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Supplemental Information

Printable Metal-Polymer Conductors for Highly Stretchable Bio-Devices

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SUPPLEMENTAL FIGURES

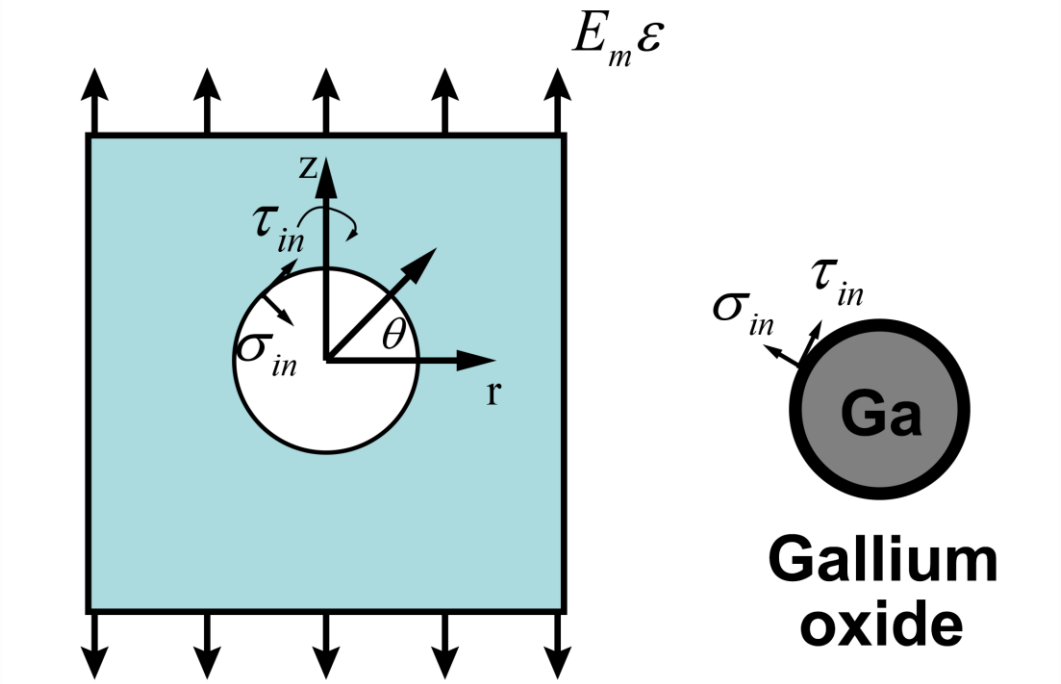

Figure S1. The diagram of uniaxial loading, related to Figure 1. The stress components at the interface of PDMS matrix and gallium oxide shell is σ_{in} and τ_{in}.

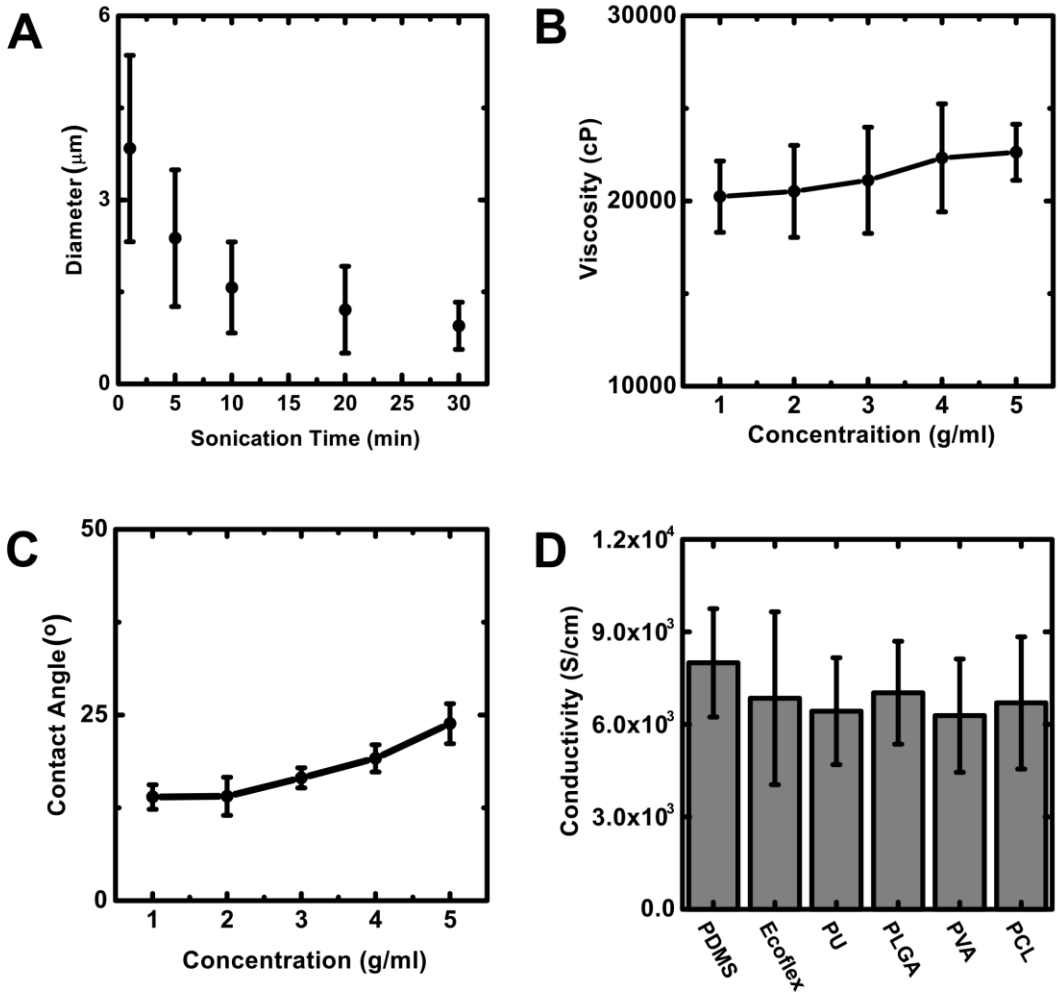

Figure S2. Characterization of the LMPs ink, **related to Figure 1.** (**A**) Average diameter of LM particles as a function of sonication time. (**B**) The viscosity of the ink as a function of the concentrations of the ink. (**C**) The contact angle between the LMPs inks with different concentrations and the PET film. (**D**) Conductivity of MPC cast by different polymers. Data are expressed as mean ±SD.

