# Supplementary Information

Artificial Visual Memory Device Based on Photo-Memorizing Composite and One-Step Manufacturing

## Section S1. Investigation on the flexibility of samples

The Young's modulus of polymeric samples is measured through the investigation of stress-strain behavior of different samples, including 3D-printed TPU and TPU-CB samples and pure TPU that is fabricated through direct solvent evaporation in petri dish. As shown in Fig. S1a, the 3D-printing process increases the Young's modulus of the original pure TPU material; moreover, the addition of CB nanoparticles in TPU dramatically increases the Young's modulus of the printed samples. To evaluate the flexibility of the printed sample, we investigated the resistances of the printed samples with different bending angles. The dimension of the printed samples is 50 mm × 10 mm × 1 mm, and the distance between the two sites connecting with ohmmeter through copper wire is 30 mm, and bending angle (α) is defined as the included angle of the two connecting lines that connect the two sites and centroid (as shown in inset of Fig. S1b). From the results shown in Fig. S1b, we figure out that the resistances of the printed samples almost remain constant under different bending angles, and this gives a corroborative evidence that the as-printed TPU-CB hybrid material is a kind of promising material for flexible or even wearable devices.

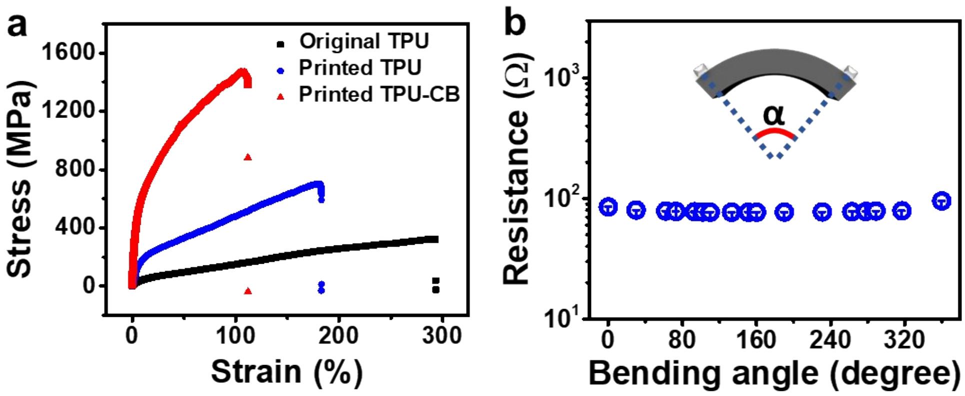


Fig. S1 a) Stress-strain behavior test results of the original TPU, printed TPU and printed TPU-CB samples. b) Flexibility investigation of as-printed sample with a dimension of 50 mm × 10 mm × 1 mm under different bending angles.

## Section S2. Experimental section

*Preparation of TPU-CB composite filament for additive manufacturing process*

Thermoplastic polyurethane filaments (TPU, 85A, NinjaFlex) were dispersed in dimethylformamide (DMF, 99 %, Alfa Aesar). As stated in Fig. S2, carbon black (CB, VULCAN® XC-72, CABOT) was then dispersed in TPU/DMF mixture through stirring overnight. After that, solvent evaporation was operated to make the liquid mixture into a black cake-like TPU-CB composite. Afterwards, the TPU-CB composite was teared into pieces and poured into an extruder (FILABOT EX2 FILAMENT EXTRUDER); after extrusion, filament with 1.75 mm diameter was obtained.

*Additive manufacturing process for artificial visual system*

Firstly, we designed a 3D model, i.e. Wheatstone bridge consisting of four electrical resistors ($R_1$, $R_2$, $R_3$ and $R_4$) with approximate resistance value, via 3Ds max software. The 3D model was composed of two sections: an internal conductive circuit and a non-conductive part. The non-conductive part was designed to encapsulate the conductive Wheatstone bridge, and four small windows were reserved to expose the conductive circuit for connecting with input voltage and output imaging elements, and the region right above resistor $R_4$ was reserved to expose the resistor under irradiation stimulation. Secondly, the 3D data was cut into accommodate separate object layers or components from bottom to up. Then the segmented/layered graphical data is sent to the 3D printer. Thirdly, dual-nozzle 3D-printer was used to print the device with one nozzle extruding pure TPU and the other one extruding TPU-CB composite. Finally, an artificial visual memory system consisting of 3 × 3 pixels array was obtained.

