Dynamic diselenide-mediated graphene composite networks: Towards shape-reprogrammable and conductivity-stable flexible electronics

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1. Materials

Se powder, sodium borohydride, 3-bromo-1-propanol, tetrahydrofuran, saturated sodium bicarbonate solution, anhydrous sodium sulfate, methylene chloride, methanol, polycaprolactone (PCL, Mn=2000), N,N-dimethylformamide (DMF), hexamethylene diisocyanate (HDI), Triethanolamine (TEA), dibutyltin dilaurate (DBTDL). All of which were provided by Aladdin (Shanghai, China), were used directly without further purification.

2. General information

^1H NMR spectra were performed on a Bruker ARX400 MHz spectrometer. The deuterated solvent was $CDCl_3$.

FT-IR spectra were scanned from smooth 0.2 mm thick polymer films using a Nicolet 760 FT-IR spectrometer according to the FT-IR attenuated total reflection (ATR) method. Ten scans at a resolution of 4 cm^{-1} were signal averaged and stored for further analysis.

XPS measurement was recorded with the Nexsa instrument (Thermo Electron Corporation, US). was carried out using anode voltage and current of 15 kV and 10 mA, respectively

XRD experiments were performed using a BRUKER AXS D8 Advance diffractometer with a 40 kV FL tube as the X-ray source (Cu Kα) and a LYNXEYE-XE detector.

TGA curves were recorded on a computer-controlled TA Instrument TG Q50 system, under the following operational conditions: a heating rate of 10 °C/min, a temperature range of 50-600 °C, a sample weight of approximately 5.0 mg, using film samples in platinum crucibles, and 60 mL/min N_2 flow. Three or four repeated readings (temperature and weight loss) were made for the same TG curve, and each included to at least 15 points.

DSC testing was performed using a TA Q200 instrument with nitrogen as the purged gas. Indium and zinc standards were used for calibration. Samples were first heated from -20 °C to 150 °C at a heating rate of 10 °C/min and kept at 150 °C for 2 min, subsequently, cooled to -20 °C at a cooling rate of 10 °C/min, and finally heated a second time from -20 °C to 150 °C.

The UV-Vis spectra were recorded on a UV-2600i spectrophotometer in the range of 200-900 nm^{-1}. The samples were immersed in DMF, and the immersion solution was subsequently tested. For the UV-lamp control group, the immersion solution was exposed to UV light (365 nm) for varying periods before testing. After exposure, the samples were removed from the solution and exposed to natural photo for a corresponding duration before testing in another time.

SEM was obtained using a Hitachi TM3030 benchtop microscope operated in low vacuum mode, samples were cut, plated, and sections were taken for photographing.

The tensile tests were performed on samples using a ZQ-990L tensile machine (ZQ-990L, Dongguan, China). The tensile speed was set to 2 mm min^{-1} and strain-stress curves were recorded for analysis.

Thermal Shape Memory Test: The sample is cut into the corresponding model, heated above Tm, deformed through folding, bending, or stretching, and then cooled to fix the deformed shape. Subsequently, the temperature is gradually increased, and the shape change at different temperatures is recorded.

Photo-responsive Shape Memory Test: The sample is cut into a corresponding shape to test its optical response. After thermally induced stretching deformation and fixation, the sample is irradiated with a 365nm ultraviolet lamp, and its photoinduced shape change process is collected.

Verification method for flexible electrical carriers: Composite a layer of conductive graphene on one side of the sample surface, fold it into different shapes, connect it to a circuit respectively, and verify whether it can serve as a flexible electrical carrier by observing whether a small bulb lights up.

Crosslinking degree test：Samples were cut into three distinct geometries: (1) rectangles (20 mm×10 mm×1 mm), (2) squares (10 mm×10 mm×1 mm), and (3) equilateral triangles (side length 10 mm), with three replicates for each group. The initial mass of each specimen was recorded. The samples were immersed in 20 mL of DMF at room temperature for 24 h to ensure equilibrium swelling. After removing surface solvent, the swollen mass (m1) was measured. Finally, the samples were dried to a constant weight to determine the mass of the crosslinked network (m2). At swelling equilibrium, the mass of the solvent can be calculated from equation (1) as follows:

$$m1 = m0 - m2 \qquad (1)$$

where m0 is the mass of sample after swelling equilibrium (g), m1 is the mass of the cross-linking portion, and m2 is the mass of the solvent in the system when swelling (g). The volume swelling Q at equilibrium can be calculated from equation (2):