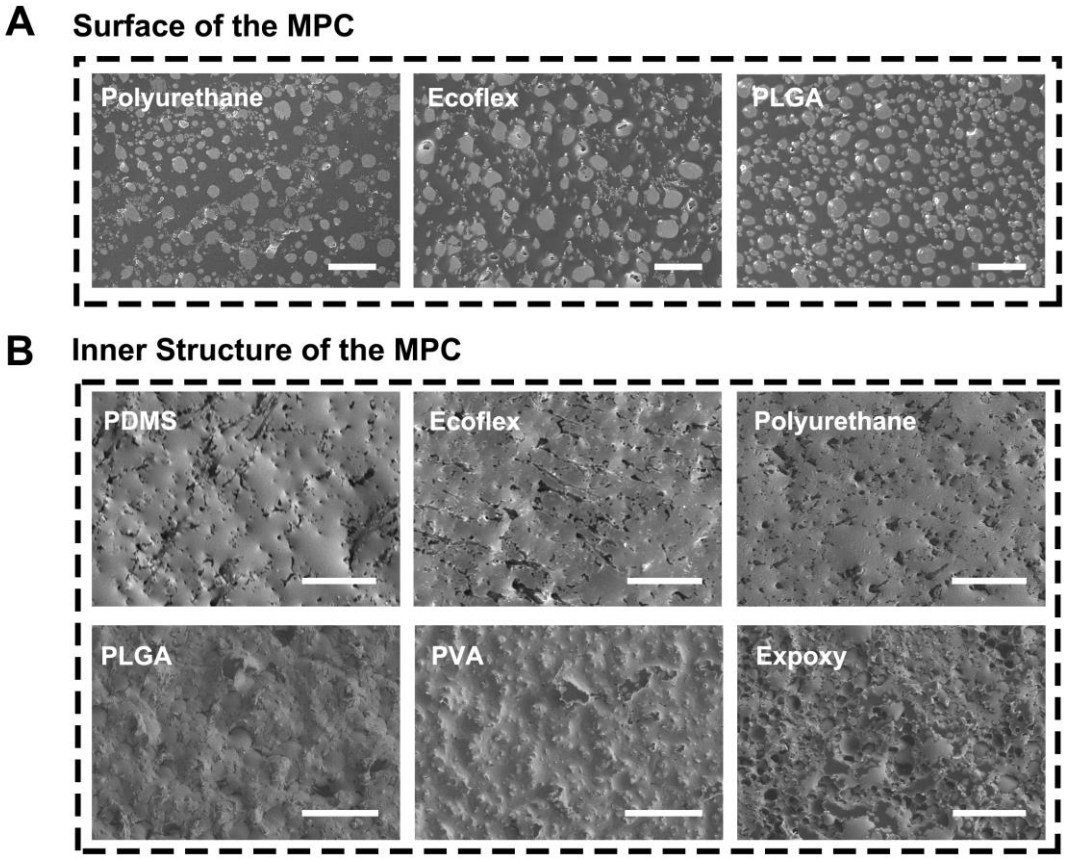

Figure S3. Characterization of the MPC cast by different polymers, **related to Figure 2.** (**A**) The surface appearances of MPC cast by polyurethane, Ecoflex, and PLGA, and it present an appearance of LM islands dispersing in the sea of polymer. Scale bar, 20 μm. (**B**) The pattern surfaces in partial transfer which represent the inner structure of the MPC; they all have continuous metallic phase. Scale bar, 20 μm.

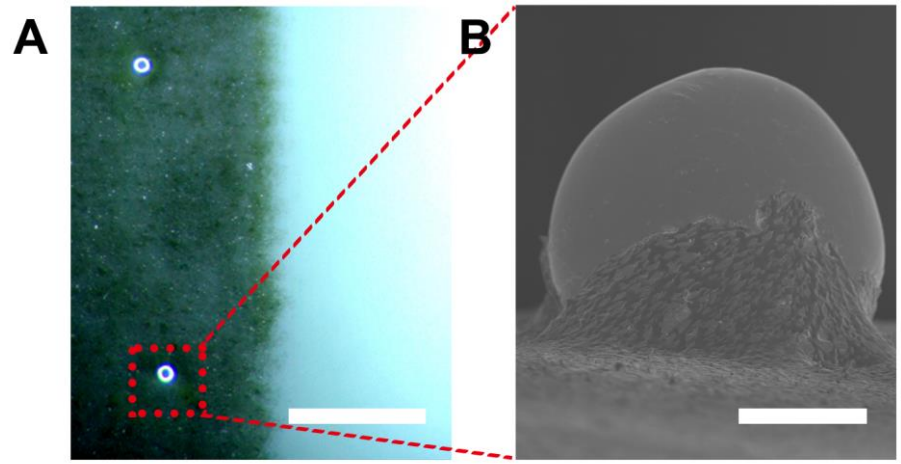

Figure S4. Characterization of the MPC after the stretch cycle, related to Figure 2. (A) Optical image of the MPC after the stretch cycle, several liquid metal droplets are squeezed out from the MPC, scale bar 500 μm. **(B)** SEM image of the squeezed liquid metal droplet. Scale bar 30 μm.

