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Supplementary Information

Phototunable Memories and Reconfigurable Logic Applications Based on Natural Melanin

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1. Marerials and Instruments

Synthetic melanin powder and Dimethyl sulfoxide (DMSO) organic solvent were purchased from Sigma-Aldrich Corp. (China).

The 15mg/ml melanin solution for device fabrication was prepared as following processes: 15 mg melanin powder was dissolved in 1 ml DMSO solvent. Then, the melanin suspension solution was kept ultrasound for 30 minutes to obtain uniform melanin solvent, following by a filtration process. The uniform melanin solvent was used in device fabrication for further experiments.

The UV-vis spectra of melanin film was measured by UV-Vis Spectrophotometer (Agilent Cary 60), and Raman spectroscopy was tested on a LABRAM-HR spectrometer. X-ray photoelectron spectra (XPS) were tested by an ESCALAB 250 spectrometer. All the electrical measurements of our melanin-based resistive switching device were performed using parameter analyzer (Keysight B1500A). The AFM topographic images were obtained in room temperature environment in a ScanAsyst mode on a Bruker Dimension Icon AFM (probe: ScanAsyst-AIR). Photo-induced carriers behavior of melanin film was detected using AFM electric technique in KPFM mode (probe: SCM-PIT). The surface potential measurement was carried out in KPFM mode under dark and light illumination with different wavelengths and intensities. The scan height between surface and probe tip is 100 nm (scanning size: 10 µm × 10 µm; scanning rate: 0.8 Hz; resolution: 256 pixels × 256 pixels).

2. Device fabrication

First of all, a 200-nm-thick indium tin oxide (ITO) grown on a glass substrate through a shadow mask was used as the bottom electrode of our melanin-based memristor. Then, pre-prepared 15 mg/ml melanin solution was spin coated on the 200-nm-thick clean ITO substrate to function as resistive switching layer. The spin coating speed is 500 rpm for 5 s followed by 2000 rpm for 120 s. The melanin thin film was annealed on a heating stage at 80 ℃ for 4 h to remove residual organic solvent. The annealing process helps us get a more uniform melanin thin film. Finally, the patterned silver electrode (30 nm) was deposited on the melanin film by thermal evaporation method with the deposition rate of 0.1 Å/s. The fabrication processes of memristive device is illustrated in Fig. S1. Fig. S2a shows a picture of as-fabricated melanin-based memristor with a vertical structure. Cross-sectional SEM image of the memristive device is presented in Fig. S2b.

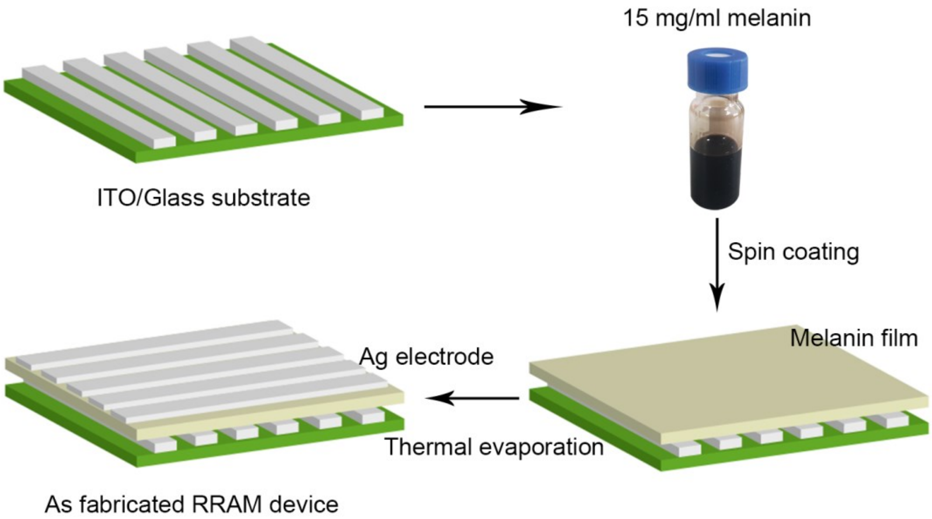

Fig. S1 Fabrication processes of melanin-based memristive device. 15 mg/ml melanin solution was spin coated on clean ITO substrate to function as resistive switching layer (speed: 500 rpm and 2000 rpm, time: 5 s and 120 s). Ag electrode was fabricated on the melanin film by thermal evaporation method (deposition rate: 0.1 Å/s, thickness: 30 nm).

