Supporting Information

Electronic Transport in the Biopigment Sepia Melanin

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Raman Spectroscopy of dry and wet Sepia melanin powders

The Raman Spectroscopy surveys of dry and wet Sepia melanin powders from pellets before and after the electrical resistive switching do not show any peak and or shoulder attributable to graphitic carbon **(Figures S6 A, B, C and Table S6)**. Typical Raman modes of graphitic carbon are indeed located at ca. 2750 cm^{-1} ($2D_2$ band) and at 2700 cm^{-1} ($2D_1$ shoulder)[1].

High-resolution X-ray photoemission spectra (XPS) of dry Sepia melanin powders

The high-resolution C_{1s} XPS spectra of dry Sepia melanin powders obtained from pellets before and after the electrical resistive switching do not indicate the presence of graphitic carbon **(Figure S6 D and E, Tables S7 and S8)**.

Typical signatures of graphitic carbon are a C_{1s} peak at BE=291.4 eV and an unusually thin C_{1s} component at BE=284.6 eV. The high-resolution C_{1s} XPS spectra of dry Sepia melanin powder show a satellite peak at BE=291.4 eV; this is expected in eumelanin because of the cyclic carbon structure. The C_{1s} component at BE=284.7 eV is broad and not as sharp as expected in graphitic carbon **(Figure S6 E)**.

The concentration of C-O, C-OH, or C-O-C groups (BE=286.7 eV) is high compared to the other chemical groups observed **(Tables S7 and S8)**. The concentration of C-O groups, compared to C-N and C=C groups, is also higher than expected. Nevertheless, the C_{1s} spectra before and after switching of Sepia melanin powders are similar, except for a slight increase in C-O and decrease in C-N after switching.

X-ray diffraction (XRD) survey of dry Sepia melanin powders

In agreement with Raman spectroscopy and XPS surveys, XRD patterns of dry Sepia melanin powders, obtained from pellets before and after the electrical resistive switching, show a broad XRD spectrum with a small shoulder around $2\theta \sim 27°$, not due to graphitic carbon **(Figure S7)**. The typical (002) and (004) graphitic planes correspond indeed to sharp peaks located respectively at $2\theta \sim 27°$ and $2\theta \sim 54°$.[2]

Supporting Information References

(1) Ferrari, A. C., Raman Spectroscopy of Graphene and Graphite: Disorder, Electron-Phonon Coupling, Doping and Nonadiabatic Effects. *Solid State Communications* **2007**, *43*, 47–57.

(2) Saenger, K. L.; Tsang, J. C.; Bol, A. A.; Chu, J. O.; Grill, A.; Lavoie, C., In Situ X-Ray Diffraction Study of Graphitic Carbon Formed during Heating and Cooling of Amorphous-C/Ni Bilayers. *Applied Physics Letters* **2010**, *96*, 2010–2013.