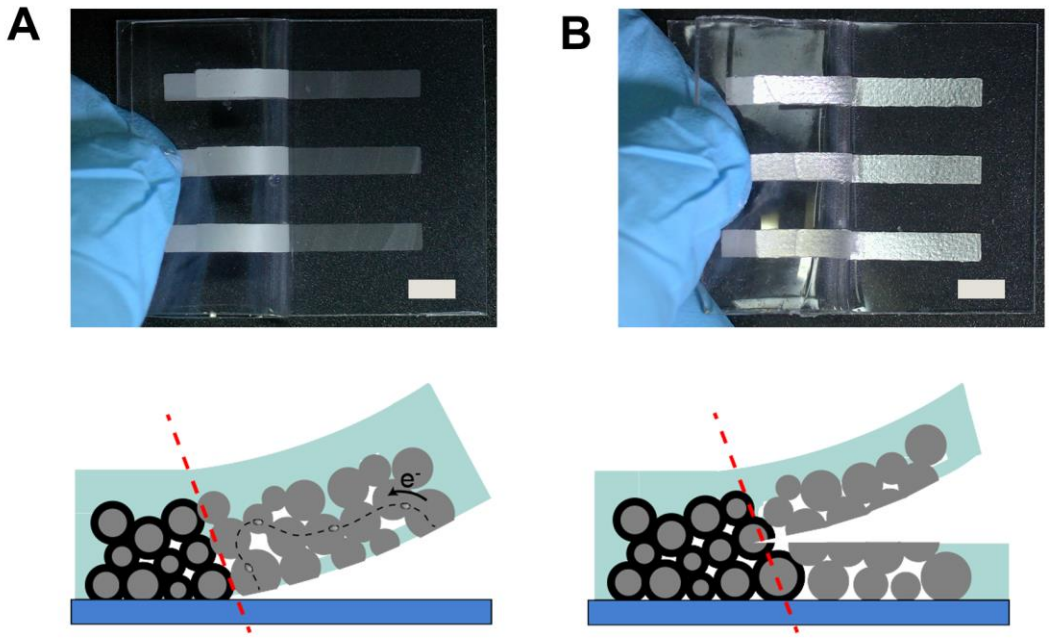

Figure S5. Entire transfer and partial transfer, **related to Figure 3.** (**A**) Entire transfer of the MPC patterns to the SL (PDMS), leaving only oxide on the IPL (PET

film). (**B**) Partial transfer of the MPC patterns, and both of the IPL and SL have integrated MPC pattern. Scale bar 10 mm.

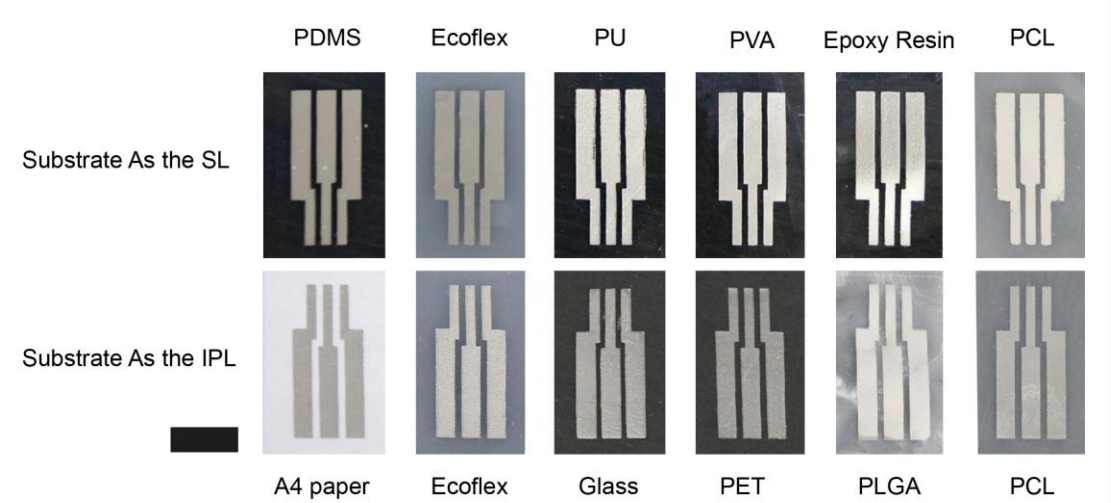

Figure S6. MPC transfer to different substrates, related to Figure 3. Scale bar, 10 mm.

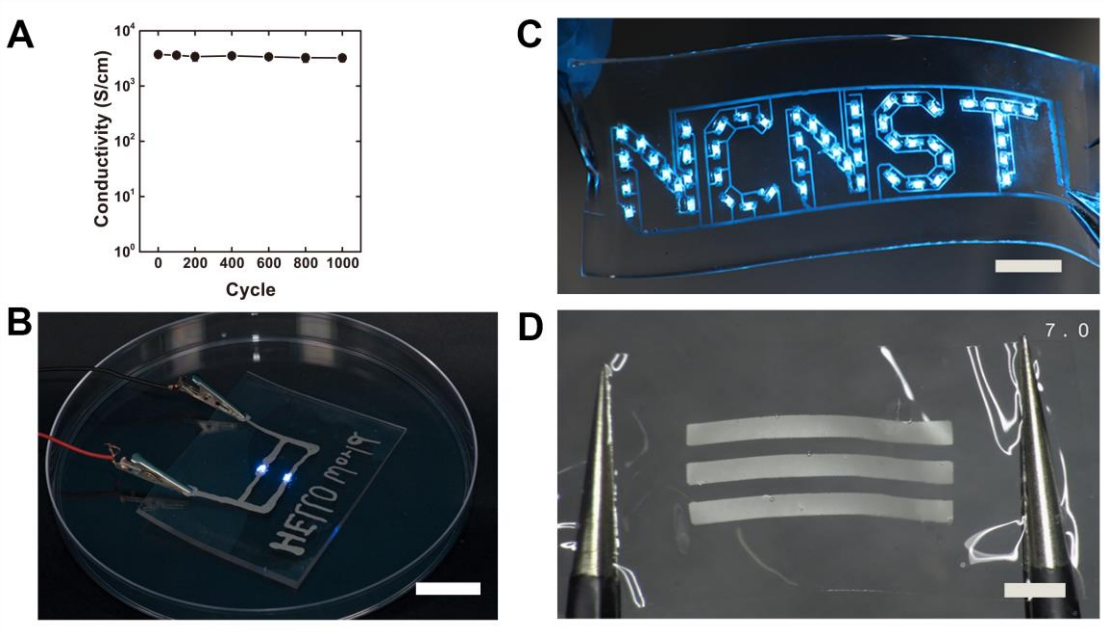

Figure S7. MPC patterns as interconnects, related to Figure 3. (**A**) Conductivity changes with the bending for 1,000 cycles. (**B**) We use handwriting method to fabricate a flexible and stretchable LED circuit on the PDMS substrate. Scale bar, 15

mm. (**C**) A simple LED display interconnected by MPC on PDMS substrate, scale bar, 20 mm. (**D**) MPC patterns fabricated on ultrathin PDMS film (30 μm). Scale bar, 4 mm.

