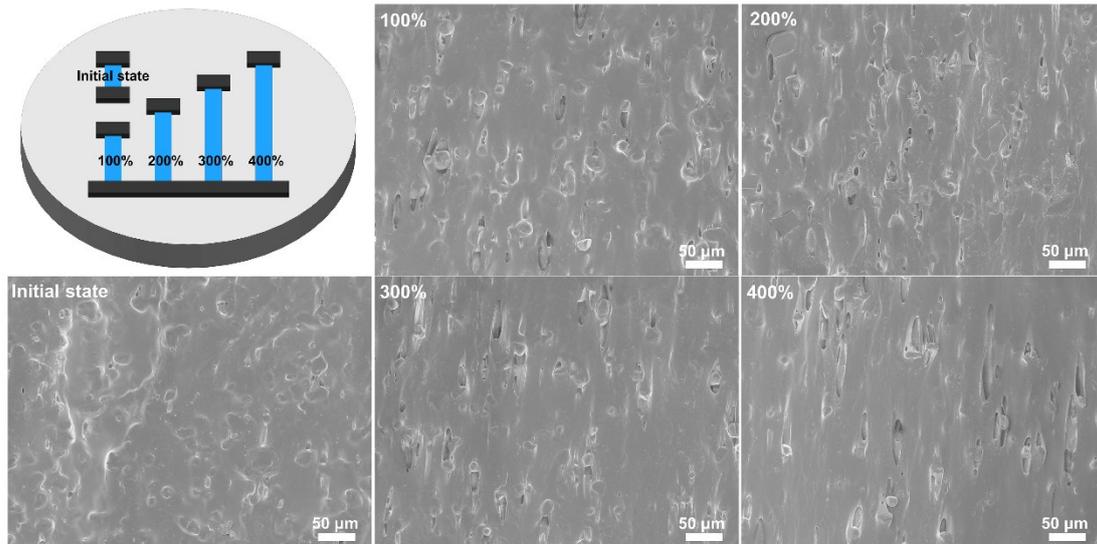


Fig. S9 The illustration of sample preparation and corresponding SEM images of phosphor layer under different tensile states.

Table S1 Compositions of the four inks (unit: g).

	Inner electrode layer	Phosphor layer	Outer electrode layer	Encapsulation layer
Ag powder	100			
TPU	9.6			
ZnS:Cu(G)		100		
DS		66.7		100
DI water			100	
PVA			29.3	
PEO			2.3	
LiCl			9.8	

Table S2 Luminance of different light-emitting ZnS/DS composites with 60 wt% of phosphor particles at ~ 1.8 V/ μm and 3 kHz based on 2D planar device with a phosphor layer thickness of ~ 200 μm .

Light-emitting color	Luminance ($\text{cd}\cdot\text{m}^{-2}$)
Green (ZnS: Cu (G))	110.9
Blue (ZnS: Cu (B))	60.6
Orange (ZnS: Cu, Mn)	0.19

References:

- S1. A. D. Valentine, T. A. Busbee, J. W. Boley, J. R. Raney, A. Chortos, A. Kotikian, J. D. Berrigan, M. F. Durstock and J. A. Lewis, *Adv Mater*, 2017, **29**, 1703817.