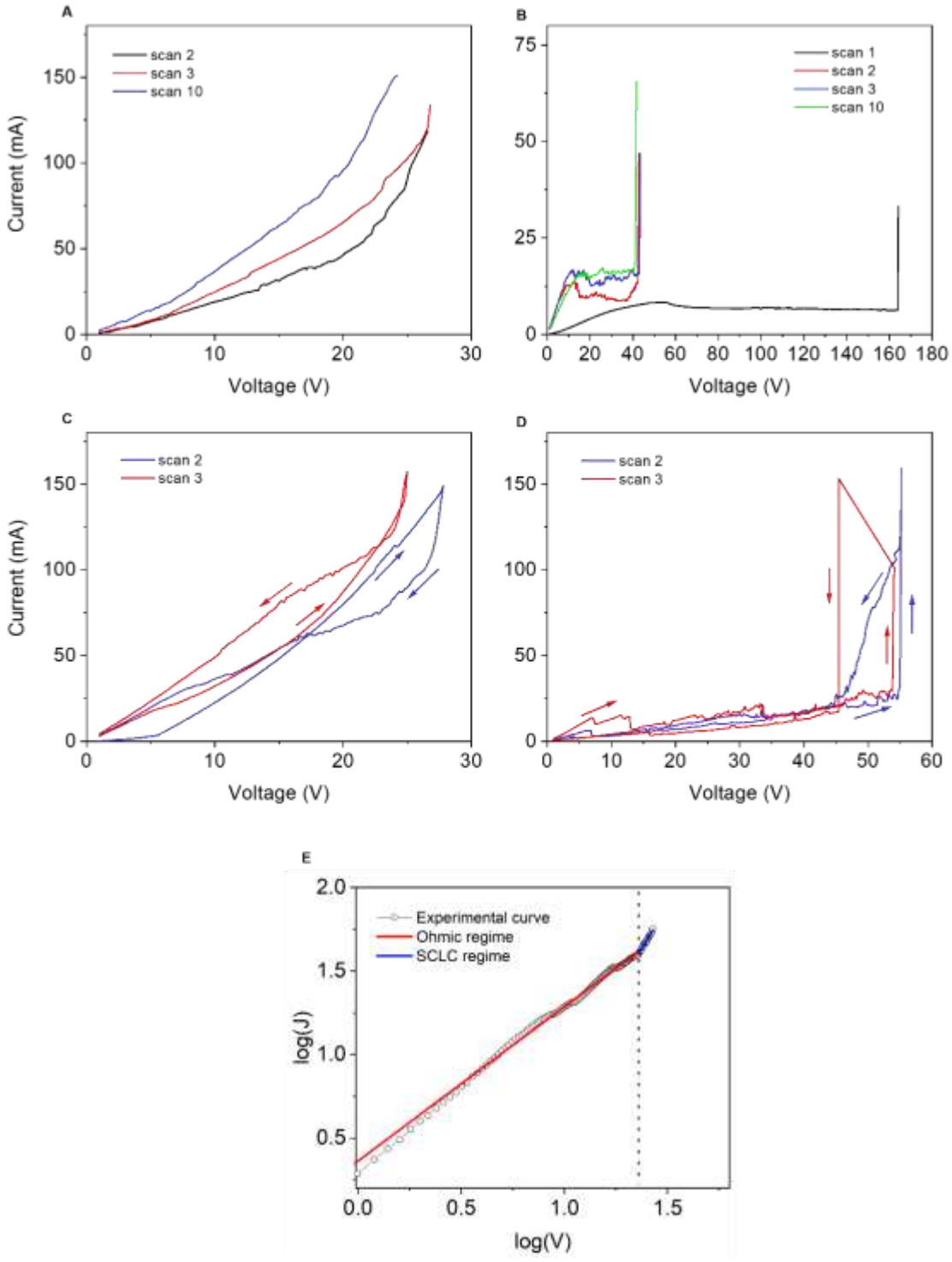


Figure S1. Sequential current-voltage scans of Sepia melanin pellets. Dry: (A) forward scan only and (C) forward and backward scans (cycles); 19.0% wt wet: (B) forward scan only and (D) forward and backward scans (cycles). In (E) log (J)-log (V) plot for dry pellets showing the change

of slope between the Ohmic and the Space Charge Limited Current (SCLC) regime (red and blue solid line with slope of 0.93±0.06 and 2.09±0.02 respectively).

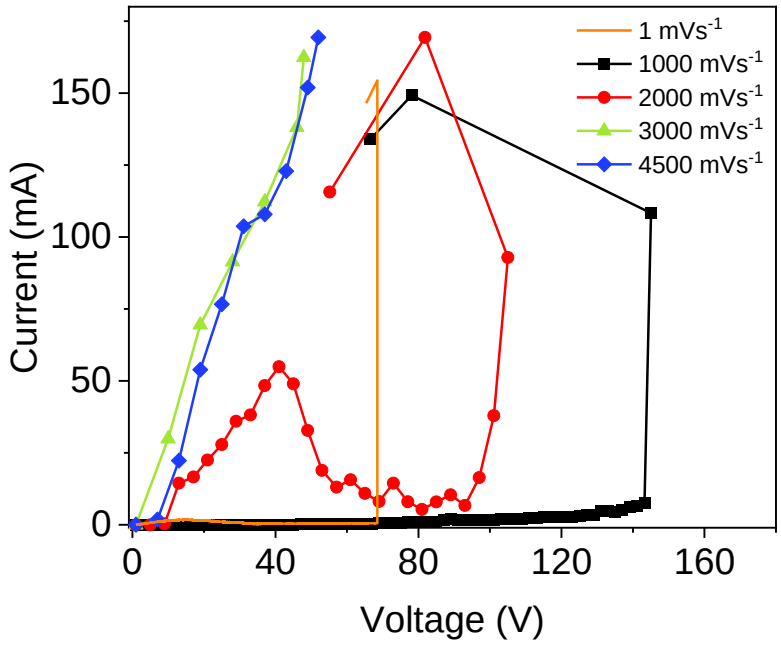


Figure S2. Sequential current-voltage acquisitions from low to high scan rates for wet pellets.

