Supplementary Materials for

Stimulus-Driven Liquid Metal and Liquid Crystal Network Actuators for Programmable Soft Robotics

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1. Materials and methods

Komeigatabacter xylinum (K. xylinus) (ATCC 10245) was purchased from the American Type Culture Collection. Bacto peptone, D-mannitol, yeast extract, hydrochloroauric acid trihydrate (HAuCl₄·3H₂O, 99.9%), and NaOH of analytical grade were purchased from Sinopharm Chemical Reagnent. Co., Ltd. (China). Sodium bromide (NaBr), sodium hypochlorite solution (NaClO, available chlorine $\geq 5.0\%$), 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO, 98%) and thioglycolic acid (TGA) were purchased from Aladdin Chemical Reagent Co. Ltd (Shanghai, China). Cetyltrimethylammonium bromide (CTAB), sodium borohydride (NaBH₄), silver nitrate (AgNO₃) and hydroquinone were supplied by Sigma-Aldrich (USA). Eutectic gallium-indium (EGaIn, 78.6 wt% Ga and 21.4 wt% In, melting point ~ 15.8 °C) was obtained from Yantai Aibang Electronic Materials Co. Ltd. (China). The polymerizable liquid crystal monomers were purchased from Jiangsu Hecheng Display Technology Co., Ltd (China). Pre-strained polystyrene (also known as Shrinky-Dinks) was purchased from corporate America (USA).

The surface morphologies of BC nanofibers were examined by Atomic Force Microscope (AFM; CSPM 4000, Benyuan, China). The microstructures of the as-prepared samples were observed by Field Emission Scanning Electron Microscopy (FESEM; S4800, Hitachi, Japan). High Resolution Transmission Electron Microscopy (HRTEM) images were obtained on JEM-2000FX (JEOL, Japan) with an acceleration voltage of 200 kV. Dynamic light scattering (DLS) was conducted on Malvern Zetasizer Nanoseries (Nano ZS90) for zeta potential and hydrodynamic particle size determination. The chemical compositions of samples were characterized by Fourier Transform Infrared Spectroscopy (FT-IR, BRUKER AXS GMBH, FT-IR-650). The absorption spectra of the as-prepared samples were recorded with a UV-visible spectrophotometer (Shimadzu, UV3600, Japan). The adhesion force between the colloidal LM coating and the substrate was tested by scratch method using Micron scratch meter (MCT of Swiss CSM Instruments Co., Ltd., Switzerland). The continuous-wave (CW) 808 nm NIR laser (MDL-N-808-10W, Changchun New Industries Optoelectronics Technology Co.) with tunable power of 0-5 W was used as the excitation source in our experiment. Surface temperature of samples obtained were recorded by an infrared camera (IRC, R500Ex-Pro-D, Japan). The mechanical tensile properties were characterized using an electronic tensile testing machine (XQ-1C, Xinxian, China). In addition, the tensile strength of the samples was tested by the standard of GB/T 528-2009, and the loading rate was 2 mm/min. Photographic images of samples obtained were carried out by Canon camera (DS126631, Japan). The tracking position of the soft robotics were recorded by using Kinovea software.

2. Synthesis and characterizations of the colloidal liquid metal (LM) ink

2.1 Synthesis and characterizations of BC and TOBC

Synthesis of pure BC: BC was produced by *Komeigatabacter xylinum* (ATCC 10245), which was inoculated into 10 mL of a Hestrin and Schramm medium in a flask at 30 °C in an incubator.^[1,2] The inoculum included 0.5 wt% yeast, 2.5 wt% D-mannitol, and 0.3 wt% bacto-peptone. Before culturing, the inoculum was autoclaved at 121 °C for 20 min. The flasks were incubated at 30 °C for 7 days in a static condition. Afterwards, the pellicle of BC obtained was soaked into 0.1 M NaOH at 80 °C for 4 h to eliminate chemicals and residual bacteria. Finally, the pre-treated BC was repeatedly washing until neutral pH.

TEMPO-mediated oxidation of BC (TOBC): TEMPO-mediated oxidation was applied to modify BC with NaBr, TEMPO and NaClO according to the previously reported strategy.^[3] A detailed procedure for the synthesis of TOBC was as follows: Firstly, the BC pellicles (1.0 g) were suspended into deionized water (100 mL) containing TEMPO (0.018 g) and NaBr (0.1 g) under stirring. 12 wt% NaClO solution (3.1 g) was slowly added to the BC slurry under gentle agitation at room temperature. The pH of the slurry was adjusted to ~ 10 by adding 0.5 M NaOH solution. The obtained TOBC was then filtered and washed with deionized water for several times.