*Resistance matching in using Wheatstone bridge to amplify small signals*

In the 3 × 3 pixels arrayed device, each pixel is a discrete unit consisting of four parts: a fully 3D-printed device consisting of conductive Wheatstone bridge circuit to transfer optical information to easy-readable electrical form, and non-conductive substance for packaging, conductive copper wires for the transmission of electrical signal, and an

LED bulb as an imaging element. Moreover, a discrete power unit is connected to each pixel. Due to the intrinsic positional accuracy of the 3D printer (0.0025 mm in vertical direction and 0.011 mm in horizontal direction) and 0.1-0.2 mm for printing accuracy, a certain difference does exist among each printed pixel. Therefore, the values of resistors in the printed circuit are different from others and vary with time under illumination. As a result, the input voltage that is needed to active the operation of LED for one pixel is different from others. Therefore, when we obtain a newly printed device consisting conductive Wheatstone bridge, we will firstly measure the values of four resistors in the circuit, i.e. $R_1$, $R_2$, $R_3$ and $R_4$. Based on the Wheatstone theory,

$$P_B = \left(\frac{R_2}{R_1 + R_2}\right) \cdot U_{AC}$$

$$P_D = \left(\frac{R_4}{R_3 + R_4}\right) \cdot U_{AC}$$

and the output voltage equals to the potential difference of point B and D, i.e.

$$U_O = P_B - P_D = \left(\frac{R_2}{R_1 + R_2} - \frac{R_4}{R_3 + R_4}\right) \cdot U_{AC}$$

The critical value of LED ON and OFF is 1.8 V according to the experimental result; hence, $U_o$ is set as 1.8 V. Finally, input voltage that is needed to active the operation of LED, i.e. $U_{AC}$, can be calculated according to the results of resistance measurement.