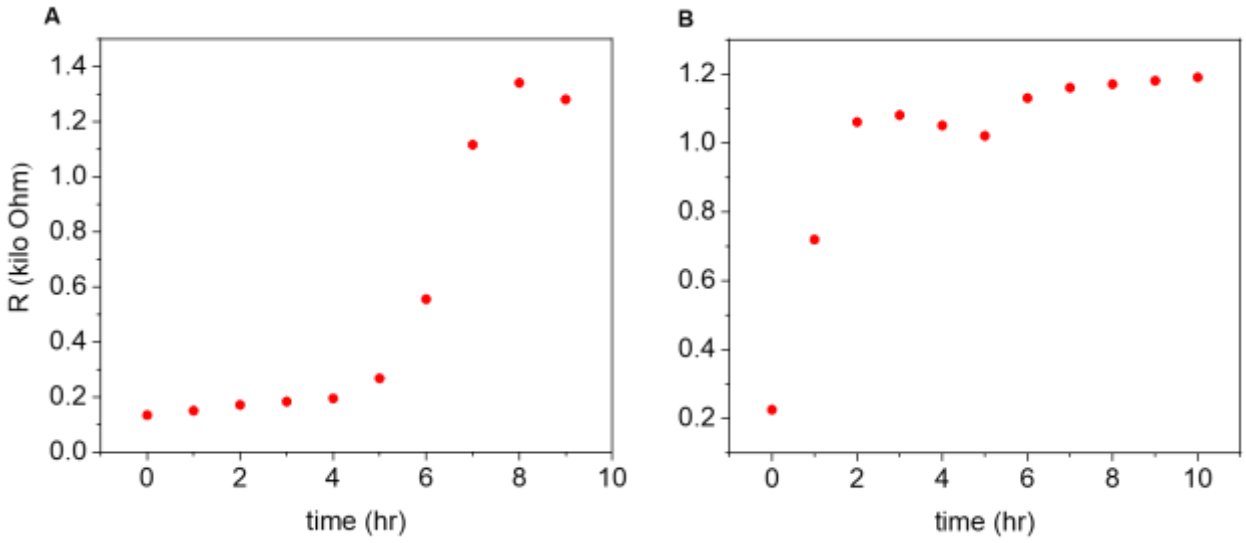


Figure S3. Resistance vs time in unbiased conditions (i.e. without electrical bias) after the electrical resistive switching for Sepia melanin pellets. (A) dry and (B) 19.0% wt wet.