Morphologies and characterizations of BC and TOBC: AFM image clearly presents that pure BC nanofibers have a reticular three-dimensional (3D) structure, are ultrafine, and are formed of fiber ranging from 10 to 70 nm with an average diameter of about 30 nm with high aspect ratio (several micrometers long), as shown in **Figure S1(A-C)**.^[4] Meanwhile, the average diameter of the obtained TOBC decreased to ~14 nm by carboxyl modification. To further confirm the successful oxidation of the hydroxyl groups, **Figure S1D** showed the FITR spectra of BC and TOBC. The FTIR spectrum of the original BC shows broad absorption band in the region of 3342 cm⁻¹, which is assigned to O-H stretching vibration. The absorption band at 2900 cm⁻¹ for BC is attributed to the presence of C-H stretching vibrations, which is in well agreement with the characteristic bands of BC reported in the literature.^[5] Meanwhile, the absorbance bands at 1165, 1110, 1060, and 1035 cm⁻¹ correspond to stretching vibrations of C1-O-C4, C2-O, C3-O, and C6-

O, respectively.^[6] After TEMPO oxidation occurred, a band appeared at 1601 cm⁻¹, which indicates the C=O stretching of the carboxylic group evident in the TOBC, thereby indicating the successful oxidation of the hydroxyl groups.^[7]



Figure S1. Morphologies and characterizations of BC and TOBC. AFM surface morphologies of (A and B) a film of pure BC. (C) Histogram variation of BC and TOBC nanofibers diameter, and (D) FT-IR spectra ranging from 400 to 4000 cm⁻¹ of BC before and after oxidation.

2.2 Synthesis and characterizations of miniature gold nanorods (MiniGNRs)

Synthesis of MiniGNRs: MiniGNRs synthesis method was reported by a hydroquinone-based seedless growth.^[8] Briefly, HAuCl_{4(aq)} (0.4 mL, 0.01 M) and CTAB_(aq) (10 mL, 0.1 M) were added to AgNO_{3(aq)} (120 μ L, 0.01 M). Then, HCl (20 μ L, 1 M) and aqueous hydroquinone (525 μ L, 0.1 M) were added to the growth solution under gentle agitation at room temperature. The color of the growth solution turned from orange to clear with a very light-yellow color. The as-prepared ice cold NaBH_{4(aq)} solution (20 μ L, 0.01 M) was injected into the growth solution using micro-syringe after 15 min of stirring. The mixture was stirred for 1 min and aged for 2 h at room temperature.

The obtained MiniGNRs solution was then cleaned by centrifuging at 12000 rpm for 40 min twice. **Synthesis of miniature carboxylated gold nanorods (MiniGNR-COOH):** Subsequently, MiniGNR-COOH were synthesized by introducing alcohol solution (0.02 M) containing 0.5 mL of thioglycolic acid (TGA) to 10 mL of MiniGNRs aqueous solution. The mixture was stirred for 24 h, and then centrifugation at 12000 rpm for 20 min. Finally, the obtained MiniGNR-COOH were dispersed in 15 mL of deionized water for later use.

Morphologies and characterizations of MiniGNRs and MiniGNR-COOH: TEM images clearly show that the size distribution of the as-synthesized MiniGNR-COOH is very uniform, as shown in Figure S2A. The size distribution of the MiniGNR-COOH in Figure S2B ranged from 16 to 25 nm with an average length of about 20 nm with an average aspect ratio of 4. To demonstrate the successful modification, structural information of the as-synthesized MiniGNRs before and after modification were further studied by FT-IR (Figure S2C). Two strong absorption peaks of MiniGNRs at 2925 cm⁻¹ and 2850 cm⁻¹ are attributed to C-H stretching vibration of CTAB on the surface of MiniGNRs. The absorption peak at 1487 cm⁻¹ is attributed to asymmetric C-H vibration of CTAB (CH₃-N⁺). The typically absorption peak for TGA at 2570 cm⁻¹ is assigned to S-H vibration. Significantly, the absorption peaks at 1598 cm⁻¹ and 3436 cm⁻¹ correspond to stretching vibration of C=O and O-H, implying the successful synthesis of the MiniGNR-COOH. It is well known that UV-vis absorption measurement is a simple strategy applicable to the analysis of the optical absorption properties of a compound. Hence, the optical properties of the obtained MiniGNRs before and after modification were analyzed by UV-vis spectroscopy. Figure S2D clearly exhibited that the as-synthesized MiniGNRs have two bands: a strong long-wavelength band at 810 nm due to the longitudinal oscillation of electrons and a weak short-wavelength band around 505 nm due to the transverse electronic oscillation.^[9] UV-vis absorption of the as-prepared MiniGNR-COOH presented a predominant absorption band located at 811 nm and a weak absorption band located at 507 nm compared to as-prepared MiniGNRs before modification. The resulting indicated that the introduction of carboxyl group has little effect on UV-vis absorption of MiniGNRs.



Figure S2. Morphologies and characterizations of MiniGNRs and MiniGNR-COOH. (A) The TEM image of as-synthesized MiniGNR-COOH, and the corresponding (B) size distribution. (C) FT-IR spectra ranging from 400 to 4000 cm⁻¹ of MiniGNRs before and after modification. (D) UV-vis absorption spectra of the obtained MiniGNRs (black line) and MiniGNR-COOH (red line) in aqueous solution.