$$Q = \frac{V1 + V2}{V2} = \frac{m1/\rho1 + m2/\rho2}{m2/\rho2} \qquad (2)$$

where Q is the volumetric solidity, V1 is the volume of solvent in the swelling equilibrium system (cm^3), m1 mass of solvent in the swelling equilibrium system (g), $\rho1$ is the density of the solvent, V2 is the volume of the cross-linked polymer in the swelling equilibrium system (cm^3), m2 is the mass of the cross-linked polymer in the swelling equilibrium system (g), and $\rho2$ is the density of the polymer (g/cm^3). At equilibrium, the volume of the polymer (V_p) is given by: $V_p = Q^{-1}$.

The Flory–Rehner equation is applied to calculate the parameters of the sample at swelling equilibrium. Specifically, it enables the calculation of the cross-link density of the polymer chains within the network structure under swelling equilibrium conditions.

$$-\left[\ln\left(1-\vartheta_p\right)+\vartheta_p+\chi\vartheta_p^2\right]=NV_s\left[\vartheta_p^{1/3}-\frac{\vartheta_p}{2}\right] \quad (3)$$

The average molecular weight between two cross-linking points can be obtained from equation (4):

$$-\left[\ln\left(1-\vartheta_p\right)+\vartheta_p+\chi\vartheta_p^2\right]=\frac{\rho_2}{M_c}V_s\vartheta_p^{1/3} \quad (4)$$

where N is the cross-link density, Vs is the molar volume of the solvent (80.7 mL mol^{-1}), χ is the polymer–solvent interaction parameter (−1.36), and Mc is the average molecular weight between cross-links.

Calculation of crystallinity from DSC: The degree of crystallinity (Xc) of the PCL-based shape memory polyurethanes (MS-SMPUs) was calculated based on the melting enthalpy (ΔH_m) obtained from the second heating scan of the Differential Scanning Calorimetry (DSC) measurements. The calculation was performed using the following equation:

$$X_c(\%)=\frac{\Delta H_m}{\Delta H_m^{\circ}\times w}\times 100\%$$

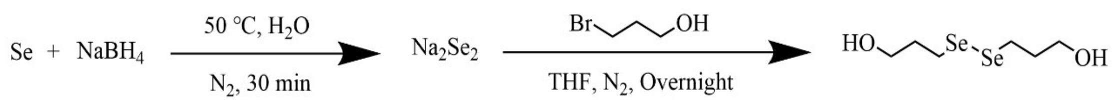
Where:

ΔH_m (J/g) is the experimental melting enthalpy of the sample, determined by integrating the area of the endothermic melting peak in the DSC thermogram.

ΔH_m° is the theoretical melting enthalpy of 100% crystalline poly(*ε*-caprolactone) (PCL), which is taken as 139.5 J/g according to literature values[1].

w represents the weight fraction of the PCL soft segments in the polyurethane network. In this study, the PCL content was approximately 70 wt% (based on the feed ratio of PCL in the synthesis formulation).

3. Supplementary Figures and Tables



Scheme S1 Synthesis route of $(HOC_3H_6Se)_2$

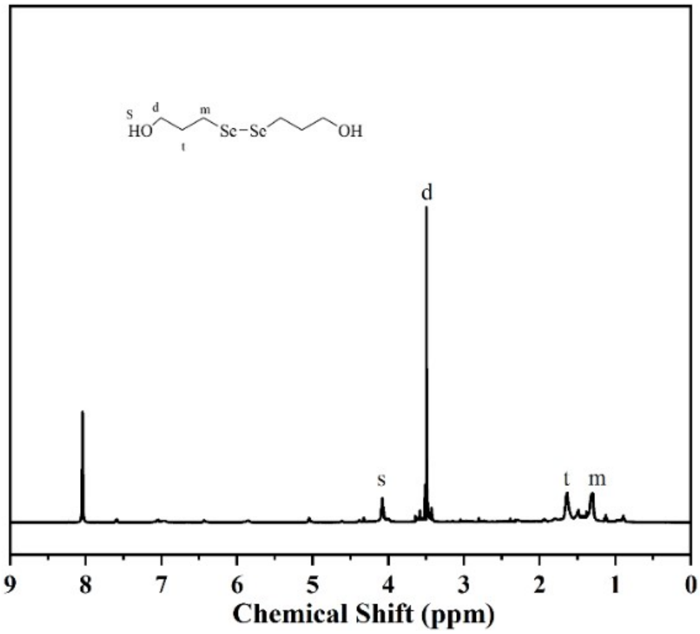


Fig. S1 ^{1}H NMR spectra of $(HOC_3H_6Se)_2$.