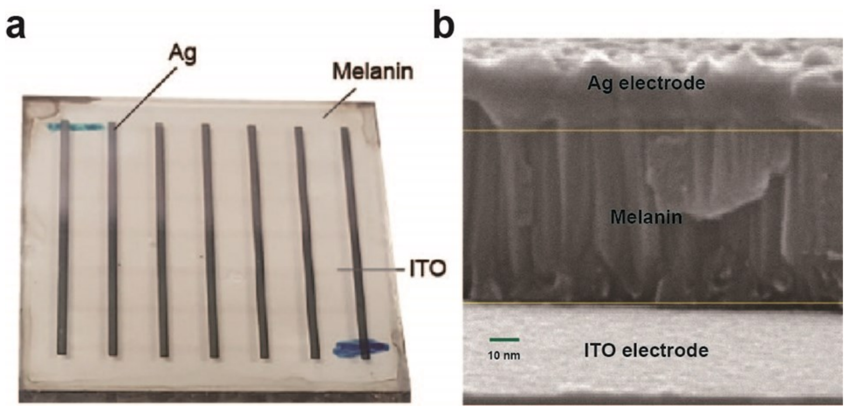

Fig. S2 a) Picture of as-fabricated Ag/melanin/ITO memristive device with a sandwich structure. b) Cross-sectional SEM image of the memristive device (Ag electrode: 30 nm, melanin film: 60 nm, ITO electrode: 30 nm).

3. Monomeric components of melanin

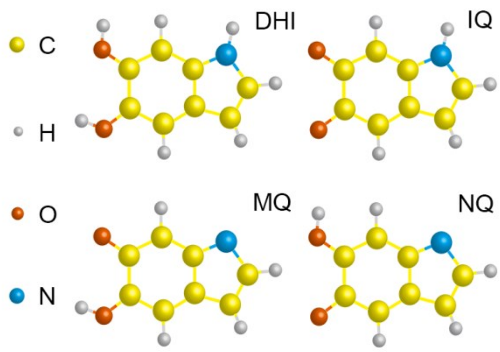

Fig. S3 Considered monomeric components of melanin in this study: 5,6-dihydroxyindole (DHI) and its three redox forms (indolequinone (IQ), quinone methide (MQ), and quinoneimine (NQ)).

4. Melanin solutions of different concentrations and corresponding melanin films

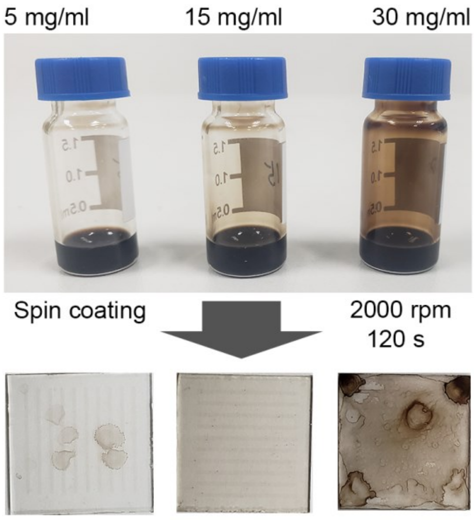

Fig. S4 Melanin solutions of different concentrations (5, 15 and 30 mg/ml) and corresponding melanin films for memristive devices preparation. The melanin films are fabricated by spin coating with 2000 rpm for 120 s. When the concentration is 15 mg/ml, the quality of the melanin film prepared by spin coating is the best.

5. Chemical moieties used to fit the XPS spectra of a melanin thin film

Table S1. Chemical moieties used to fit the XPS spectra of a melanin thin film.