NIR photothermal properties of MiniGNR-COOH in deionized water: To further explore NIR photothermal properties of the as-prepared MiniGNR-COOH in deionized water, the temperature changes of the obtained MiniGNR-COOH in aqueous solution with different concentrations were captured by an infrared camera (IRC, R500Ex-Pro-D, Japan) under NIR light irradiation (808 nm, 0.4 W cm⁻²), as shown in **Figure S3A**. The surface temperature of aqueous solution of MiniGNR-COOH increased with the increase of time compared to pure aqueous solution, indicating that MiniGNR-COOH had excellent absorption at 808 nm and high photothermal conversion capacity. To further prove the excellent NIR photothermal properties of MiniGNRs, the simulation of a single MiniGNR shows an enhancement of the electric field on the nanorod surface, and thus a high light-to-heat conversion efficiency would be expected (**Figure S3B**).^[10]



Figure S3. NIR photothermal properties of MiniGNR-COOH in deionized water. (A) The temperature change of MiniGNR-COOH in deionized water with different concentrations by NIR light irradiation (808 nm, 0.4 W cm⁻²). (B) The COMSOL simulation of electric field enhancement of single MiniGNR, the color bars represent the ratio between the enhanced electric field and the incident electric field.

2.3 Synthesis and characterizations of the colloidal LM ink

Firstly, to prepare TOBC suspension, 0.04 g of TOBC was added to 20 mL of aqueous solution, and then formed a uniformly dispersed solution under sonication (TL-250Y, Jiangsu Tianling Ltd; power of 650 W with 20% amplitude) for 10 min in ice-bath water. Subsequently, 0.1 g of EGaIn bulk (melting point ~ 15.8 °C) was firstly added into the above aqueous TOBC suspension (20 mL, $\phi_{\text{TOBC}} = 0.2 \text{ wt\%}$), and the ultrasonication was performed for 30 min in ice-bath water (TL-250Y, Jiangsu Tianling Ltd; power of 650 W with 80% amplitude). Then, 1 mL of MiniGNR-COOH aqueous solution ($\phi_{\text{MiniGNR-COOH}} = 0.4 \text{ wt\%}$) was further added into the above EGaIn/TOBC dispersion and the ultrasonication was performed for another 10 min in ice-bath water (TL-250Y, Jiangsu Tianling Ltd; power of 650 W with 80% amplitude). Finally, size-grading was achieved by centrifugation at 4000 rpm. The resultant colloidal LM ink obtained was stored at $pH \sim 7$ under N₂ protection. We have investigated the effects of TOBC and MiniGNR-COOH concentrations on the properties of colloidal LM ink, as shown in Figure S4. An optimal concentration of TOBC, 0.2 wt%, is critical to the formation of stable and uniform LM nanoparticles. A lower concentration of TOBC would destabilize the LM nanoparticles, while a higher concentration could result in an unevenly size distribution since excess nanofibers may hinder the ultrasonic dispersion of LM nanoparticles.



Figure S4. (A-F) SEM image of TOBC/EGaIn with different TOBC suspension concentrations: 0; 0.1; 0.2; 0.3; 0.5 and 1.0 wt%, under ultrasonic 40 min with 650 W with 80% amplitude and 20 kHz.

Figure S5A clearly shows that pure EGaIn nanoparticles are irregularly sphere and unevenly distributed ranging from 70 to 400 nm under ultrasonic 40 min (**Figure S5A**¹). Compared to pure EGaIn nanoparticles, the SEM image of EGaIn droplets in the presence of nanocellulose (0.2 wt%) indicates the formation of relatively stable spherical LM nanoparticles (**Figure S5B**), and the droplet size varied from 40 to 130 nm with an average droplet diameter of 85 nm (**Figure S5B**¹). Interestingly, it was found that the introduction of 0.02 wt% MiniGNR-COOH could further stabilize and downsize the EGaIn nanoparticles in the presence of 0.2 wt% TOBC. **Figure S5(C-C¹)** indicates the formation of stable and uniform spherical LM nanoparticles with an average size of ~ 70 nm, which might result from synergistic coordination of Ga³⁺ with carboxyl groups of MiniGNR-COOH and TOBC. To further analyze the structural information of the colloidal LM ink, the energy-dispersive X-ray spectroscopy (EDX) in combination with SEM shows that the resulting LM nanocomposites consist of 15.84 wt% (C), 7.23 wt% (O), 56.43 wt% (Ga), 12.33 wt% (In), and 8.17 wt% (Au), as shown in the **Figure S6**.



Figure S5. SEM image and size distribution of EGaIn, TOBC/EGaIn and TOBC/EGaIn/MiniGNR-COOH nanoparticles. (A-C) SEM images of pure EGaIn, TOBC/EGaIn and TOBC/EGaIn/MiniGNR-COOH nanoparticles under ultrasonic 40 min with 650 W with 80% amplitude and 20 kHz, corresponding (A^{1} - C^{1}) histogram variation of EGaIn droplets diameter, respectively.



Figure S6. Energy-dispersive X-ray spectroscopy (EDX) of the colloidal LM ink.



Figure S7. TEM image of the obtained colloidal LM ink after the solvent evaporation.

