# Supplementary Materials for

# 4D Printing of Carbon-Fiber-Reinforced Liquid Crystal Elastomers for Self-Deployable Solar Panels

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#### **1. Experimental Procedures**

#### **1.1 Materials**

Short carbon fiber (SCF) from Nanjing Weida Composite Material Co., Ltd., China. Polyimide film tape (3M 3M7414L). 1,4-bis(4-(3-acryloyloxypropyloxy)benzoyloxy)-2-methylbenzene (RM257) from Jiangsu Hecheng Display Technology Co., Ltd., China. Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), and 2,2-(ethylenedioxy)diethanethiol (EDDET) were all purchased from Heowns Biochemical Technology Co., Ltd., Tianjin, China. Dipropylamine (DPA, Macklin Biochemical Co., Ltd., Shanghai, China). 2,2-dimethoxy-2-phenylacetophenone (I-651) was acquired from Rhawn, China. 2,6-di-tert-butyl-4-methylphenol (BHT) and 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA) from Macklin Biochemical Co., Ltd., Shanghai, China.

#### 1.2 Preparation of photopolymerizable SCF

For the preparation of TMSPMA-modified SCF, the SCF was treated by  $O_2$  plasma irradiation (FEMTO plasma cleaner, 5 min) to activate surface (generate hydroxyl groups). Then, the TMSPMA solution (1 wt % in a 1:1 water-ethanol mixture) was added dropwise onto the SCF drip addition on the SCF, followed by curing (80 °C, 60 min).

### **1.3 Preparation of printable SCF-LCE inks**

The chemical compositions of printable SCF-LCE inks are listed in Fig. 1b and S2a and consist of the diacrylate mesogen RM257, the chain extender EDDET, and the tetrathiol crosslinker PETMP, the catalyst DPA, the thermal polymerization inhibitor BHT, and the photoinitiator I-651, and the photothermal filler SCF. The preparation procedures for SCF-LCE inks are described below: RM257 (1000 mg), SCF (20, 40, 60, and 80 mg corresponding to 2 wt%, 4 wt%, 6 wt%, and 8 wt%) and BHT (1 mg) were dissolved at 80 °C. Then, EDDET (270 mg), PETMP (40 mg), and I-651 (6 mg) were added. After DPA (15  $\mu$ l) was added to initiate the Michael addition reaction, reacted for 3 h at 65 °C, the SCF-LCE ink was obtained and is ready for printing.

## 1.4 Printing of the SCF-LCE film

The SCF-LCE inks were extruded through a metal nozzle using a direct-ink-writing 3D printer (Bio-Architect, Regenovo). Original images, which were used to program the printing trajectory

and parameters, were imported into the 3D Max (Autodesk) and subsequently imported into the 3D printer software. The writing speed and the pneumatic pressure were manually set on the basis of the relation between the line width and vink/vnozzle.

## 1.5 Adhesion of the polyimide tape

To ensure a better bond between the polyimide tape and the SCF-LCE, we first treat the SCF-LCE film with  $O_2$  plasma in a plasma cleaner for 2 minutes, grafting hydroxyl groups onto its surface. Then, under 80°C, while the SCF-LCE film is in a contracted state, we attach the polyimide tape to its surface and apply a 1 kg weight. After 5 minutes, the weight is removed, and the polyimide tape is successfully bonded to the SCF-LCE surface.

#### **1.6 COMSOL simulation**

A finite element analysis model was set up to verify the shape-bending mechanism of SCF-LCE bilayer actuators by using COMSOL Multiphysics software 5.4. In the simulation, the SCF-LCE composites were modeled as a bilayer structure. One layer was defined with isotropic material properties without thermal expansion behavior, while the other was defined with directional thermal expansion along the printing pathway. The input thermal expansion coefficient was set to be negative to represent the thermally induced shrinkage of monodomain LCE. To align the material direction along mesogen alignment, two coordinate systems were established: the global coordinate system was used to construct the geometrical model, and the local coordinate system described the local material distribution and orientation in the current configuration.