Element	Binding energy (eV)	Assignment
C	284.7	C-C aromatic
	285.3	C-C aromatic
	285.8	-C-N
	286.5	-C-OH, -C-N
	288.0	-C=O
	289.2	O=C-OH
N	399.2	$-NH_2$
	400.3	Pyrrole
	401.8	$-NH_3^+$
O	531.3	O=C
	532.1	O=C in COOH
	532.8	HO-C in COOH
	533.5	HO-C aromatic

6. Typical forming curve

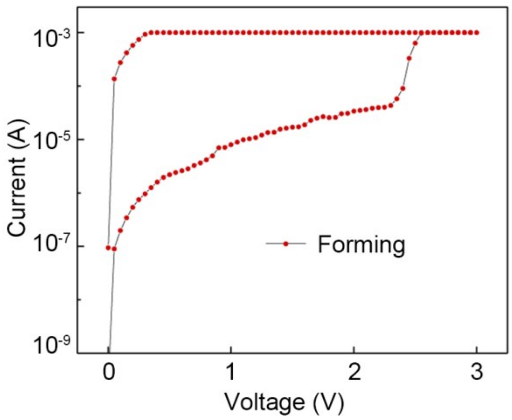

Fig. S5 Typical forming curve of Ag/melanin/ITO memristor at 1 mA compliance current (sweeping rate: 50 mV, temperature: 30 ℃).

7. Influence of melanin solution concentration on the *I-V* performance

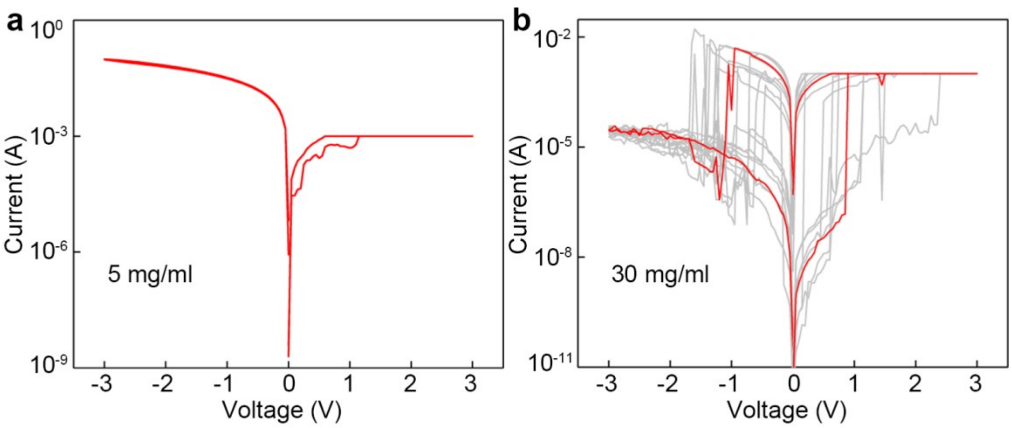

Fig. S6 The concentration influence of melanin solution for resistive switching layer on Ag/melanin/ITO memristors *I-V* performance. a) Typical *I–V* characteristic of ITO/melanin/Ag memristive devices with 5 mg/ml melanin. b) *I–V* characteristic of ITO/melanin/Ag memristive devices with 30 mg/ml melanin (compliance current: 1 mA, sweeping rate: 50 mV).

8. Performance comparison of biomaterials based memristive devices

Table S2. Performance comparison of melanin-based memristive device and other biomaterials based memristive devices.

Biomaterial unit	Device structure	Light response	SET voltage	RESET Voltage	ON/OFF ratio	Ref
Ag-doped Chitosan	Mg/Ag-doped chitosan/Mg	No	1.63 V	-0.82 V	10^2	[41]
Starch	Au/starch/ITO	No	0.9 V	-1.5 V	10^3	[42]
Fibroin	Mg/fibroin/Mg	No	1.5 V	-0.7 V	10^2	[43]
Ferritin	Pt/ferritin/Pt	No	1.3 V	-0.4 V	10^5	[44]
Gelatin	Al/gelatin/ITO	No	-0.7 V	2.4 V	10^6	[45]
Chicken albumen	Al/ Chicken albumen /ITO	No	-0.3 V	3.6 V	10^3	[46]
DNA	Au/CuO-DNA-Al/ Au	No	2.25 V	-2.25 V	50	[47]
RNA	QD-STV/RNA /Au	No	1.8 V	-1.5 V	10^2	[48]
Tobacco mosaic virus (TMV)	Al/TMV-Pt nanoparticles/Al	No	3.1 V	-2.4 V	10^3	[49]
Melanin	Ag/melanin/SS	No	0.6 V	-0.6 V	10	[50]
Melanin	Ag/melanin/ITO	Yes	0.2 V	-0.6 V	10^4	This work