TEM was further used to characterize the microstructure of the colloidal LM ink after the solvent evaporation (**Figure S7**). TEM image shows that LM nanoparticles are surrounded around by TOBC nanofibers and MiniGNRs and formed a spider web. There may be two mechanisms at play in the whole reaction: First, there are abundant functional groups (-OH and -COOH) on the surface of TOBC that have strong hydrogen bonding with the carboxyl group (-COOH) on the surface of MiniGNR-COOH. Meanwhile, LM nanoparticles of the colloidal LM ink was further stabilized due to the spontaneous oxidation on the surface under continuous ultrasonication and the coordination of Ga³⁺ with carboxyl groups (-COOH) of MiniGNR-COOH and TOBC. Meawnhile, The stability of the colloidal LM ink was also further studied as shown in **Figure S8**. Through 30 days of observation, the results clearly show that the resultant colloidal LM ink was capable of remaining stable up to days at pH ~ 7 under N₂ protection, with negligible precipitation, which might be derived from their negatively charged surfaces (zeta potential: ~ -32 mV at pH = 7) as well as the strong hydrogen bonding or Ga³⁺ coordination among LM nanoparticles, MiniGNR-COOH and TOBC nanofibers (**Figure S9**).



Figure S8. Visual observation of the colloidal LM ink maintaining stable up to days at $pH \sim 7$ under N₂ protection with negligible precipitation.



Figure S9. The zeta potentials of pure BC, TOBC, TOBC/EGaIn and TOBC/EGaIn/MiniGNR-COOH suspensions in deionized water.

To further investigate NIR photothermal properties of the obtained colloidal LM ink, the temperature changes of TOBC, TOBC/EGaIn and TOBC/EGaIn/MiniGNR-COOH in aqueous solution were recorded by an infrared camera under 808 nm NIR light irradiation (0.5 W cm⁻²) (**Figure S10**). When the NIR light was continuously irradiated for 7 s, the temperature difference on the surface of TOBC aqueous solution was 2.0 °C, indicating that TOBC had almost no 808 nm NIR light absorption and photothermal conversion capability. NIR photothermal properties of TOBC/EGaIn suspensions has been improved and the temperature difference was 30.1 °C compared to TOBC aqueous solution, due to the photothermal effect of LM nanoparticles. Significantly, NIR photothermal properties of the colloidal LM ink was further improved and

temperature difference reached 43.4 °C by introducing MiniGNR-COOH, ascribed to the photothermal synergies between MiniGNR-COOH and LM nanoparticles. The photothermal properties of the colloidal LM ink can be significantly enhanced upon increasing the concentration of MiniGNR-COOH from 0 to 500 μ g mL⁻¹ (**Figure S11**), which was mainly due to the further improvement of the photothermal effect with the increase of the MiniGNR-COOH content.



Figure S10. Temperature change of TOBC, TOBC/EGaIn and TOBC/EGaIn/MiniGNR-COOH in aqueous solution were acquired under NIR light irradiation (808 nm, 0.5 W cm⁻²), the inset shows corresponding photothermal real images captured by an infrared camera.



Figure S11. Temperature changes of TOBC/EGaIn/MiniGNR-COOH in aqueous solution under NIR light irradiation (808 nm, 0.5 W cm⁻²) with different the MiniGNR-COOH content: 0; 100;

200; 500 µg mL⁻¹.

3. Drop-casting deposition of the colloidal LM ink on different substrates

3.1 Fabrication and characterizations of LM-based nanostructured film

Fabrication of LM-based nanostructured film: The colloidal LM ink was poured onto a polytetrafluoroethylene (PTFE) substrate. Subsequently, LM-based free-standing nanostructured film was formed after solvent evaporation. The cross-sectional SEM and EDX elemental-mapping images further confirmed the gradient distributions of LM nanoparticles across the thickness of self-assembled nanostructured film, while MiniGNR-COOH exhibited a homogeneous distribution throughout the whole film (**Figure S12**).



Figure S12. The cross-sectional SEM and EDX elemental-mapping images of free-standing ultrathin nanostructured film automatically detached from the PTFE substrate.



Figure S13. (A) Schematic diagram of the formation process of the LM-based free-standing nanostructured film and the corresponding (B) interaction mechanism between the components.

The entire process of LM-based free-standing nanostructured film formation can be divided into three stages: drying, stratification, and coalescence (**Figure S13A**). When the stable colloidal LM ink comprising TOBC, MiniGNR-COOH and EGaIn droplets was placed onto a PTFE substrate, the mass-transfer-limited evaporation of water forces the particles into a close-packed structure. The deposition velocity of the EGaIn droplet is faster than that of TOBC-MiniGNR-COOH due to the former's larger density. During the evaporation process, the LM nanoparticles tend to precipitate primarily to the lower layer while free TOBC nanofibers were mainly distributed in the upper layer to form free-standing nanostructured thin film. Figure S13B illustrates the interactions among LM nanoparticles, TOBC and MiniGNR-COOH. Strong hydrogen bonding could be formed between the carboxyl group (-COOH) of MiniGNR-COOH and the abundant functional groups (-OH and -COOH) on the surface of TOBC. Meanwhile, LM nanoparticles were stabilized due to the spontaneous oxidation on the surface under continuous ultrasonication and synergistic coordination of Ga³⁺ with carboxyl groups (-COOH) of MiniGNR-COOH and TOBC.