The parameters of film are provided in Fig. S15. The "Solid Mechanics" and "Thermal Expansion" physical modules were used to simulate the thermal actuation and study the steady state temperature-induced deformation at a reference temperature of 25 °C. The temperature distribution is essentially uniform because the thickness of the actuator (< 500  $\mu$ m) is typically less than 1/50 of the length in the other two dimensions (~25 mm). therefore, the heat conduction inside the actuator is very fast. Based on the bimetal thermostat analysis the deformation radius is

$$\rho = \frac{(h_1 + h_2) \Big( 3(1+m)^2 + (1+mn) \Big( m^2 + \frac{1}{mn} \Big) \Big)}{6(\alpha_{11} - \alpha_{22})(1+m)^2} \frac{1}{T - T_0}$$

Here,

$$m = \frac{h_2}{h_1}, \ n = \frac{E_2}{E_1}$$

Where 1 and 2 represent LCE and PI, respectively.  $h_1$  and  $h_2$  are the thickness of PI film and LDPE film, respectively,  $E_1$  and  $E_2$  denote their moduli of elasticity,  $\alpha_{11}$  and  $\alpha_{22}$  denote their coefficients of expansion,  $T_0$  is the room temperature (25 °C) at which the sample is flat. Upon a temperature increment, the defined material structures exhibited folding deformation that accurately captured the experimental results of 4D printed composites.

#### **1.7 Characterization and Measurement**

FT-IR spectra were collected on a Tensor II (Bruker, Germany) spectrometer by dispersing completely dried samples in compressed KBr pellets. Differential scanning calorimetry measurements were conducted on a TA Instruments S4800 at 10 °C min<sup>-1</sup>. The examination used the up-down-up mode, and the first heating was used to remove the thermal history, while the first cooling and the second heating were used for analysis. The Optical images were imaged by consumer-grade digital cameras (DS126631, Canon) and POM images were obtained using polarized microscopy (Olympus BX60) equipped. 2D-Wide-angle X-ray diffraction (Xenocs Xeuss 2.0) was performed to explore the transformation of liquid crystal-isotropic phases during the heating and cooling process and changes in the order parameter S during phase transitions. SEM images were performed with a Hitachi S-4800 field-emission scanning electron microscope. UV-Vis spectra were observed by using a FUV-6BK spectroscope (BANGWO Co., Ltd., Guangzhou, China). The rheological properties of the SCF-LCE inks were characterized using a Discovery HR-2 Hybrid Rheometer (TA Instruments). A 20 mm parallel plate geometry was used. The shear rate was swept from 0.01 to 1000 s<sup>-1</sup> using a plate gap of 1 mm. An iodine-tungsten lamp (PHILIPS 250W BR125) was used as the light source. A STG-500 transformer (Zhejiang Huizheng Electric Co., LTD., Zhejiang, China) and a CEL-NP2000 power meter (Zhongjiao Jinyuan Technology Co., LTD., Beijing, China) were used to adjust the light power. An IR camera Fluke TiX500 was used to measure the temperature of the samples to evaluate photothermal performance. The UV light irradiation was carried out with the help of a Xenon light source (100 W, UVGL-58, UVP Co.) through a filter at 365 nm. The stress-strain curves were obtained by

Universal Testing Machine (Suns890, Shenzhen Suns Technology Co., Ltd.). Laser particle size analyzer (Malvern Mastersizer 2000) was conducted on for particle size determination.

## 2. Results and Discussion

# **2.1 Supplementary Figures**



Fig. S1 Length-size distribution of SCF dispersions in deionized water. (a) An average SCF of 9  $\mu$ m. (b) An average SCF of 75  $\mu$ m. (c) An average SCF of 200  $\mu$ m.



**Fig. S2** Chemical structures of the compounds used in the experiments. (a) Other compounds used in our experiments. (b) Schematic representation of the main components (diacrylate monomer and chain extender) making up the CLE oligomer.