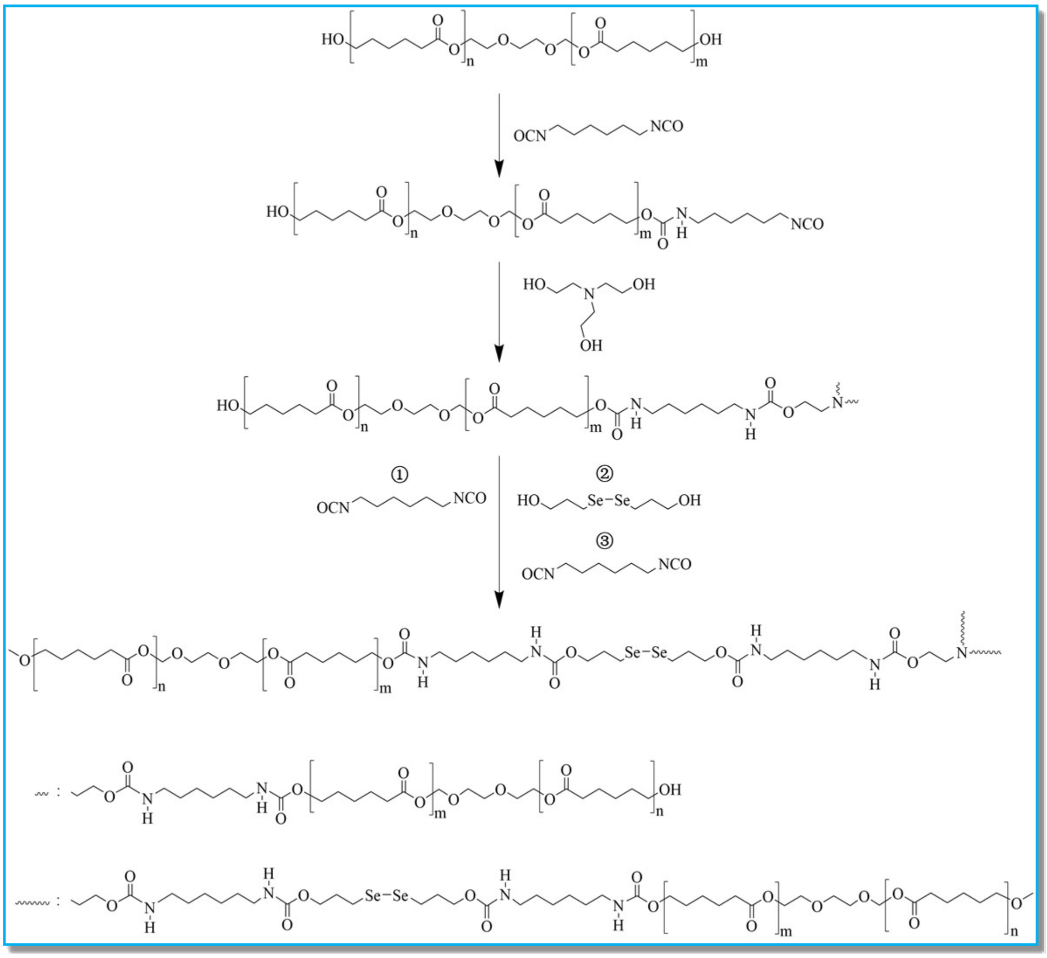


Fig. S2 Synthesis route of the Se-SMPUs.