To evaluate NIR photothermal properties of the obtained three samples, the temperature changes of pure BC, TOBC/EGaIn and TOBC/EGaIn/MiniGNR-COOH free-standing nanostructured film were recorded by an infrared camera under 808 nm NIR light irradiation (**Figure S14**). When the NIR light was continuously irradiated for 2.5 s, the temperature difference on the surface of pure BC film was 1.5 °C, indicating that BC had almost no 808 nm NIR light absorption and photothermal conversion capability. Compared to pure BC, NIR photothermal properties of TOBC/EGaIn free-standing nanostructured film has been improved and the temperature difference was 32.6 °C, mainly attributed to the photothermal effect of LM nanoparticles. Significantly, NIR photothermal properties of free-standing nanostructured TOBC/EGaIn/MiniGNR-COOH thin film was further improved and temperature difference reached 52.7 °C by introducing the MiniGNR-COOH, ascribed to the photothermal synergies between LM nanoparticles and the MiniGNR-COOH. The results further proved that the MiniGNR-COOH have excellent photothermal conversion capability, which is consistent with the results in **Figures S3** and **S10**. Meanwhile, results of NIR photothermal properties of free-standing nanostructured TOBC/EGaIn/MiniGNR-COOH film upon exposure to different light intensities

are shown in **Figure S14E**. The results showed that with the increase of 808 nm NIR light intensities from 0.1 to 0.3 W cm⁻², the surface temperature difference of free-standing nanostructured film increases gradually and its values are $32.9 \,^{\circ}$ C, $43.9 \,^{\circ}$ C and $52.7 \,^{\circ}$ C, respectively.

To explore the electrical properties of LM-based free-standing nanostructured film before and after the introduction of the MiniGNR-COOH, the resistances of TOBC/EGaIn and TOBC/EGaIn/MiniGNR-COOH were collected by a Keithley 2450 source meter under different shape-bending states (from 0 to 360°). It should be noted that the resultant ultrathin flexible nanostructured film was found to exhibit high electrical conductivity and favorable stability (**Figure S15**), which might result from the evaporation-induced deposition of LM nanoparticles in the presence of biological nanocelluloses. To further study the effect of the MiniGNR-COOH on the mechanical properties of free-standing nanostructured film, tensile stress-strain curves of the LM-based free-standing nanostructured film before and after the introduction of the MiniGNR-COOH were tested using an electronic tensile testing machine. The tensile stress of TOBC/EGaIn and TOBC/EGaIn/MiniGNR-COOH free-standing nanostructured film are 4.32 ± 0.14 MPa and 4.93 ± 0.17 MPa, and the corresponding elongation are $5.04 \pm 0.12\%$ and $5.29 \pm 0.13\%$ (**Figure S16**), respectively. These results might result from the enhanced hydrogen bonding or Ga³⁺ coordination among LM nanoparticles, MiniGNRs-COOH and TOBC nanofibers.



Figure S14. (A-C) Infrared thermal images of pure BC, TOBC/EGaIn and TOBC/EGaIn/MiniGNR-COOH free-standing nanostructured film under NIR light irradiation (808 nm, 0.3 W cm⁻²), respectively, and the corresponding (D) surface temperature changes of different samples: pure BC (black line); TOBC/EGaIn (blue line) and TOBC/EGaIn/MiniGNR-COOH (red line). (E) Changes of surface temperature of TOBC/EGaIn/MiniGNR-COOH as a function of NIR irradiation time for different light intensities (0.1 W cm⁻², 0.2 W cm⁻², and 0.3 W cm⁻² at 808 nm).



Figure S15. Electrical conductivity of the free-standing nanostructured thin film (Length = 4.0 cm,

Width = 1.0 cm, Thickness = $20 \mu \text{m}$) before and after the introduction of MiniGNR-COOH under different shape-bending states.



Figure S16. Tensile stress-strain curves of the free-standing nanostructured thin film (Length = 4.0 cm, Width = 1.0 cm, Thickness = $20 \mu \text{m}$) before and after the introduction of MiniGNR-COOH.

Drop-casting selective deposition of the colloidal LM ink on other substrates: Besides as the free-standing LM nanostructured film, the colloidal LM ink could also be coated onto many other substrates through drop-casting technique followed by the solvent evaporation and film drying process at the ambient condition (1 atm, room temperature ~ 25 °C, relative humidity ~ 40%) (**Figure S17**).



Figure S17. Drop-casting selective deposition of the colloidal LM ink on other substrates including filter paper, polydimethylsiloxane (PDMS), aluminum foil and tree leaf.

4. LM-liquid crystalline network (LCN) soft actuators

4.1 Fabrication and characterizations of LM-LCN thin film

Free-standing LCN films were prepared by the photocopolymerization of liquid crystalline monomer mixture (C6M:RM23 = 70:30 wt%, 0.5 wt% photoinitiator DMPA) capillary-filled into a splay-aligned cell under UV irradiation (365 nm, 10 mW cm⁻²) at ~ 70 °C for 30 min.^[11] The film thickness was controlled by spacers. After polymerization, the cell was opened by scalpel and the free-standing film was obtained. We cut the above free-standing LCN film into desired strips (e.g., Length = 10 mm, Width = 3 mm, Thickness = 23 μ m). Subsequently, 100 μ L of the colloidal LM suspension was drop-casting deposited on the planar side of LCN film followed by the solvent evaporation and film drying processes at the ambient condition, and gradually formed LM-LCN thin film. SEM was used to further characterize the cross-sectional microstructure of the obtained LM-LCN thin film. **Figure S18** clearly showed that the LM coating adhered closely to the LCN, which could be attributed to superior interfacial adhesion properties of deposited ultrathin colloidal LM coatings.