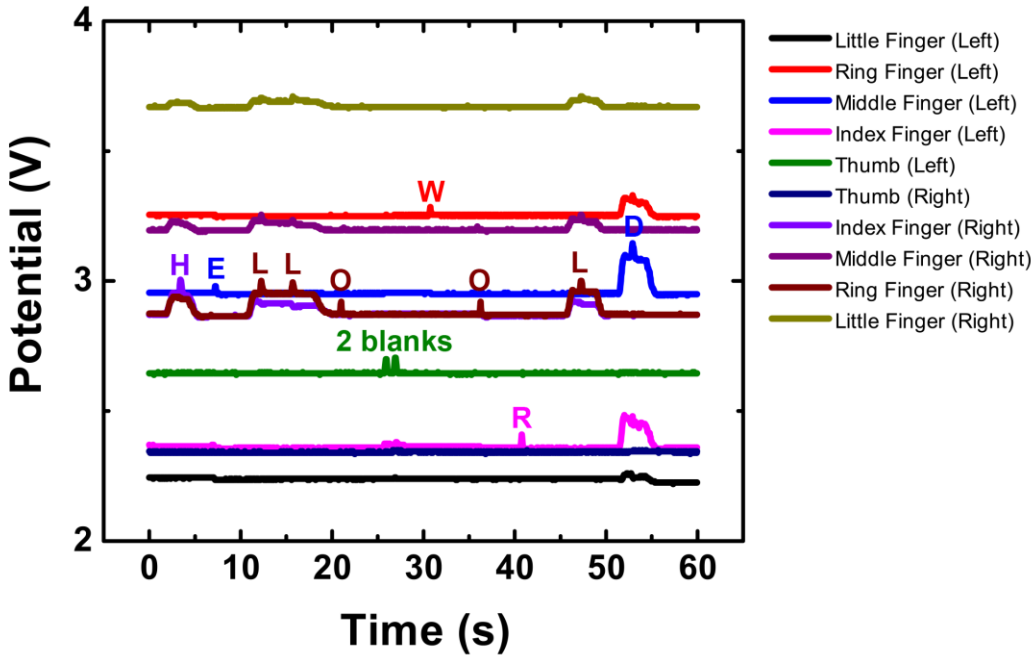

Figure S8. Potentials across the strain sensors versus time when we use the virtual keyboard to type "HELLO WORLD", related to Figure 4.

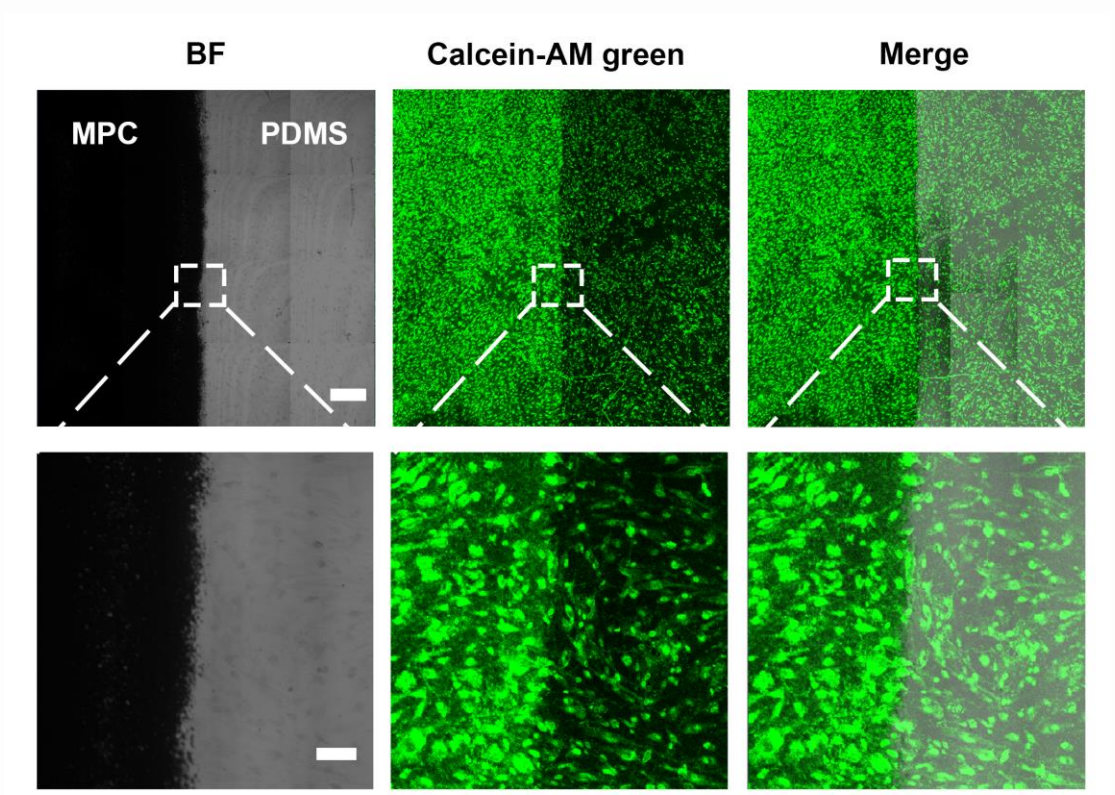

Figure S9. Viability test of the HUVECs on the MPC-PDMS interface after 7 days, related to Figure 5. Cells are stained by Calcein-AM green (Invitrogen, US), Scale bar, (top) 400 μm, (bottom) 100 μm.