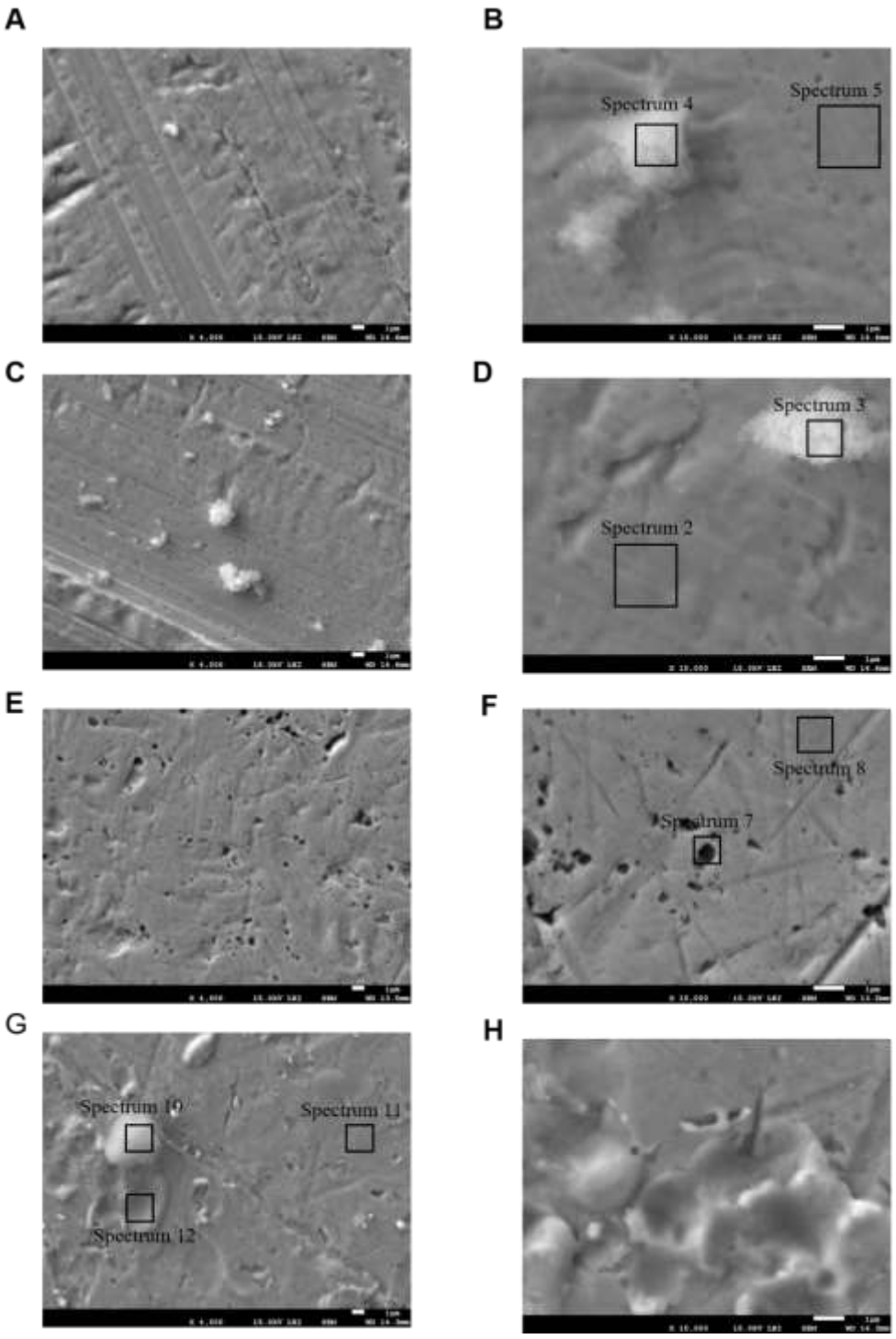


Figure S4. Scanning electron microscopy (SEM) of copper and stainless-steel electrodes. SEM images of copper and stainless-steel electrodes (A), (B), (E) and (F) before electrical resistive switching; (C) and (D), (G) and (H) after electrical resistive switching.