Figure S18. The cross-sectional SEM and EDX elemental-mapping images of LM-LCN thin film.

4.2 Electrothermally driven reversible shape-deformation of LM-LCN soft actuator

Figure S19A schematically shows the procedure of fabricating electrically conductive LM-LCN thin film. Firstly, one thin copper electrode as a fluid collector was adhered to one end of the LCN film (e.g., Length = 20 mm, Width = 4 mm, Thickness = 23 μ m) at a set distance. Then, 200 μ L of the colloidal LM ink was drop-casting deposited on the entire LCN film followed by the solvent evaporation and film drying processes at the ambient condition. **Figure S20** shows the electrical conductivity of the LM-LCN thin film. **Figure S19B** schematically shows the procedure of fabricating electrothermally driven LM-LCN soft actuator. Firstly, two copper electrodes as a fluid collector were adhered to one end of the LCN film (e.g., Length = 20 mm, Width = 4 mm, Thickness = 23 μ m) at a set distance. Then, 200 μ L of the colloidal LM ink was drop-casting deposited on the entire LCN film followed by the solvent at the ambient condition.



Figure S19. Schematic procedure of fabricating electrically conductive thin film (A) and electrothermally driven LM-LCN soft actuator (B)



Figure S20. Electrothermally driven reversible shape-deformation of the LM-LCN soft actuator. (A, B) Electrical conductivity of the obtained LM-LCN thin film. (C-E) Electrothermally driven reversible shape-deformation of the as-prepared LM-LCN soft actuator under different DC voltages (0.5; 1.0 and 1.5 V).

It is worth noting that the LM-LCN film could also be electrothermally actuated through applying a low direct-current (DC) voltage thanks to the excellent electrical conductivity of colloidal LM coating layer (**Figure S20**). This Joule-heating effect would also enable an electrical actuating behavior: a curve-shaped LM-LCN film bended up to different angles under different voltages, whose bending angle was controllable by the applied voltage. When the applied voltage is 0.5 V, the bending angle of the obtained LM-LCN soft actuator film is approximately 9.3 °C (**Figure S20C**). When switching off the voltage, the bending film recovered in several seconds. As the applied voltage increases (1.0 V and 1.5 V), the corresponding bending angles are 16.4 °C and 32.7 °C, respectively (**Figure S20(D-E**)).

4.3 NIR light-driven reversible shape-bending deformation of LM-LCN soft actuator

Figure S21A illustrates the shape-bending deformation process of LM-LCN soft actuator under NIR light irradiation (808 nm, 0.2 W cm⁻²). The LM-LCN soft actuator underwent a fast bending within 2 s and would autonomously revert to the original state in 3 s upon tuning off the NIR irradiation and the corresponding infrared thermal images are shown in **Figure S21B**. Results of NIR photothermal properties of LM-LCN soft actuator upon exposure to different light intensities are shown in **Figure S21C**. **Figure S21D** shows that the reversible shape-deformation of LM-LCN soft actuator could be repeatedly for many times without any noticeable degradation.

To further investigate the influence of LM coating thickness on the actuation performance of LM-LCN soft actuator, we designed LM-LCN composite films with different LM coating thickness (0.3, 0.9 and 5.0 μ m) and the corresponding total thickness is 23.3, 23.9 and 28.0 μ m, respectively. The actuation performance of LM-LCN soft actuator with different thickness were monitored by a thermal camera and Canon camera upon irradiating with 808 nm NIR light (0.2 W cm⁻²), as shown in Figure S22. The bending angle and surface temperature of LM-LCN soft actuator are 81° and 59.6 °C, respectively, when the designed LM-LCN thin film with thickness of 23.3 μ m under the NIR light (808 nm, 0.2 W cm⁻²) is continuously irradiated for 2.5 s, as shown in Figures S22(A-A¹). When the thickness of LM coating is 0.9 μ m, the bending angle and surface temperature of LM-LCN thin film are 130° and 73.3 °C, respectively, as shown in Figure 22(B-B¹). The results shows that the actuation performance of LM-LCN soft actuator was greatly enhanced with an increasing thickness of LM coatings on 23.0 μ m-thick LCN film, which can be attributed to an increasing content of LM and MiniGNR-COOH, and subsequent enhanced photothermal effect. However, when the LM coating thickness increases to a certain extent such as 5.0 μ m, the LM-LCN soft actuator exhibits a decreased actuation performance, where a large thickness of the LM coating could restrict the shape-deformation of LCN layer (**Figure 22(C-C**¹)).Results of NIR photothermal properties and bending angle change of LM-LCN soft actuator with different LM coating thickness are shown in **Figure S23**.



Figure S21. NIR light-driven reversible shape-bending deformation of LM-LCN soft actuator. (A) Photographs showing the shape-bending process of LM-LCN soft actuator upon NIR light irradiation (808 nm, 0.2 W cm⁻²) and (B) the corresponding infrared thermal images. (C) Changes of surface temperature of LM-LCN soft actuator as a function of NIR irradiation time for different light intensities (0.1 W cm⁻², 0.2 W cm⁻², and 0.3 W cm⁻² at 808 nm). (D) Reversible shape-bending deformation cycles of LM-LCN soft actuator upon repeatedly switching on/off NIR light irradiation (808 nm, 0.2 W cm⁻²).



