1 Electronic Supplementary Material (ESI) for Materials Horizons.

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3 Metal-hygroscopic Polymer Conductors that Can Secrete Solders for

4 Connections in Stretchable Devices

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25 Experimental Section

Fabrication of the MHPC. The MHPC ink was fabricated by 26 sonicating liquid metal and hygroscopic polymer solutions. We mixed 1g 27 PVP (Aladdin, Mn = 1300000, China) with 20 ml hexyl alcohol (98%, 28 MACKLIN, China) and stirred for 24 h to obtain the PVP solution. We 29 added 3 g gallium-indium alloy (Ga:In = 4:1, Hawk, HK3284, China) 30 and 1 mL PVP solution into a 5 mL centrifuge tube and sonicated for 60 s 31 with a amplitude of 20% using a probe sonicator (S-450D, Branson,). We 32 obtained the MHPC ink. We also used other polymers such as 33 polyethylene oxide (PEO), hydroxypropyl methylcellulose (USP2910, 34 MACKLIN, China), thermoplastic polyurethane (TPU) (BASF, 9390, 35 Germany), Poly (ethylene-co-vinyl acetate) (vinyl acetate 40 wt. %, 36 Sigma-Aldrich, USA) and different solutions like pure water, 37 tetrahydrofuran (99%, MACKLIN, China), ethanol, decanol (98%, 38 MACKLIN, China) to fabricate the ink. 39 We use a manual screen printer (NS101-S, Leniya, China) to print 40 the MHPC ink on different substrates such as polyurethane (0.01mm, 41 0.02mm, 0.03mm, Ensinger, China), ecoflex (0030, Smooth-on, USA) 42 and acrylic foam (4905, 3M VHB, USA). Before the printing on the AF 43 film, plasma treatment (PDC-MG, ING HENG, China) should be 44 conducted to eliminate the tackiness of the film. After the evaporation of 45 the solvent in room temperature for 20 min or in an oven at 80 °C for 3 46

min, we use a humidifier (SC-3C40B, Midea, China) to produce vapor to 47 change the environmental humidity (RH 100%) around the MHPC. After 48 vapor treatment for 30 s, we let the MHPC dry in atmosphere 49 environment in room temperature (the typical relative humidity in Beijing 50 varied from 5% to 20%) for 10 min. The RH was measured by a thermos-51 hygrometer (PC-5110, AS ONE, Japan). We repeat the wet-dry cycles for 52 several cycles to make the MHPC conductive and secrete LMSs in 53 different numbers and diameters. 54

Fabrication of the stretchable system. The fabrication process was 55 shown in figure S24. The fabrication starts from drilling holes on the 56 stretchable films. We screen printed commercial pigment to locate the 57 holes on the films and drilling holes on the stained locations using 58 punchers (20839-1, EASYUSE, China) (Biopsy Punch, World Precision 59 Instruments Inc., USA). After alignment, we screen printed MHPC on 60 one side of the stretchable film to obtain the back side of the third PCAT 61 layer. After the evaporation of the solvent, we screen printed MHPC on 62 the front side of the third PCAT layer. We carried out 3 wet-dry cycles on 63 both sides of the third PCAT layer to make MHPC conductive and secrete 64 LM eruptions. We dilute the pressure sensitive adhesive (PSA) (Wuqing 65 SY002, Yihui, China) using n-hexane (98%, MACKLIN, China) with a 66 weight ratio of 1:2 (PSA: n-hexane), and spin coat the diluted PSA on the 67 front side of the first PCAT layer using a spin coater (200 r/min, 30 s, 68

KW-4A, SETCAS, China). We obtained the prepared third PCAT layer 69 after baking it in an 80 °C oven for 20 min. We used the same method to 70 obtain the second and third PCAT layer. We aligned the contact pads of 71 the three PCAT layers and stacked together, electrical and mechanical 72 connections will form between layers because of the PSA and the LMSs. 73 We connect the ECEs on the first layer PCAT by light pressure. The 74 ECEs were ordered from the Shanghai Ren Ren Technology Co., Ltd. 75 Finally, we spin coat (2000 r/min, 40 s) a thin layer of Ecoflex for 76 encapsulation. 77