9. SCLC model mechanism

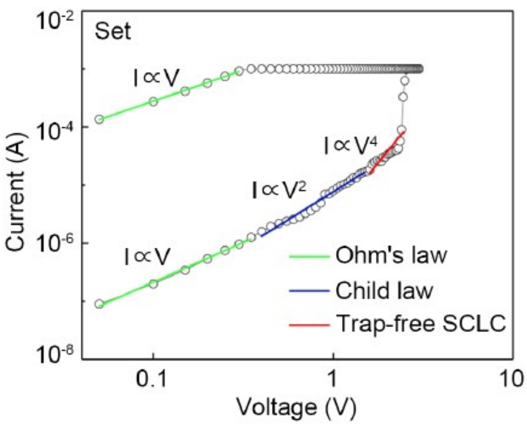

Fig. S7 Nonlinear *I–V* curve and fitted lines of the Ag/Melainn/ITO memristive device at SET process (compliance current: 1 mA, sweeping rate: 50 mV). The fitting lines of four regions illustrate that the conduction can be divided into three parts including Ohm's law ($I \propto V$), Child law ($I \propto V^2$) and trap-free SCLC ($I \propto V^4$).

10. *I–V* performance of the memristor with different sweep rates

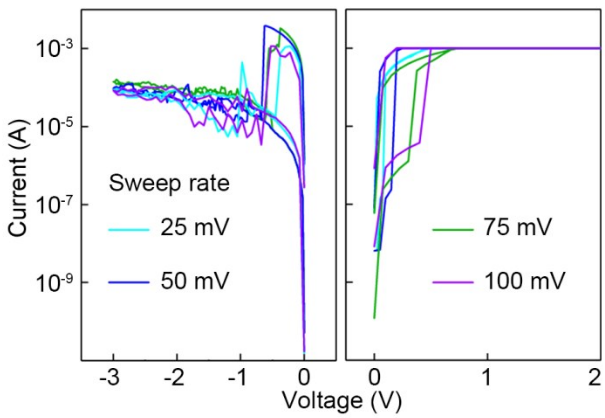

Fig. S8 The continuous *I–V* tests of the memory device with different sweep rates from 25 to 50, 75 and 100 mV with constant compliance current of 1 mA.

11. Photograph of probe station for electrical test under light illumination

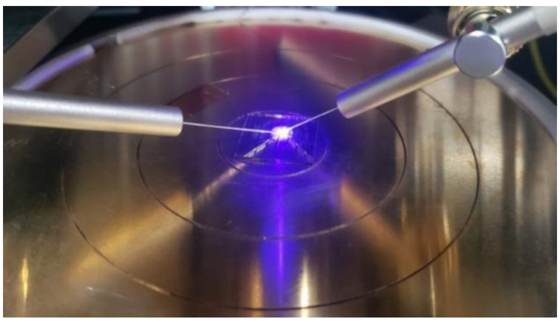

Fig. S9 Photograph of probe station for the electrical test of Ag/melanin/ITO memristive device under illumination condition.

12. Histogram and Gaussian distribution of SET voltage under light condition

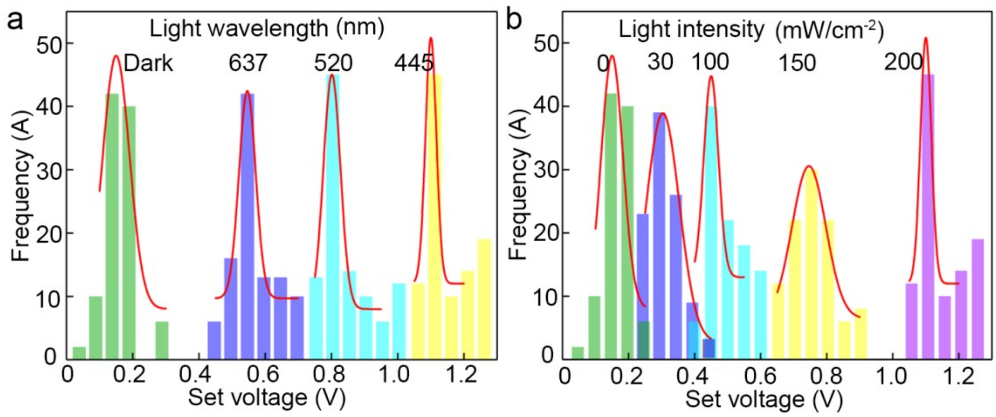

Fig. S10 a) Histogram and Gaussian distribution of SET voltage with various light wavelengths (dark, 637, 520, 445 nm) with constant light intensity of 200 mW/cm². b) Histogram and Gaussian distribution of SET voltage with different light intensities (0, 30, 100, 150, 200 mW/cm²) with fixed light wavelength of 445 nm.