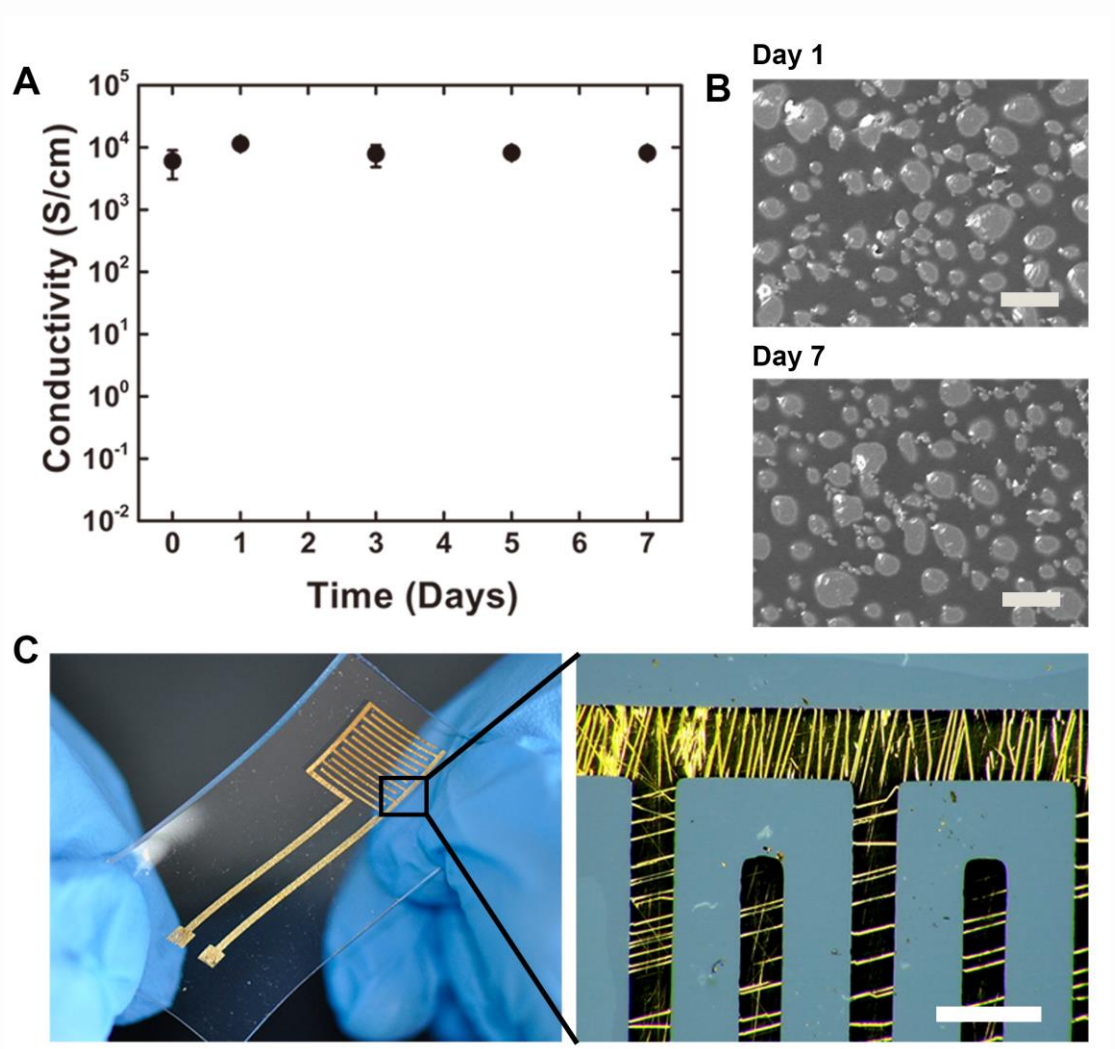

Figure S10. Tolerance of the MPC and the gold electrode, related to Figure 5. (**A, B**) Degradation exploration of the MPC. (**A**) Conductivity of the MPC dependence on culturing time. (**B**) SEM characterization of the surface of MPC electrodes exposed in DMEM. Scale bar, 10 μm. (**C**) The gold electrode on the PDMS substrates lost its conductivity after the tensile cycle due to the forming of cracks. Scale bar, 500 μm. Data are expressed as mean ±SD