**Fig. S3** Diagram of modified carbon fiber using TMSPMA. (a) The SCF is treated by  $O_2$  plasma irradiation to activate surfaces and generate hydroxyl groups. Then, the TMSPMA solution is dropwise applied onto the SCF. Silane hydrolyzes into silanol. During curing, the silanol groups condense with hydroxy. (b) After photopolymerization, the double bonds of TMSPMA crosslink with the LCE network. As a result, SCF and LCE combine firmly.



**Fig. S4** The FTIR spectra of SCF, SCF-TMSPMA. The feature absorption peak at 1127 cm<sup>-1</sup> (Si-O) and 1715 cm<sup>-1</sup> (C=O) implied the successful silanization grafting of TMSPMA on SCF surface.



**Fig. S5** Viscosity of the 2 wt% SCF-LCE inks as a function of the shear rate at different temperatures. The SCF-LCE ink exhibits clear shear thinning effects at all temperatures studied, ranging from 30 to 70 °C.



Fig. S6 (a) The influence of the printing temperature on the actuation strain of SCF-LCE films. (b) The influence of the printing speed on the actuation strain of SCF-LCE films. SCF-LCE was printed at a printing speed of 5 mm s<sup>-1</sup> at 30 °C, 40 °C, 50 °C, 60 °C, and 70 °C printing temperatures. When the printing temperature was 30 °C and 40 °C, the drive strain was 33% and 28%, respectively. However, when the printing temperature exceeded 50 °C, the drive strain decreased to less than 10% (Fig. S6a). This behavior can be attributed to the entropic elasticity in liquid crystal elastomers, which drives the mesogens towards a disordered state. As the temperature increases, the enhanced mobility of the mesogens accelerates their disorientation in the SCF-LCE. In addition, higher printing speeds lead to larger actuation strains. However, at a printing temperature of 30 °C, the high viscosity of the ink prevents the formation of a continuous SCF-LCE film at a speed of 6 mm s<sup>-1</sup>. Therefore, a printing temperature of 40 °C was selected to investigate the influence of printing speed on the actuation strain of SCF-LCE films. The actuation strain increases from 20% to 33% as the printing speed rises from 4 mm s<sup>-1</sup> to 6 mm s<sup>-1</sup> (Fig. S6b). Notably, the actuation strain of SCF-LCE remains at 33% even when the printing speed exceeds 6 mm s<sup>-1</sup>. This suggests that a printing speed of 6 mm s<sup>-1</sup> achieves the maximum orientation of the SCF-LCE. Therefore, a printing speed of 6 mm s<sup>-1</sup> should be selected for optimal performance. Finally, a printing temperature of 40 °C and a printing speed of 6 mm s<sup>-1</sup> were selected for subsequent experiments.



**Fig. S7** Optical images of the DIW printed SCF-LCE filaments under different printing speeds and different printing temperature. Upon observing the appearance of the filaments under each printing condition, it was found that at a printing temperature of 30 °C and a printing speed of 5 mm s<sup>-1</sup>, uneven extrusion occurred due to the ink viscosity, which affected the bonding between the filaments. At a printing temperature of 40 °C, extrusion remained stable and uniform. Therefore, a printing temperature of 40 °C was selected.



Fig. S8 Temperature change profiles of SCF monomer powder exposed to an iodine tungsten lamp at a light power intensity of 400 mW  $\cdot$  cm<sup>-2</sup>.



Fig. S9 Actuation strain of LCE films with varying SCF content.



Fig. S10 Actuation strain of Pure LCE.



**Fig. S11** (a) Light-induced actuation strain of SCF-LCE films reinforced with carbon fibers of varying lengths. (b) Stress-strain curves of SCF-LCE films containing carbon fibers of different lengths at room temperature. (stretching rate: 5 mm min<sup>-1</sup>).



**Fig. S12** (a) Schematics for the T-Peel test. (b) Peeling force per unit width versus displacement curves for the SCF-LCE film and PI tape. A universal testing machine was employed to perform T-peel tests, in which the PI tape was peeled from the surface of the SCF-LCE film. The bonding strength was calculated by dividing the steady-state (or plateau) peeling force with the sample width.