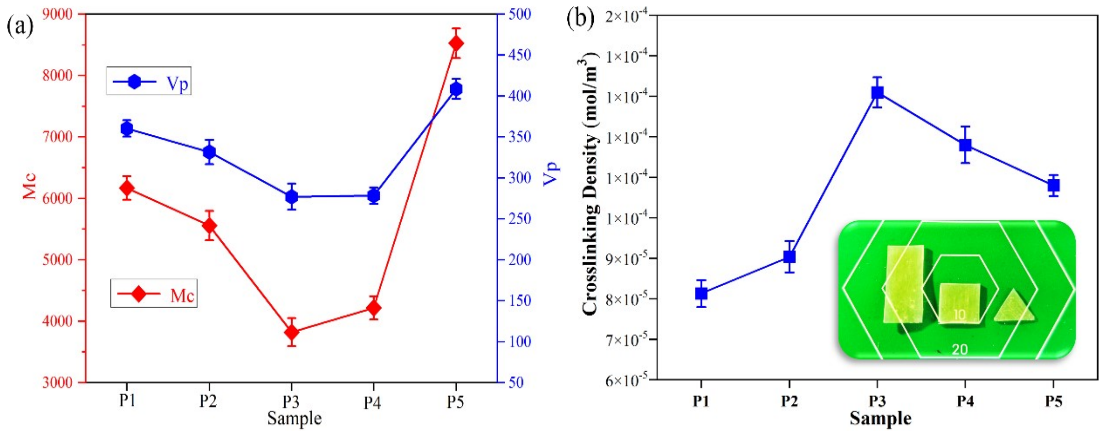


Fig. S3 Swelling related parameters (a) polymer volume ratio and average molecular weight between cross-linking points; (b) crosslinking degree.

Table S1 Composition of the MS-SMPUs

Sample	PCL	HDI	TEA	$(HOC_3H_6Se)_2$
P1	2g	0.57g	0.07g	0.066g
P2	2g	0.68g	0.12g	0.066g
P3	2g	0.85g	0.19g	0.066g
P4	2g	0.96g	0.26g	0.066g
P5	2g	1.13g	0.34g	0.066g

Table S2 The ratio of theoretical elements compared to the values obtained by XPS.

Name	XPS test Atomic %	Theoretical calculation of Atomic %
C1s	76.1	70.97
N1s	2.57	2.32
O1s	20.17	24.08
Se3d	1.16	1.86

Table S3 Thermal properties of the MS-SMPUs.

Sample	**T_{d1} (°C)^a**	**T_{d2} (°C)^a**	**T_{d3} (°C)^a**	**T_m (°C)^b**	**crystallinity (Xc)**
P1	236.4	381.6	462.9	37.6	24%
P2	241.3	382.1	467.8	39.6	25%
P3	238.2	389.9	469.1	40.6	27%
P4	240.2	387.5	471.1	41.1	30%
P5	236.9	390.8	474.4	38.6	26%

a. The weight loss temperatures of the samples under nitrogen [$T_d(N_2)$] were measured by TGA heating experiments at a rate of 20 °C min^{-1}.

b. Evaluated by DSC during the second heating process at a rate of 10 °C min^{-1} under nitrogen atmosphere.

Table S4 Elongation at break and yield strength.

Sample	Elongation at break (%)	Stress (Mpa)
P1	211.24	13.94
P2	582.99	10.34
P3	322.32	11.29
P4	433.44	15.44
P5	413.77	14.04
MS-SMPUs-G	258.16	7.22
Before UV irradiation	325.53	11.24
After UV irradiation	309.29	13.26

Table S5 Shape fixation and recovery.

No.	L1（cm）	L2（cm）	fixation rate（%）	recovery rate（%）
1	4	3.01	97.6	99.0
2	4	3.09	97.6	91.0
3	4	3.10	95.7	90.0
4	4	3.12	94.6	88.0
5	4	3.16	92.8	84.0
6	4	3.16	92.2	84.0
7	4	3.20	90.9	80.0
8	4	3.21	90.1	79.0
9	4	3.24	89.7	76.0
10	4	3.30	89.3	70.0

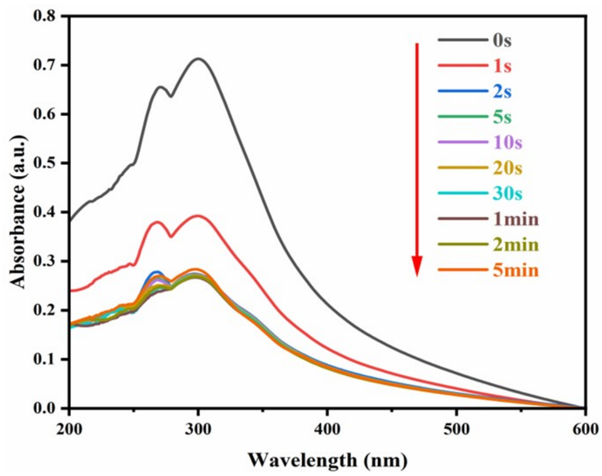


Fig. S4 UV-Vis Spectra of MS-SMPUs under different UV irradiation times.