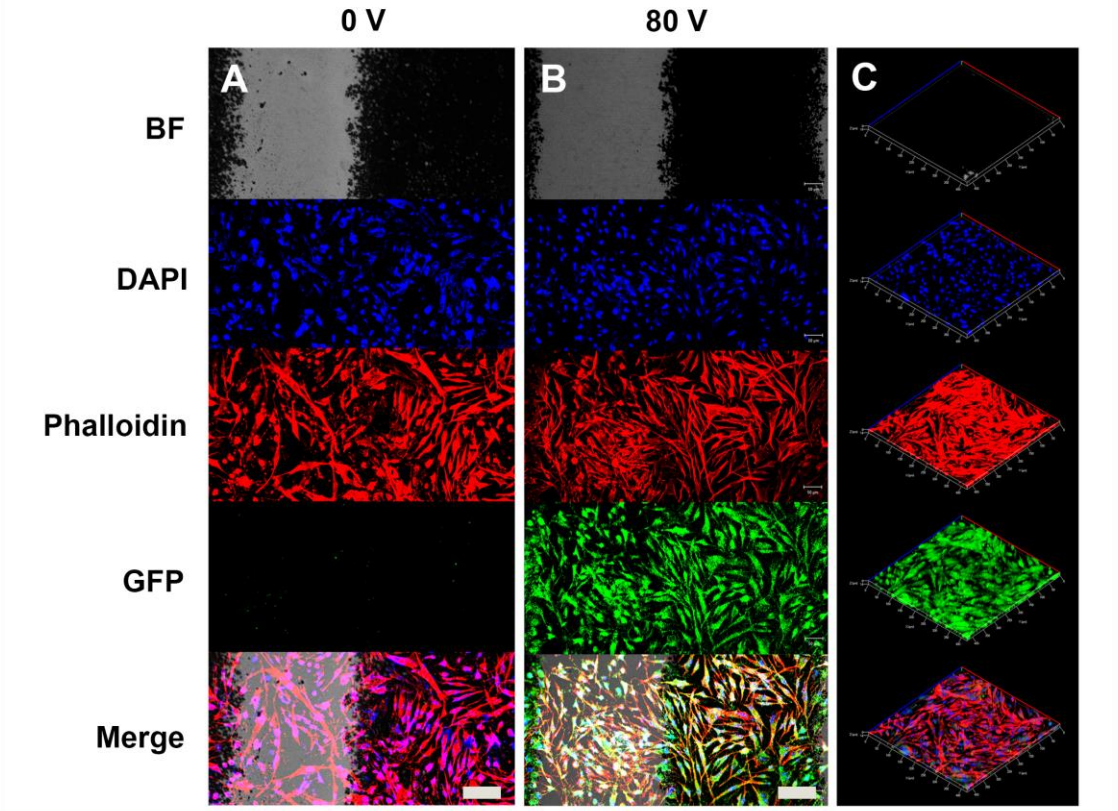

Figure S11. GFP plasmid delivery in Fibroblasts, related to Figure 5. A, B, Fluorescent cytoskeleton staining of fibroblasts on and adjacent to the MPC (**A**) without and (**B**) with electroporation. Scale bar, 100 μm. **(C)** 3D distribution of fibroblasts on the MPC treated by electroporation. The nucleus (blue) and F-actin (red) are stained by Hoechst 33342 and Alexa Fluor 568-labelled phalloidin, respectively.

SUPPLEMENTAL TABLES

Table S1. Typical value of parameters we used in this study, related to Figure 1.

The Young's modulus and Poisson's ratio of Gallium Oxide [a]	E_s=8 GPa μ_s=0.3	The Young's modulus and Poisson's ratio of PDMS	E_m=1.2 MPa μ_m=0.5
The yield stress of Gallium Oxide [a]	σ_y=200 MPa	The thickness of the PDMS	h =50 μm
The radius of droplets	**R**=3 μm	The thickness of Gallium oxide film [b]	t =0.5 nm
The typical curvature of the PDMS film	κ=1 mm^{-1}		

[a] (Dickey et al., 2008)

[b] (Boley et al., 2015)

TRANSPARENT METHODS

Mechanical Calculation. We obtained micro particles of gallium alloy through sonication. The surface of these droplets will form an oxidation layer (Lin et al., 2015; Boley et al., 2015). The thickness of the oxide layer is about 0.5 nm (Boley et al., 2015). This thin oxide layer will keep the shape of the droplets and make it behave like an elastic material (Boley et al., 2015; Lawrenz et al., 2015). When the film experience a large enough stress, it will yield and flow readily (Lawrenz et al., 2015). According to the data of Dickey et al.'s previous research (Dickey et al., 2008), the Young's modulus (E) and the yield stress (σ_y) of the oxidation layer are estimated to be 8 GPa and 200 MPa respectively.

To prove the stress during stripping can effectively break the oxide layer of LMPs embedded in elastomers, we performed theoretical calculation. We analyze the stress of liquid metal particles on the bending part (Fig. 1a). The model can be simplified as a gallium particle embedded in a PDMS (polydimethylsiloxane) matrix. When we peeled the PDMS film off the glass matrix, the liquid metal particle patterns will be conductive. Based on this, we will give a theory explanation of this phenomenon.

When we peel the PDMS film off a substrate like PET, the film will have a curvature. The gallium droplets are at the bottom of the PDMS. So they will suffer a large stress and the oxide layer of the gallium droplets will yield.

According to the bending theory, the stain at the bottom of the PDMS can be written as

$$\varepsilon = \frac{\kappa h}{2} \quad (1)$$

In which, h is the thickness of the PDMS and κ is the curvature radius of the PDMS. We will calculate the relation of the stress of gallium droplet and the PDMS strain ε. As shown in fig. S1, the PDMS matrix is assumed as an infinite solid and the gallium droplet with a thin oxide layer is assumed as a thin walled sphere with a radius *R* and a thickness *t*. Far from the sphere, the matrix is subjected to a tensile stress $\sigma_z = E_m\varepsilon$, with all other stress componets zero. The stress field of PDMS matrix σ'_{ij} is

$$\sigma'_r = \frac{B}{2} + \left[A - \frac{3}{2}C\right]\frac{1}{r^3} + \frac{D}{2r^5} + \frac{1}{2}\left[B - 9\frac{C}{r^3} + 3\frac{D}{r^5}\right]\cos 2\theta \quad (2)$$

$$\sigma'_\theta = \frac{B}{2} - \frac{A}{2r^3} - \frac{D}{8r^5} - \left(\frac{B}{2} + \frac{7D}{8r^5}\right)\cos 2\theta \quad (3)$$

$$\sigma'_\varphi = -\frac{A}{2r^3} - \frac{3D}{8r^5} - \frac{5D}{8r^5}\cos 2\theta \quad (4)$$

$$\tau'_{r\theta} = \left(-\frac{B}{2} - \frac{3C}{2r^3} + \frac{D}{r^5}\right)\sin 2\theta \quad (5)$$

And in which, *A*, *B*, *C*, *D* are constants which are determined by the boundary conditions. Then the stress filed of the oxide layer of the gallium droplet σ_{ij} can be written as

$$\sigma_\theta = \frac{R}{t}\left(H + I\cos 2\theta\right) \quad (6)$$

$$\sigma_\varphi = \frac{R}{t}\left[\sigma_a - H + \left(\sigma_b - I\right)\cos 2\theta\right] \quad (7)$$

Where *H*, *I* and σ_b are constants. And the boundary condition is at $r \to \infty$,

$$\sigma'_r = \frac{E_m\varepsilon}{2} + \frac{E_m\varepsilon}{2}\cos 2\theta \quad , \quad \tau'_{r\theta} = -\frac{E_m\varepsilon}{2}\sin 2\theta \quad (8)$$

And finally, we can obtain the maximum Tresca's equivalent stress of the oxide layer is

$$\sigma_{\max} = \frac{5RE_m\varepsilon}{2t} \quad (9)$$

The typical value of parameters we used in this study are listed in table S1. Substituting the value in table 1 in the Equation (9), we obtain

$$\sigma_{\max} = 4500 \text{ MPa}$$

And this value is great larger than the yield stress of gallium oxide (about 200 MPa). So the oxide layer of the gallium droplet will yield.