**Fig. S13** (a) Method of measuring the unfolding force. (b) The folding actuation force of the bilayer actuator as a function of angle when the iodine tungsten lamp light irradiation is removed.



**Fig. S14** Repeated folding deformation of SCF-LCE bilayer actuator. The following figure shows the sample's appearance during ten heating-cooling cycles, where the high and low temperatures were set to 80 °C and room temperature, respectively. The bottom figure displays the folding curvature at 80 °C in each cycle. It was observed that the sample exhibited consistent and repeatable deformation in each cycle, with the magnitude of folding deformation remaining stable throughout.



**Fig. S15**  $\rho$  represents the material density, v represents the Poisson's ratio,  $\alpha_{11}$ ,  $\alpha_{22}$ , and  $\alpha_{33}$  represents the directional thermal expansion coefficients. We used COMSOL software to conduct FEA of SCF-LCE bilayer actuator deformation It is important to note that although the SCF-LCE composites also undergo shape changes in the transverse direction of the composite filament upon temperature change, the corresponding thermal expansion coefficient was set to 0 due to its minimal effect on the overall deformation of the structures.



**Fig. S16** Length changes of the hinge in the triple-fold solar panels as a function of time under light irradiation.



Fig. S17 Photograph of the photovoltaic power generation from the self-deployed solar panels.



**Fig. S18** Power generation performance of self-deployed solar panels under cyclic unfolding. Under 400 mW cm<sup>-2</sup> of light irradiation, the self-deployed solar panel can fully deploy within 40 s during the cycle and achieve its maximum power generation efficiency.



**Fig. S19** Current changes of unfolded (static) solar panels and self-deployed solar panels photovoltaics generated under 400 mW cm<sup>-2</sup> of light irradiation. The self-deployed solar panels exhibit lower photoelectric efficiency only during the initial deployment compared to static solar panels. Once deployed, the photoelectric efficiency of the self-deployed solar panels is comparable to that of static solar panels and exhibits stable photoelectric efficiency.

Sample	Material Designs	Туре	Prepara tion method	Program mability	Bend	Contr actile Strain	Tensile Stress	Ref.
LCE-SCF	Photopolymeriza ble short carbon fiber monomer	Film/Bilay er structure	DIW	Yes	Yes (0.40 mm <sup>-1</sup> )	27%	13.5 MPa	This work
LCE/ Continuous fiber	Carbon Fiber, Polyester Fiber, Conductive Fiber	Embedded film	DIW	Yes	Yes (0.11 mm <sup>-1</sup> )	N/A	~73 MPa	Ref. 1
CFRLCEs	Continuous aramid fiber	Off-center Core–shell Fiber	DIW	Yes	Yes (0.33 mm <sup>-1</sup> )	N/A	~70 MPa	Ref. 2
LCECs	Unidirectional continuous carbon fibers, Carbon nanotubes	Solid Film	Mold	Yes	Yes	57.1%	3.6 MPa	Ref. 3
LCEC	Unidirectional carbon fiber fabric	Solid Film	Mold	No	Yes (~0.12 mm <sup>-1</sup> )	N/A	9.59 MPa	Ref. 4
LCEC	Carbon fiber fabric	Solid Film	DIW	Yes	Yes	N/A	4.58 MPa	Ref. 5
SWNT-LCE	Functionalized carbon nanotubes	Solid Film	Mold	No	Yes	30%	0.125 MPa	Ref. 6
MLCE/CNT	Carbon nanotubes, Dispersant	Film/Bilay er structure	Mold	No	Yes	~48%	3.85 MPa	Ref. 7

 Table S1 Comparison of performance of different LCE-based soft actuators in literatures.

## **2.3 Supplementary Movies**

- Movie S1: The light-driven unfolding of a SCF-LCE bilayer actuator.
- Movie S2: Various bending patterns of SCF-LCE bilayer actuator under light.

Movie S3: The light-responsive self-deployed solar panels for the space station model.

### 3. References

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