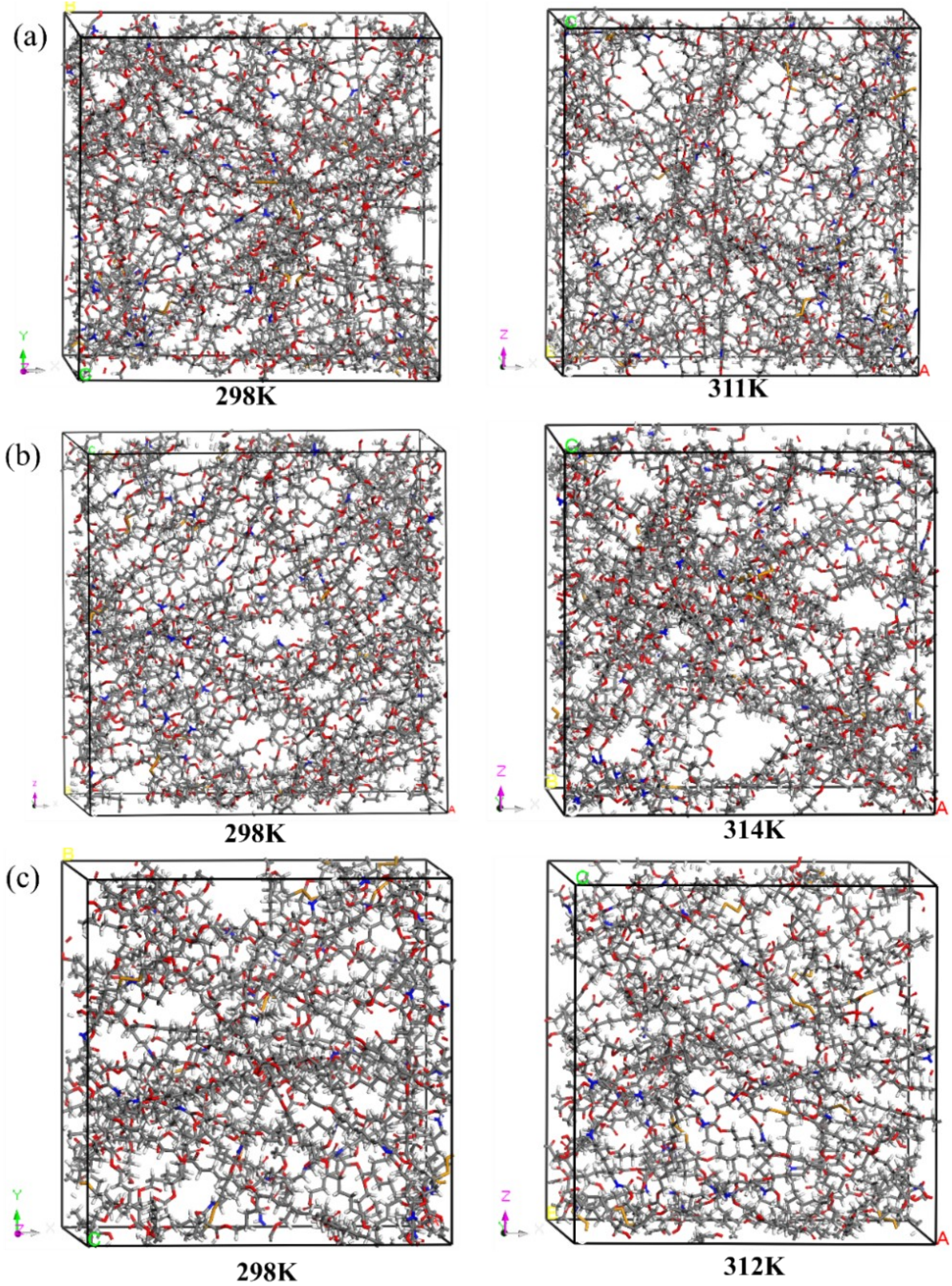


Fig. S5 The changes in the unit cell before and after T_m. (a) P1, (b) P3, (c) P5.

Table S6 The packed cell dimensions and molecular weights of the constructing model polymer.