Preparation of the low-melting metal particle inks. 1 g, 1.5 g, 2g, 2.5 g, 3 g, 4 g, and 5 g EGaIn (Gallium Indium eutectic, 99.99%, Sigma-Aldrich) was added into 5 mL centrifuge tube filled with 1 mL n-Decyl alcohol (98%, MACKLIN, China), respectively and sonicated by a sonicator (Scientz, Scientz-IID). For screen printing, we sonicated the EGaIn for 1 min with the power of 300 W. For microfluidic patterning, 5 min with 300 W is required.

We also adopted alloy with melting point 47 °C (Sn 8.30, Pb 22.60, Bi 44.70, Cd 5.30, In 19.10, Taobao, China) to prepare the low-melting metal particle inks. 2.5 g alloy was added to 1 mL n-Decyl alcohol (98%, MACKLIN, China). We heated the alloy in an oven at 80 °C for 10 min to melt the alloy and sonicated the melting alloy for 1 min with the power of 300 W.

Screen printing of the LMPs ink. The printing of liquid metal particle was realized by a screen printing equipment (Taobao, China). We used the liquid metal particle ink to print desired patterns on various substrates including PET, PCL, PLGA, PDMS films, A4 paper, and glass with 200 mesh screen printing plates.

Microfluidic patterning of the LMPs ink. The microstructures are obtain by soft lithography. Briefly, we used silicon wafer or printed circuit boards (PCB) as the master molds. To obtain silicon wafer as the master wafer, we followed standard photolithography. Master fabrication for the microfluidic channels begins with spin coating negative photoresists (SU8 2035, MicroChem Corp., US) on a silicon wafer at 1200 rpm for 30 s (100 μm thick). After baking the photoresist at 95 °C for 5 min, the wafer was exposed to UV light for 90 s through a mask. After baking the wafer at 95 °C for 10 min, we immersed the wafer into a developer (SU8 developer, MicroChem Corp, US.) and washed it for 5 min.

We also use the PCB (Jiekecengfeng Corp., China) as the master wafer. The thickness of the copper film is 150 μm. We cast a layer of PDMS onto the master mold. After baking in an oven at 80 °C for 40 min, we removed the PDMS replica from master. We spread LM particle inks onto the patterned PDMS. Before the evaporation of the solvent, we filled the microfluidic channel with EGaIn particle ink using a blade or squeegee, and excess ink was scraped off the substrate.

The fabrication of MPC by casting and peeling. After evaporation of the solvent, we used various polymers for casting on the patterned LMPs. We dissolved poly (carprolactone) (PCL, Mn=80000 g/mol, Sigma-Aldrich, US) pellets in dimethylformamide (DMF, ThermoFisher Scientific, US) and CH_2Cl_2 (Aladdin, China) with a ratio of 1:3 (w/w) at 5 wt% to prepare the PCL solution. We prepared the 5 wt% poly (vinyl alcohol) (PVA) (1795, Aladdin, China) solution (w/w) by dissolving PVA in ultrapure water (Milli-Q Reference, MERCK, France) in water bath at 95 °C for 1 hour. We dissolved poly (DL-lactide-co-glycolide) (PLGA 75:25, Mw=114 kDa, Lakeshore Biomaterials, US) particles in acetone/DMF with a ratio of 2:1 (w/w) at 5 wt% to prepare the PLGA solution. We prepared the PDMS prepolymer by mixing base and curing agent with a ratio of 10:1, 15:1, 20:1, 25:1, 30:1, and 35:1 (w/w). We prepared the Ecoflex prepolymer by mixing part A and part B with a ratio of 1:1 (w/w). We prepared the epoxy sealant prepolymer (epoxy sealant, Ausbond, US) by mixing part A and part B with a ratio of 5:4 (w/w). We prepared the polyurethane (PU) (polyurethane sealant, Ausbond, US) prepolymer by mixing part A and part B with a ratio of 1:1 (w/w). These prepolymers were thoroughly mixed and degassed in a mixer (AR-100, THINKY, Japan).

We cast polymer solutions or prepolymers onto the LMPs patterns. These cast polymer solutions were placed in a chemical hood in room temperature for 24 h to volatile solvents. While the cast PDMS, PU, and epoxy resin prepolymers were placed in 80 ^{o}C oven for 40 min or in room temperature for 12 hours.

After curing, these polymer films were peeled off from the substrates. Thus conductive MPC on different polymer substrates were obtained either on IPL or SL. To obtain MPC patterns on the PDMS ultrathin film (30 μm), we spin-coated the PDMS at 4500 r for 20 s after the casting process.

Particles and MPC characterization. Inks (2.5 g/mL for 1 min) for Scanning Electron Microscopy (SEM, S4800, Hitachi, Japan) characterizations were fabricated by sonicating EGaIn for 1 min, 5 min, 10 min, 20 min, and 30 min, respectively. We deposited 100 μL suspension on conductive tape via micropipette (Eppendorf, Germany) and allowed them to dry in 80 ^{o}C oven for 10 min. MPC for SEM characterizations were prepared by screen printing using different polymers as SL (PDMS, Ecoflex, PLGA, PVA, PCL, PU, and epoxy resin).

The LM dissolved MPC for SEM characterizations were fabricated by immersing the MPC patterns (2.5 g/mL) on 0.1 M sulfuric acid for 10 h. We use the LM dissolved MPC for the thickness measurements. Briefly, we cut the sample with a blade and characterized the cross section of the sample using SEM.