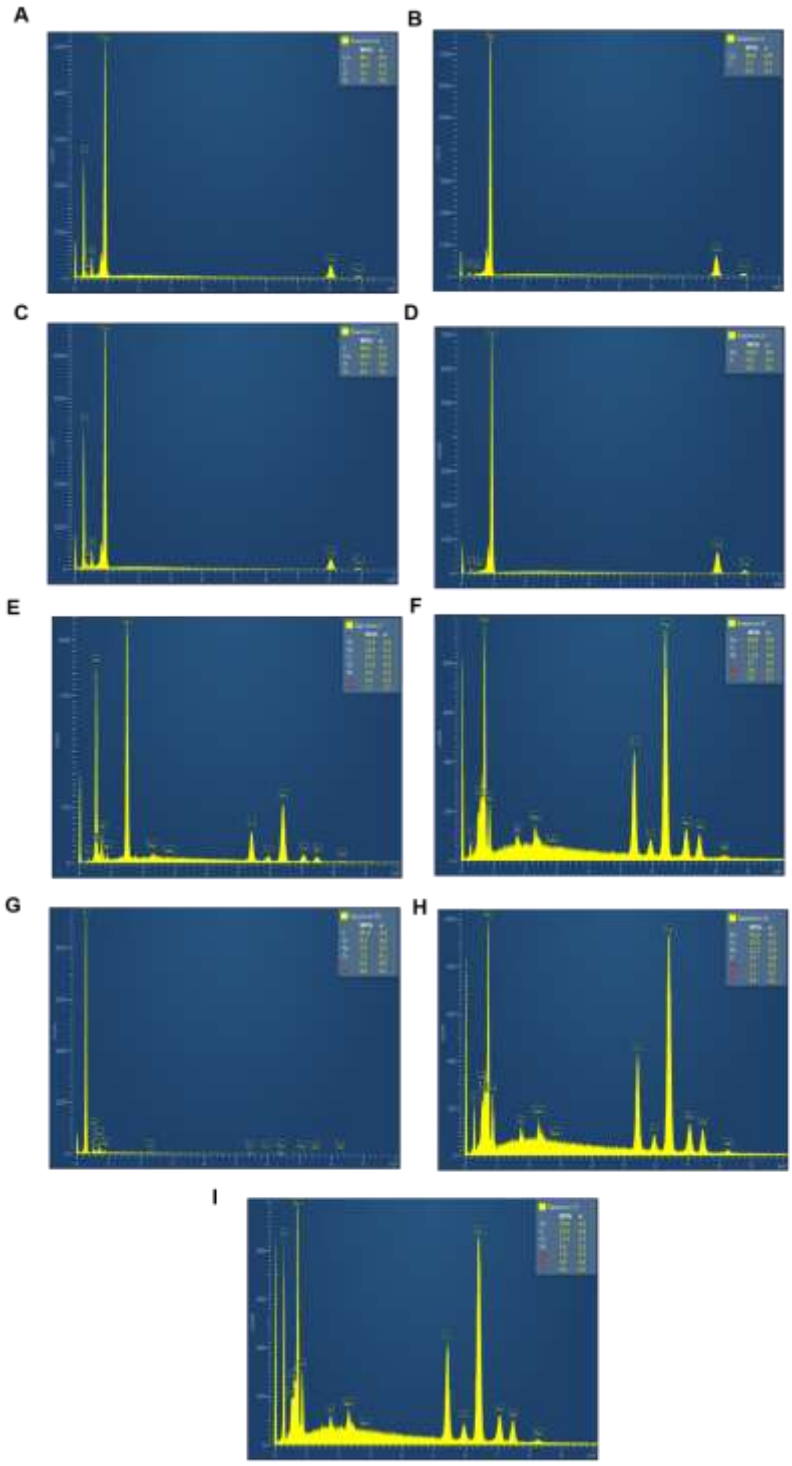


Figure S5. EDX spectra of copper and stainless-steel electrodes. EDX spectra of copper and stainless-steel electrodes (A), (B), (F) and (G) before electrical resistive switching; (C), (D), (E), (H) and (I) after electrical resistive switching **(Figure S4)**.