Characterizations. We used SEM (8220, Hitachi, Japan) to directly
characterize the surface of the MHPC (PVP based). To investigate the
inner structure of the MHPC, we immersed the MHPC in pure water for
24 h to dissolve the PVP before the SEM characterizations. We also used
the optical microscopy (M30x-HD, Optilia, Sweden) to characterize the
growing process of the LMSs. We obtained the thickness of the MHPC
by a stylus profiler (Bruker, Dektak-XT, USA).

The shrinkage degree of the polymer in different humidity can be reflected by the bending degrees of a polymer coated silicon strips. Briefly, we print the polymer solution (the same as the PVP solution for preparing the MHPC ink) on the silicone (0.25mm, HT6240, Rogers, US) via screen printer. We let the solvent n-hexane evaporate in an oven at 60 °C for 10 min. The PVP coated silicones are cut into small samples with

91 size of 3 mm* 45 mm. The bending test of the silicones strips in different
92 humidity were carried out in a sealed glass chamber connected with a
93 humidifier.

The peel strength of the PSA between the PU and polyimide is achieved by 180 degree peel method (figure S10a) using the universal testing machines (3365, INSTRON, USA).

We use the electrochemical station (1040C, CHI, China) and screw 97 driven slide (FSL 40, FUYU, China) for the strain-conductivity and 98 cycle-resistant tests. We used MHPC (2*20 mm) on PU strips 99 (10*50*0.05 mm) for the stretchy test. The electrochemical station served 100 to apply 0.001 V voltage on both ends of the MHPC and collect the 101 current while the slide are responsible for stretching the MHPC to 102 different strains. The strain-stress and strain-load curve of different soft 103 materials were measure by universal testing machines (3365, INSTRON, 104 USA). 105

The measurements of body temperature, heart rate and SpO₂ were achieved by our system connected to an Arduino. The chips we adopted for monitoring the body temperature are LM35 (National Semiconductor, USA). The oximetry chip (MAX30102EFD, Maxim integrated, USA) and the corresponding codes for detecting heartbeat and SpO₂ were purchased from Maxim Integrated. The oximetry chip (MAX 30102) on our system contains red LED, IR LED and photodiode that can collect the

113 PPG signals (light absorption) at two different wavelengths (red 660 nm

- and Infrared red 880 nm) based on the amount of light reflected to a
- 115 photodiode. The circuit designs and layouts of the oximeter are based on
- 116 commercial SpO₂ modules (MH-ET Live).





Figure S1. Fabrication and optical image of the MHPC. (a) Fabrication of the MHPC, (i) sonicating the liquid metal into MHPC ink in a hygroscopic polymer solution. (ii) Screen printing the MHPC on a substrate. (iii) Changing the humidity around the MHPC using a humidifier. (b) Optical image of the MHPC before and after the wet-dry cycles, scale bar, 10 mm.



127 Figure S2. SEM characterization of the MHPC in different phase corresponding

to figure 2c. (a) SEM characterization of the MHPC after 0 (I), 1 (II), 2 (III), 3 (IV)
wet-dry cycles, respectively. Scale bar, 30 um. (b) Illustration of the conductive paths

130 between the liquid metal particles during the wet-dry cycles. Dash line, the width of the

131 conductive paths.



- 141 suggest that PVP shrink greater in lower humidity. (c) Curvature of the silicone strips
- 142 and MHPC conductivity after the first wet-dry cycle versus different humidity.
- 143
- 144



Figure S4. Measurements of the thickness of the MHPC. (a) Scanning direction of
the probe. (b) The height of the MHPC after different wet-dry cycles, the measurements
avoid the LMEs.