Measurement of the liquid metal consumptions and transfer amount of the MPC. We used screen printing method to print liquid metal particles (2.5 g/mL) on PET films as a shape of a strip (3*30 mm). After the evaporation of solution in an oven at 80 ^{o}C for 10 min, we cast PDMS of different ratio (10:1, 15:1, 20:1, 25:1, and 30:1) on different PET films, respectively. The PDMS films were peeling from PET films after curing in 80 ^{o}C for 40 min. We weighed these PET films using a precision balance (AL104, METTLER TOLEDO, Swizerland) before printing, after printing, after evaporation, and after peeling off, respectively.

Tensile test. Samples for stretching test were prepared by screen printing inks with concentration of 1 g/ml, 2 g/ml, 3 g/ml, 4 g/ml, and 5 g/ml, respectively. We made the MPC into a strip shape (800 μm in width and 4 cm in length) using PET as the IPL and Ecoflex as the SL. The MPC strips were connected with a 100 Ω resistance and mounted on a homemade frame. We measured resistance of the MPC using multimeter (8846A, FLUKE, US) when they were gradually stretched to 500% strain.

Cycling test. Samples for stretching cycling test were prepared by screen printing EGaIn inks with concentration of 2.5 g/ml. Samples for bending cycling test were prepared by screen printing 47 ^{o}C low melting alloy particle inks with concentration of 2.5 g/ml. We made the MPC into a strip shape (800 μm in width and 2 cm in length) using PET as the IPL and PDMS (10:1) as the SL. We performed the stretching cycling test for 10,000 cycles using a dynamic mechanic analysis (DMA Q800, TA Instruments, US) under a strain rate of 100% /min with maximum strain of

50%. We performed the bending tests on dynamic mechanic analysis under a strain rate of 100% /min with a displacement of 1 cm for 1,000 cycles

Circuits assembly. To assembly a functional circuits, we first used a pipette to add 2 μL EGaIn onto each contact pad of interconnects. Subsequently, we gently rubbed EGaIn into the surface of electronic components to wet their pins and connected electronic components with the touch pads. Finally, a layer of elastomer was cast to encapsulate the circuits.

Fabrication and characterization of the strains sensors and virtual keyboard. We printed EGaIn LMPs ink (2.5 g/mL) on PET films by screen printing as serpentine shapes with the width of 200 μm. After solvent evaporation at 80 ^{o}C for 10 min, we spin-coated the PDMS (10:1) at 1000 r for 20 s on the LMPs patterns. . After curing at 80 ^{o}C for 30 min, the PDMS films with serpentine MPC (strain sensors) were carefully peeled off from PET films. We used silica adhesive (3145 RTV, Dow Corning, US) to attach strain sensors on a glove to monitor the motion of different fingers by capturing resistance change.

We wore the strain sensors-mounted glove to monitor motions of fingers. The strain sensors were connected to electrochemical workstation (1040C, CH Instruments, US). We tested the resistant changes of the sensors by using the technique amperometric i-t curve at potential 0.001 V.

The virtual keyboards were achieved by connecting the glove to Arduino (MEGA 2560, ITALY), and processed signals using MATLAB.

Cell culture, staining and characterization. Samples for cell experiments were prepared by screen printing inks with concentration of 2.5 g/ml. We made the MPC using PET as the IPL and PDMS (10:1) as the SL. Before cell culture, we sterilized all the samples by radiation with a cobalt radiation device (Co 5 60, 10-130 Gymin-1, Peking University, China). The MPC was incubated with fibronectin solution (50 μg/ml) for 6 h at room temperature to promote the adhesion of cells. We seeded human umbilical vein endothelial cells (HUVECs, ATCC, US) and human aortic fibroblasts (Science Cell, US) on the surface of the MPC, and culture them in DMEM supplemented with 10% fetal bovine serum (5% CO_2, 37 ^{o}C) for 7 days. HUVECs were stained with live/dead kit (Invitrogen, US) for cell viability test. Briefly, we fixed cells with 4% paraformaldehyde aqueous solution for 10 min. Subsequently, we stained the cells with the dyes at a concentration of 1 μg/mL for 20 min, and removed excess dyes by 3 times rinsing the cells with phosphate buffered saline (PBS). (Invitrogen, US) We stained the nucleus with Hoechst 33342 (Invitrogen, US) at a concentration of 1 μL/mL for 5 min, and removed excess dyes by 3 times rinsing the cells with PBS. We stained the F-actin with Alexa Fluor 568-labelled phalloidin (Invitrogen, US) at a concentration of 200 units/mL for 20 min, and removed excess dyes by 5 times rinsing the cells with PBS. The fluorescent images of cells was taken by laser scanning confocal microscopy (LSM 710, Zeiss, Germany). Before SEM characterization, we fixed cells with 4% paraformaldehyde aqueous solution for 30

min and dehydrated the sample with ethanol at the concentrations of 50%, 75%, and 100% for 10 min, sequentially.

Electroporation. We printed the MPC electrodes for electroporation with 2.5 g/mL EGaIn LMPs, using PDMS (10:1) as the SL and PET as the IPL. We deposited 100 nm thick gold on the surface of PDMS by evaporation (Ohmiker-50B, Cello Technology Corporation, Taiwan) to fabricate gold electrodes as a control group. Human aortic fibroblasts were used to verify the electroporation of green fluorescent protein (GFP, RiboBio, China). We incubated the MPC electrodes with the fibronectin plasma solution (50 μg/ml) for 6 h at room temperature to promote adhesion of cells. Subsequently, fibroblasts were delivered on the MPC electrode (PDMS as the substrates) and cultured for 24 h. We washed the sample 3 times before electroporation and immersed the surface of the electrodes in GFP solution at a concentration of 40 μg/ml. We applied 5 electrical pulses using an electroporator by exerting a square wave pulse (Electro Square Porator ™ ECM 830, BTX, USA). The voltage is 80 V, the pulse duration is 100 μs, and the pulse interval is 1 s. After culturing for 24 h, we stained the cells as above-mentioned and used confocal microscopy to image the cells.

SUPPLEMENTAL REFERENCES

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