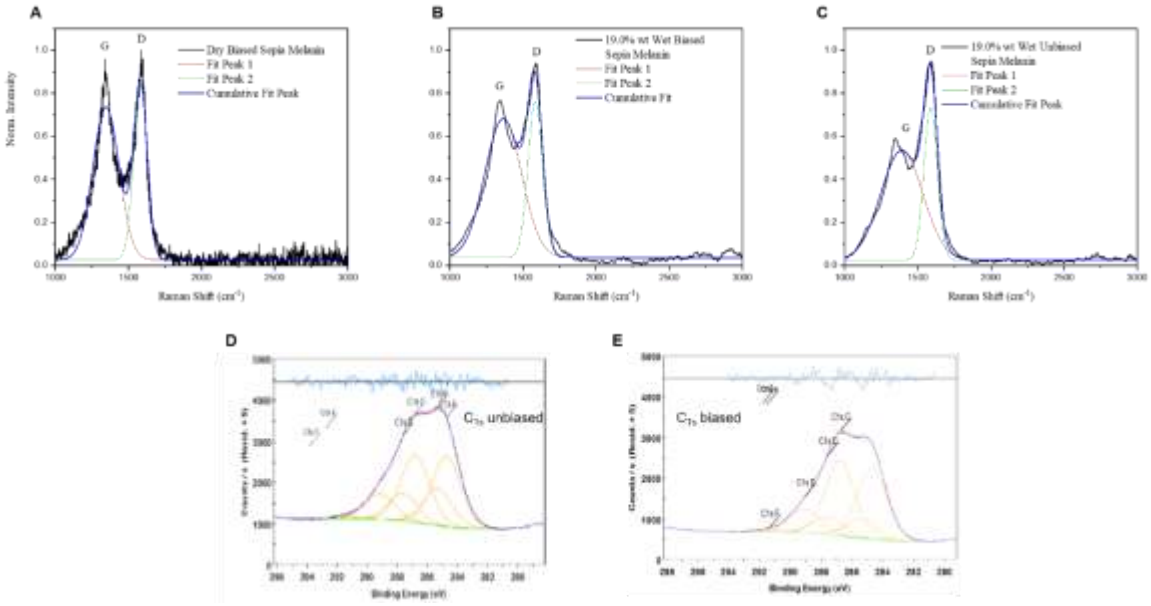


Figure S6. Raman and XPS characteristics of dry and wet Sepia Melanin pellets. Raman spectra after resistive switching for pellets dry (A) and wet **(**B) pellets. Raman spectrum before resistive switching for wet pellets (C). High resolution C_{1s} XPS spectra of dry pellets before switching (D) and after switching (E).

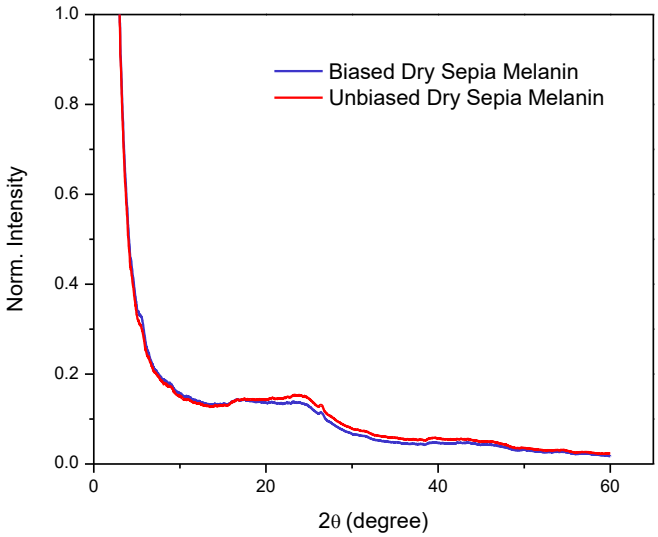


Figure S7. Structural characterization of dry Sepia Melanin. XRD patterns before and after resistive switching.

	%RH	%wt gained
Sepia Melanin	90 ± 0.3	19.0 ± 1.0
	dry	0

Table S1. Percentage of weight gained (% wt) after hydration (24 hr) at different percentages of relative humidity (% RH) for Sepia melanin pellets (see experimental section, main file).

Sample	Scan Rate (mVs^{-1})	V_T (V)	$\frac{R_{ON}}{R_{OFF}}$
Dry	1	41.7	0.191
	100	51.6	0.18
19.0% wt, wet	1	68.5	0.003
	100	55.1	0.05
	1000	143.2	0.025
	2000	97.0	0.070

Table S2. Threshold voltage (V_T) and $\frac{R_{ON}}{R_{OFF}}$ for dry and wet pellets at different voltage scan rates (see main file for the meaning of R_{ON} and R_{OFF}).

Sample	Scan Rate (mVs^{-1})	a
Dry	100 (Cycle 2)	0.959 ± 0.005
	100 (Cycle 3)	1.059 ± 0.003
	1000	1.137 ± 0.018
	2000	1.168 ± 0.081
	3000	1.344 ± 0.026
	4500	1.250 ± 0.010
19.0% wt, wet	3000	1.325 ± 0.116
	4500	1.001 ± 0.067

Table S3. Values of a in $I \propto V^a$ at a different voltage scan rates, for dry and wet pellets.

$I_0\ (mA)$	$\tau_1\ (s)$	$\tau_2\ (s)$	$A_1\ (mA)$	$A_2\ (mA)$
10.49 ± 0.07	162.9 ± 5.3	1.17 ± 0.05	12.25 ± 0.20	62.52 ± 0.88

Table S4. Fitting parameters for the transient characteristics of wet pellets, at V_T, after electrical resistive switching. The transient characteristics fit a biexponential function of the form $I(t) =$

$I_0 + \sum_{j=1}^{2} A_j \exp(-\frac{t}{\tau_j})$, where I_0 is the *quasi-plateau* current, τ_1 and τ_2 the characteristic decay times, A_1 and A_2 the amplitudes of the decay profile.