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Figure S5. MHPC fabrication using different polymers and solvents. (a) Illustration of the size of the measured MHPC. (b) Conductance of the MHPC fabricating by different polymers after 5 wet-dry cycles. (c) Conductance of the MHPC fabricating by



Figure S7. A MHPC strain sensor with a serpentine structure. (a) Illustration and optical image of the serpentine-structured MHPC. (b) Resistant change response of the serpentine-structured MHPC in different strains, dashed line, the resistant deviation of the ordinate origin. When the maximum strain reaches 100%, the resistance at the strain of 0% begin to increase with cycles (Figure S6b). This may affect the accuracy of the MHPC-based strain sensor, but has negligible influence on the MHPC-based

- 173 interconnects. (c) Resistant change dependence on different strains.



- 177 Figure S8. Optical image of the MHPC after different wet-dry cycles, red dashed178 cycles, the vanished LMEs. Scale bar, 0.5 mm.





182 Scale bar, 0.3mm



Figure S10. Characterizations of the connections. (a) Measure the peel strength if the adhesives between the PU and polyimide using 180 degree peel method. (b)

- 187 Illustration, SEM, and EDS analysis on the Cross-section of the LME connected part.188 Scale bar, 50 um.



193 Figure S11. Design drawing of the ECEs. Red, copper film on the top side. Blue,194 copper film on the bottom side.

Тор





197 Figure S12. Optical image of the top and bottom of the ECEs. Scale bar, 20 mm.

0% 30% **Image: 30% Image: 30% Image:**



150%





202

- 203 Figure S13. Optical image of the double-sided and single-layered pulse oximeter
- 204 stretched to different strains and recover to 0%. Scale bar, 20 mm.

205



b

Cycles

0

а



500

1000

207

Figure S14. Cycling test of a double-sided and single-layered pulse oximeter with an 80% uniaxial strain. (a) Optical image of the setup for the cycling test. (b) Optical image of the device after different cycles, scale bar, 20 mm.

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Figure S15. Strain-stress and strain-load curve of different elastomers. (a) Strainstress curve of Ecoflex, AF, and PU. (b) Strain-stress curve of the Ecoflex and AF. (c)
Strain-load curve of different elastomers with different thickness. Thickness, PU-t,
0.01mm; PU-2t, 0.02 mm; PU-3t, 0.03 mm; PU-20t, 0.20 mm, AF and Ecoflex, 0.20
mm.



220 Figure S16. Optical image of the LED simulated circuit stretched to different

221 strains. Scale bar, 30mm.





Figure S17. FEA simulation of the stress distribution on the stretchable device with different thickness when stretching to a strain of 50%. Scale bar, 20 mm.















241 Figure S20. Electrical-mechanical performance of MHPC printed on both sides

242 of the substrates connected by VIAs. (a) Illustration of the stretched MHPC on both

sides of the PCAT connected by VIA. (b) The change in resistance of MHPC and

244 VIA connected MHPC depends on different tensile strains. (c) The change in

245 resistance of VIA connected MHPC by stretching the patterns from 0% to 50% for

- 246 1,000 cycles
- 247



250 Figure S21. Circuit design and chip summary for the multilayered stretchable

- 251 system.





255 Figure S22. Layout designs for each separated PCAT layer and the merged 256 multilayer design.

257



260 Figure S23. Optical image of the integrated system stretched to different strains.

The stretchable system can be stretched to a strain of 50%. When the strain reaches about 100%, some ECEs will detach from the PCAT.



Figure S24. The fabrication of the stretchable system.1-2, Orientation and drilling of the VIAs. 2-3, alignment and printing the MHPC on the back of the first PCAT layer. 3-4, alignment and printing the MHPC on the top of the first PCAT layer. 5-6, fabrication of the second and thier PCAT layer. 6-7. Wet-dry treatment, PSA coat, and assembly of the three PCAT layer. 7-8, connections of the ECEs. 9, illustration of the stretchable system. Scale bar, 10 mm