Figure S22. Real images the bending process of the LM-LCN soft actuator upon switching on/off NIR light irradiation (808 nm, 0.2 W cm⁻²) under different LM coating thickness: (A) 0.3 μ m; (B) 0.9 μ m and (C) 5.0 μ m, respectively, and the corresponding (A¹-C¹) thermal imaging photographs. Fixed LCN film size: Length = 12 mm, Width = 3 mm, Thickness = 23.0 μ m.



Figure S23. (A, B) Changes of surface temperature and bending angle of LM-LCN soft actuator as a function of time upon switching on/off NIR light irradiation (808 nm, 0.2 W cm⁻²) under different LM coating thickness, respectively.

We also investigate the influence of the LCN film thickness on the actuation performance of LM-LCN soft actuator. We prepared LM-LCN composite films with different LCN thickness (23.0, 46.0 and 69.0 μ m) and the corresponding total thickness is 23.3, 46.3 and 69.3 μ m, respectively. The actuation performance of LM-LCN soft actuator with different thickness were traced by a thermal camera and Canon camera upon irradiating with 808 nm NIR light (0.2 W cm⁻²), as shown in Figure S24. The results shows that with a constant thickness of LM coating (0.3 μ m), the bending angle of LM-LCN soft actuator decreases upon increasing the thickness of the LCN film from 23.0 μ m to 69.0 μ m. Therefore, photoresponsive dynamics of LM-LCN soft actuators are closely related to several factors such as the thickness of LCN film, thickness of colloidal LM coating and power density of NIR irradiations. The performance of LM-LCN soft actuators could be optimized by balancing the trade-off among the LCN film, LM coating, and irradiation intensity of NIR light.



Figure S24. Real images the bending process of the LM-LCN soft actuator upon switching on/off NIR light irradiation (808 nm, 0.2 W cm^{-2}) under different LCN thicknesses: (A) (Size: Length =

12 mm, Width = 3 mm, Thickness = 23.0 μ m); (B) (Size: Length = 12 mm, Width = 3 mm, Thickness = 46.0 μ m) and (C) (Size: Length = 12 mm, Width = 3 mm, Thickness = 69.0 μ m), respectively, and the corresponding (A¹-C¹) thermal imaging photographs. Fixed LM coating thickness: 0.3 μ m.



Figure S25. (A, B) Changes of surface temperature and bending angle of LM-LCN soft actuator as a function of time upon switching on/off NIR light irradiation (808 nm, 0.2 W cm⁻²) under different LCN thickness, respectively.

5. Light-driven LM-shape memory polymer (SMP) soft actuators

5.1 Fabrication of irreversible shape-deformation of LM-SMP soft actuators

The colloidal LM ink was selectively drop-casting deposited on SMP (pre-strained polystyrene, also named Shrinky-Dinks) followed by the solvent evaporation and film drying processes at the ambient condition. We demonstrated self-folding of 2D SMP sheets with predesignated colloidal LM coatings into various 3D objects under the exposure of unfocused NIR light, and temporal programming of shape morphing and sequential self-folding were easily achieved by tailoring the thickness of the designed colloidal LM hinges.

V-shaped actuator: We cut the patterned SMP sheets into desired sample (e.g., Length = 25 mm, Width = 10 mm). Then, 50μ L of the colloidal LM ink as single line (Width = 1.2 mm, Length = 10 mm) can be selectively drop-casting deposited on the above SMP followed by the solvent evaporation and film drying processes at the ambient condition. Finally, the LM-SMP soft actuator showed self-folding of 2D SMP sheet into V-shaped 3D object under the exposure of NIR light.

N-shaped actuator: We cut the patterned polymer sheets into desired sample (e.g., Length = 40 mm, Width = 10 mm). Then, 100 μ L of the colloidal LM ink as two lines (Width = 1.2 mm, 12 mm spacing, Length = 10 mm) can be selectively drop-casting deposited on either side of the above SMP followed by the solvent evaporation and film drying processes at the ambient condition.

Finally, the LM-SMP soft actuator showed self-folding of 2D SMP sheet into N-shaped 3D object under the exposure of NIR light.

W-shaped actuator: We cut the patterned polymer sheets into desired sample (e.g., Length = 50 mm, Width = 10 mm). Then, 150 μ L of the colloidal LM ink as three lines (Width = 1.2 mm, 12 mm spacing, Length = 10 mm) can be selectively drop-casting deposited on alternating sides of the above SMP followed by the solvent evaporation and film drying processes at the ambient condition. Finally, the LM-SMP soft actuator showed self-folding of 2D SMP sheet into W-shaped 3D object under the exposure of NIR light.

Cube-shaped actuator: We cut the patterned polymer sheets into the plane shape of the cube before folding ($10 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$, Width = 1.2 mm). Then, 150μ L of the colloidal LM ink as five lines can be successively drop-casting deposited on the above SMP followed by the solvent evaporation and film drying processes at the ambient condition. Finally, the LM-SMP soft actuator showed self-folding of 2D SMP sheet into cube-shaped 3D object under the exposure of NIR light.