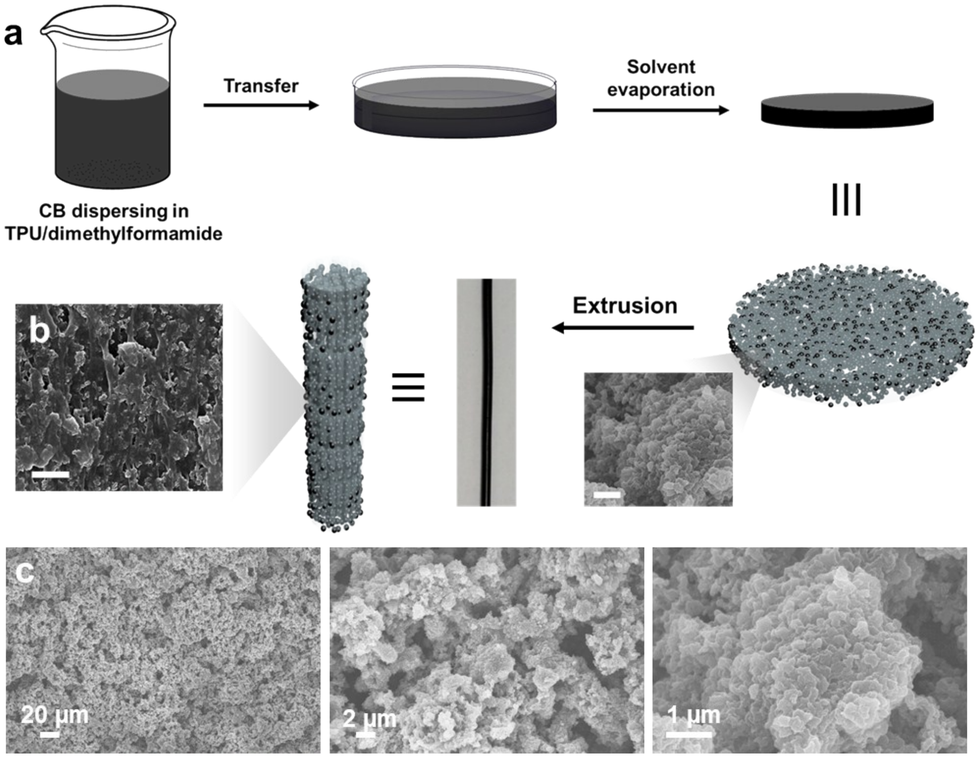


Fig. S2 a) Fabrication process of printing filaments of TPU-CB composite. Scanning electron microscope (SEM) results of b) extruded TPU-CB filaments and c) hierarchical structure of TPU-CB composite.

*Material characterization*

Scanning electron microscope (SEM; ZEISS SUPRA 55) was applied to characterize the morphology of the obtained TPU composite. According to the SEM results (Fig. S2b), the prepared filament is composed of hundreds and thousands of TPU-CB fibers, and this is induced by the mechanical stress of the nozzle during extrusion process. As a result, TPU-CB composite with nano-/micro- hierarchical structure (Fig. S2c) is constructed, which is attributed to the thorough mixing of TPU and CB nanoparticles.

*Other instruments*

Light-emitting diodes (5050, 12 V voltage, 11.52 W power) were used to visualize the photo-memorizing behavior of the 3D-printed device. KEITLEY (keithley 4200 semiconductor characterization system) was used to monitor the resistance change of conductive samples. Solar simulator (HAL 320, 350-1100 nm, 1.5 G) was used to provide simulated sunlight. The photometer (Gentec-eo UNO later power meter) was employed for obtaining the light intensity. Mechanical test system (MTS, Model 42) was used to measure the mechanical property of materials, including pure TPU, 3D-printed TPU sample and 3D-printed TPU-CB sample. The thermal imager (Fluke Ti450 Infrared Camera) was used to monitor the temperature change of the 3D-printed samples. The glass-transition temperature of TPU-CB composite was measured via differential scanning calorimetry (DSC Q10) under a steady flow of nitrogen (25 mL·min$^{-1}$) and heated at 10 °C·min$^{-1}$ from -50 to 200 °C.

**Section S3. Recyclability of TPU-CB composite**

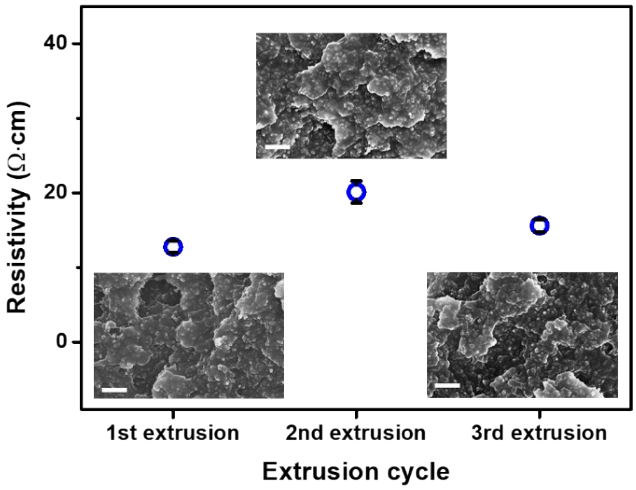


Fig. S3 Resistivity and SEM results of the as-prepared 3D-printing TPU-CB filament under different extrusion cycles.