13. *I-T* characteristic at different temperature

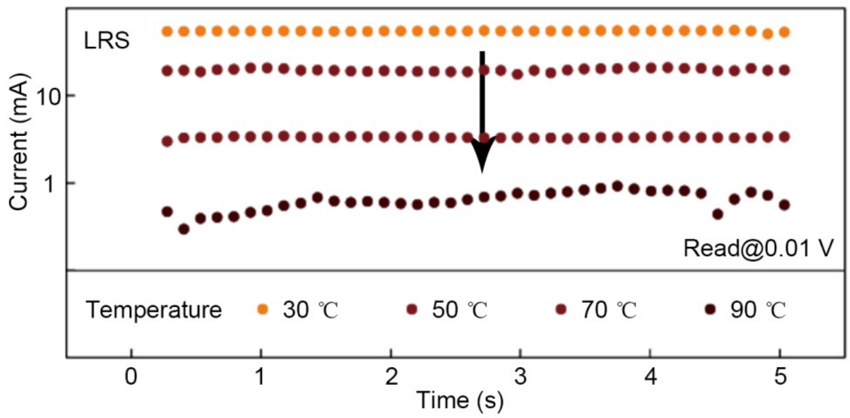

Fig. S11 The *I-T* characteristic of Ag/melanin/ITO memristive device at different temperature (30, 50, 70 and 90 ℃). The memristor was measured at LRS with fixed read voltage of 0.01 V.

14. Fundamental memristor circuit for logical functions

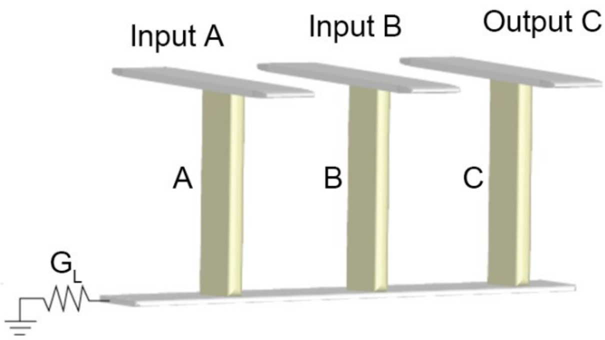

Fig. S12 Fundamental memristor circuit with two input devices A and B, one output device C and a load resistor G_L for NAND and NOR logical gates.

15. Charge trapping capacity of melanin film under various light intensities

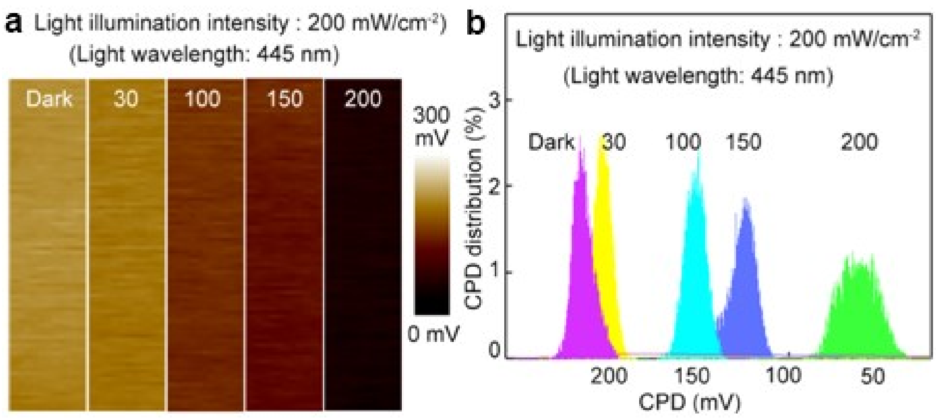

Fig. S13 Charge trapping capacity of melanin film measured by KPFM a) Surface potential of melanin thin film detected in KPFM mode under dark and light illumination of various intensities from 0 to 200 mW/cm^2 (light wavelength: 445 nm). b) Potential distribution corresponding to a).