TJU-shaped actuator: We cut the patterned polymer sheets into our university TJU logo. Then, 100, 80 and 60 μ L the colloidal LM ink as three lines (T: Width = 1.2 mm, Length = 10 mm; J: Width = 1.2 mm, Length = 14 mm; U: Width = 1.2 mm, Length = 18 mm) can be successively drop-casting deposited on "TJU" logo composed of the desired SMP followed by the solvent evaporation and film drying processes at the ambient condition. Finally, temporal programming of shape morphing and sequential self-folding of "TJU" logo were easily achieved under the exposure of NIR light.

5.2 Light-driven irreversible shape-deformation of LM-SMP soft actuators

Taking advantages of high photothermal conversion efficiency, superior interfacial adhesion and programmable coating properties of colloidal LM suspensions, we demonstrated self-folding of 2D SMP sheets with predesignated colloidal LM coatings into various 3D objects under the exposure of NIR light. Temporal programming of shape morphing and sequential self-folding were achieved by tailoring the thickness of the designed colloidal LM hinges (**Figure S26** and **Movie S4**). The onset of folding and the time required to complete folding are dependent on the intensity of the NIR light, the hinge width and surface temperature of the base support. **Figure S26A, S26C**)

display three examples of 3D shape-folding generated via NIR irradiations, the left column shows the 2D patterns before irradiation with NIR light and the right column presents the corresponding irreversible shape-deformation of V-shaped, N-shaped and W-shaped 3D objects after NIR irradiation. **Figure S26B, S26E** demonstrates the bidirectional 3D self-folding of SMP films with predesignated colloidal LM coatings. As shown in **Figure S26D**, a cube box could be obtained upon NIR irradiations, where the folding angle generated by a single hinge is typically 90°. Interestingly, temporal programming of shape morphing and sequential self-folding of "TJU" logo were achieved by tailoring the thickness of the designed colloidal LM hinges (**Figure S26E**). These empirical results indicate that various 3D structures can be realized by designing the line and pattern of the hinges.



Figure S26. Programmable self-folding of 2D SMP sheets with predesignated colloidal LM coatings into various 3D objects under the exposure of NIR light. (A) Single line (Width = 1.2 mm, Length = 10 mm) patterned on the top side of the SMP; (B) two lines (Width = 1.2 mm, 12 mm spacing, Length = 10 mm) patterned on either side of the SMP; (C) three lines (Width = 1.2 mm, 12 mm spacing, Length = 10 mm) patterned on alternating sides of the SMP; (D) cube box (10 mm × 10 mm × 10 mm, Width = 1.2 mm); (E) three lines patterned on "TJU" logo from our university by different concentrations of the colloidal LM ink: T (Width = 1.2 mm, 100 μ L, Length = 10 mm), J (Width = 1.2 mm, 80 μ L, Length = 14 mm) and U (Width = 1.2 mm, 60 μ L, Length

= 18 mm). Fixed in our experiment at 675 mW cm⁻² by placing the sheets under an unfocused NIR light bulb at a set distance (20 cm from the lamp).

Materials	Strategies	Conductivity	Light-driven		
			Light intensity P [mW cm ⁻²]	Response time <i>t</i> [s]	Ref.
LM/LCN/MiniGNRs	Coating	\checkmark	300 (NIR)	2.5	this work
LM/LCE	Mixing	\checkmark	—	—	[12]
LM/LCE	3D printing	\checkmark	800 (NIR)	25	[13]
PDA/LCN	Coating	×	4000 (NIR)	_	[11]
CNT/LCE	Mixing	\checkmark	287 (visible light)	6	[14]
LCE-dyes/LCE	Mixing	×	180 (NIR)	32	[15]
PET/LCN	Spray-coating	×	170 (UV) & 300 (blue)	15	[16]
GO/azobenzene doped LCN (ALCN)	Spin-coating	×	700 (NIR)	15	[17]
AuNR/ALCN	Mixing	×	6700 (NIR)	40	[18]
PDA/ALCN	Coating	×	100 (UV) & 1000 (NIR)	6	[19]

Table S1. Summary of representative liquid crystalline polymer-based soft actuators

6. Captions for supplementary movies

Movie S1. Programmable S-, M- and W-shaped LM-LCN soft actuators under the NIR light irradiation.

Movie S2. Light-fueled LM-LCN self-sustained soft oscillator under a constant NIR light illumination.

Movie S3. Light-driven inchworm-inspired soft crawler made of LM-LCN soft actuator on a ratcheted substrate upon cyclic NIR irradiations

Movie S4. Programmable self-folding of 2D SMP sheets into various 3D objects under the

exposure of NIR light.

Movie S5. Light-driven robotic Shadow Play showing the scene of "a police officer directing the traffic" upon NIR irradiations.

Movie S6. Light-driven robotic Shadow Play showing the scene of "a Jade Rabbit walking toward the Beauty" upon NIR irradiations.

Movie S7. Light-driven robotic Shadow Play showing the scene of "a person looking up at the shining beacon" upon NIR irradiations.

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