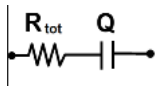
Fitting parameters 	**Dry Pellet**		**Wet pellet**	
	Before switching	**After switching**	**Before switching**	**After switching**
R_{total}	4.5 GΩ	172 Ω	9 KΩ	719 Ω
Q ($F.s^{n-1}$)	6.70×10^{-12}	6.77×10^{-9}	2.60×10^{-8}	3.80×10^{-10}
n	0.81	0.94	0.58	0.88

Table S5. Fitting parameters of the equivalent circuit of both dry and wet Sepia melanin pellet in the frequency range 3 kHz -3 Hz and 3 kHz -145 Hz for dry and wet pellet respectively. R_{tot} includes the electronic resistance R_e, the ionic resistance R_i, the interface resistance R_{if}, i.e., $R_{tot} = R_e + R_i + R_{if}$, Q (CPE the constant phase element) is the series combination of melanin's geometrical capacitance and the capacitance at melanin/metal interface that describes any deviation from an ideal capacitive response and n is a dispersion parameter that determines the physical meaning of Q. The CPE impedance is $Z_{CPE} = \frac{1}{Q\,(j2\pi f)^n}$, where f is the frequency. If n = 1, the CPE reduces to an ideal capacitor. If n = 0, the CPE reduces to a real resistor, and if n = 0.5, the CPE reduces to a Warburg element (describes any process controlled by ionic or electronic diffusion).

Wet pellet after switching					
Raman Mode #	$y_o \pm \Delta y_0$	$A \pm \Delta A$ **(cm^{-1})**	$w \pm \Delta w$ **(cm^{-1})**	$x_c \pm \Delta x_c$ **(cm^{-1})**	**FWHM (cm^{-1})**
1	0.036 ± 0.001	203.2 ± 1.9	251.1 ± 2.6	1363.9 ± 1.3	295.6
2	0.036 ± 0.001	91.8 ± 1.5	101.3 ± 1.1	1583.3 ± 0.5	215.1
Wet pellet before switching					
1	0.024 ± 0.001	183.9 ± 1.7	287.6 ± 2.5	1389.9 ± 1.4	338.6
2	0.024 ± 0.001	82.3 ± 1.2	92.3 ± 0.8	1587.4 ± 0.3	108.6
Dry pellet after switching					
1	0.026 ± 0.001	158.5 ± 1.5	177.9 ± 2.0	1346.3 ± 0.9	209.5
2	0.026 ± 0.001	95.4 ± 1.1	93.6 ± 1.2	1581.6 ± 0.6	110.2

Table S6. Fitting parameters of the deconvolution of the Raman modes of melanin pellets before and after electrical tests. The deconvolution function is a Gaussian distribution of the form $y = y_o + \frac{A}{w\sqrt{\pi/2}} \exp\{-2\left[\frac{x-x_c}{w}\right]^2\}$, where x_c is the Raman shift of the mode, w the standard deviation and A the amplitude of the distribution **(Figures S6 A, B and C)**.

Name	BE (eV)	At. %	
		Before switching	After switching
S_{2p}	166.6	0.2	0.4
C_{1s}	284.9	61.8	61.6
N_{1s}	399.1	4.5	5.6
O_{1s}	531.8	32.9	31.5
Na_{1s}	1070.7	0.5	0.9

Table S7. Atomic percentage of the elements and binding energies obtained from the XPS survey scan of the dry pellets, before and after resistive switching.

Name	BE (eV)	Identification	At. %	
			Before switching	After switching
C_{1s}	284.7	$C-C$ and $C=C$	30.7	34.0
	285.3	$C-N$	16.1	9.3
	286.7	$C-O, C-O-C, C-OH$	29.4	35.5
	287.6	$C=O$	11.9	8.5
	289.1	$O-C=O, COOH$	11.1	11.5
	291.4	$\pi \rightarrow \pi^*$ of $C=C$	0.8	1.2

Table S8. Attribution of chemical bond from high resolution XPS scans (C_{1s} only) of dry pellets before and after resistive switching **(Figures S6 D and E)**.