Model name	The packed cell dimensions $\alpha = \beta = \gamma$	M_W
P1	26.86 Å	13728.5
P3	23.39 Å	11759.0
P5	23.39 Å	10732.9

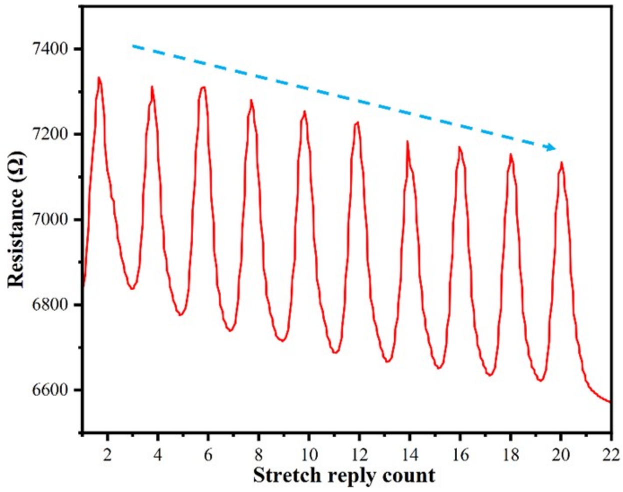


Fig. S6 Flexible Electronic Tester for MS-SMPUs-G.

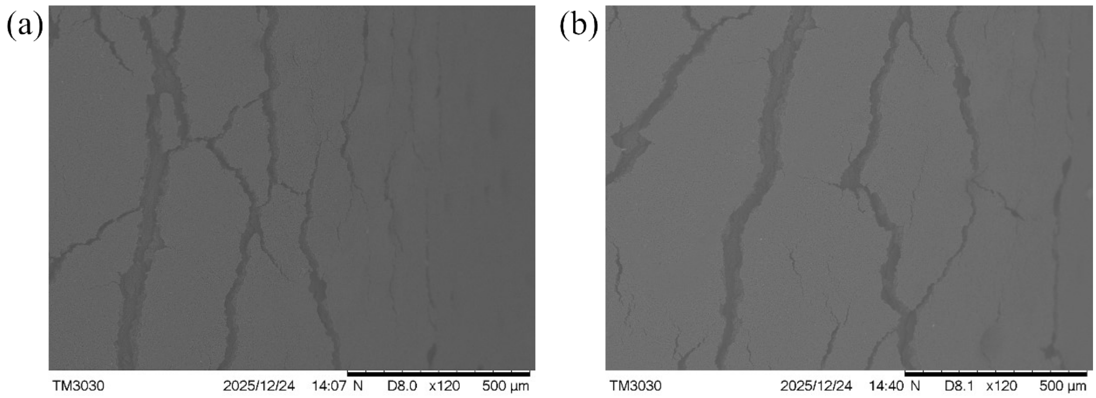


Fig. S7 SEM images of deformed graphene layers: (a) after stretching, (b) after folding.

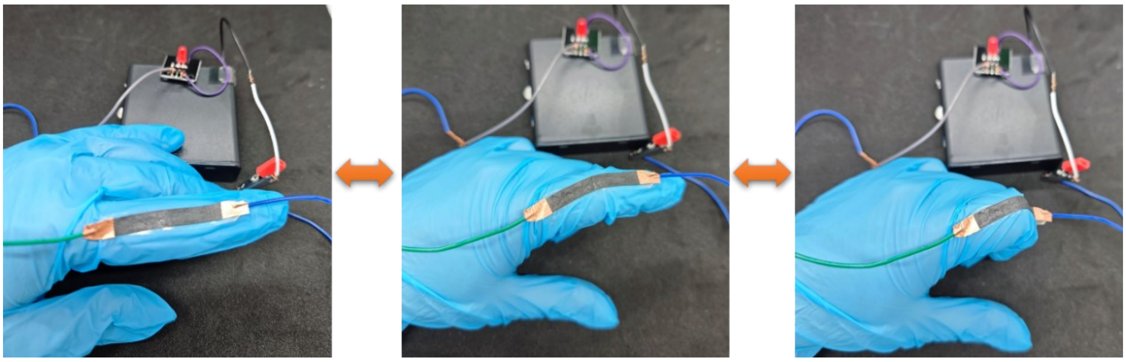


Fig. S8 Under repeated deformation, MS-SMPUs-G maintains good conductivity.

References for Supplementary Material:

[1] R. Pantani, F. De Santis, V. Speranza, G. Titomanlio. *Eur. Polym. J.*, 2016, **78**, 329-340.