**Section S4. Temperature change of pure TPU and TPU-CB composite under irradiation**

It is true that the light emitted by the light source has a certain amount of heat, and pure TPU can directly feel it. Therefore, we investigated the temperature of pure TPU and TPU-CB composite separately. As shown in Fig. S4, the temperature of pure TPU (blue bar charts) increases slowly under irradiation with an intensity of 70.3 mW·cm$^{-2}$ and keeps constant at 27.2 ± 0.2 °C after 10 min irradiation. On the contrary, the temperature of TPU-CB sample increases dramatically during the first 1 min under irradiation and always keeps higher than that of pure TPU. Hence, the heat accommodated in TPU-CB sample is attributed to the cooperation of photothermal conversion effect of carbon black nanoparticles in TPU-CB composite and the composite feeling the heat itself. The glass-transition temperature of TPU-CB composite was measured via differential scanning calorimetry (DSC Q10) under a steady flow of nitrogen (25 mL·min$^{-1}$) and heated at 10 °C·min$^{-1}$ from -50 to 200 °C. According to the result shown in Fig. 2c, glass transition region is identified to start from the point of black arrow, approximately 29.3 °C. The temperature of pure TPU under irradiation keeps lower than the critical temperature value that glass transition starts (dashed line showing in Fig. S4). Moreover, only under the temperature above $T_g$, the creep behavior of polymer chains can be observed. Therefore, pure TPU itself directly feeling the heat carried by the light emitted by the light source does not play a decisive role in the photo-memorize behavior of TPU-CB composite.

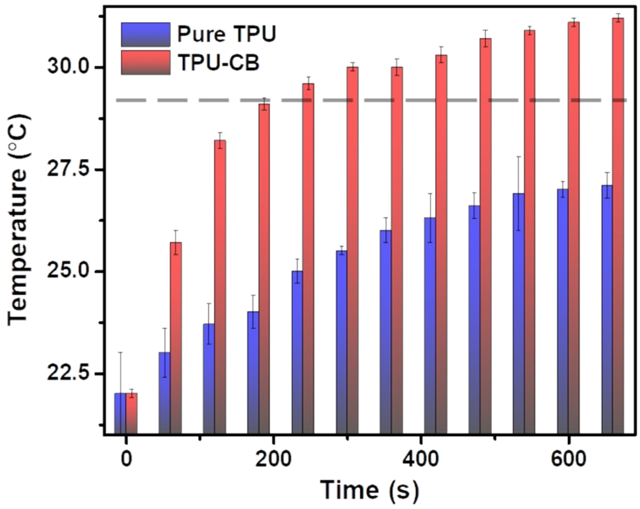


Fig. S4  Temperature measurement of pure TPU and TPU-CB composite under an irradiation intensity of 70.3 mW·cm$^{-2}$.

**Section S5. Data for the discussion about Boltzmann superposition principle**

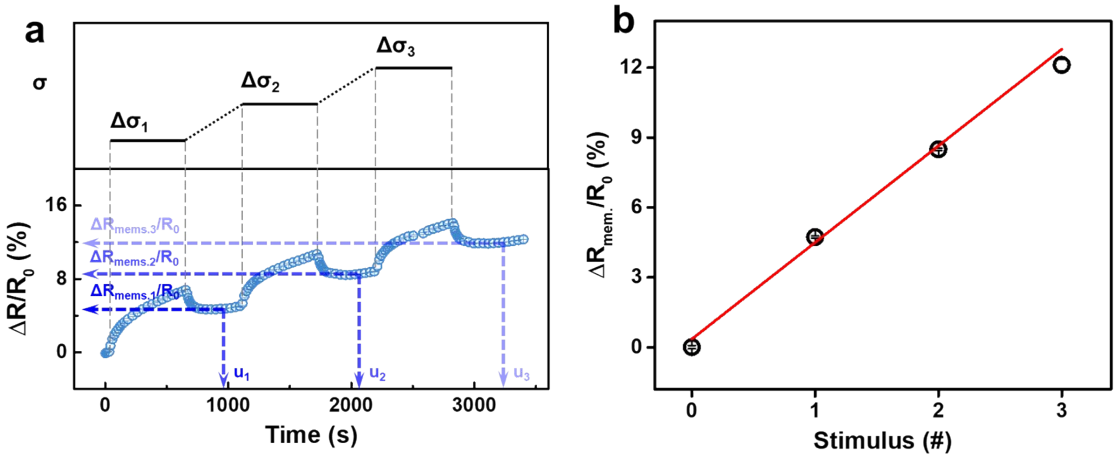


Fig. S5 Schematic illustration and data for the discussion about Boltzmann superposition principle. a) Resistance change rate under irradiation. b) Retentive memory after interval time.