Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information

S.1 *C vs f and G/ω vs f dispersion analysis*

The presence of the nanotextured silicon surface modifies the dispersive trend of the device impedance **(Figure S1).** In particular, the order of magnitude of the capacitance in the high frequency region (Figure S1, a) is greatly reduced respect to those measured on flat silicon and on melanin on ITO. Besides, a relevant low frequency contribution is present. The conductance vs frequency (*G/ω vs f)* data display also peaks in different frequency regions. These peaks relates to the presence of melanin as can be deduced from the *G/ω vs f* of structures embedding melanin. In particular the peaks are present in a high frequency range (> 1 kHz) in melanin on flat silicon devices and (down to 100 Hz) when it is assembled on nanotextured supports (see Figure S1, b) and ITO. In melanin on nanotextured silicon with short hydrophobic structures the peak features are not present. The presence of a dominant conductance peak in the low frequency region when nanotextured structure is present, indicates an interface-trap states mediated transport contribution overwhelming the bulk one. This has to be ascribed to the increased surface/bulk ratio due to the nanotexturing.

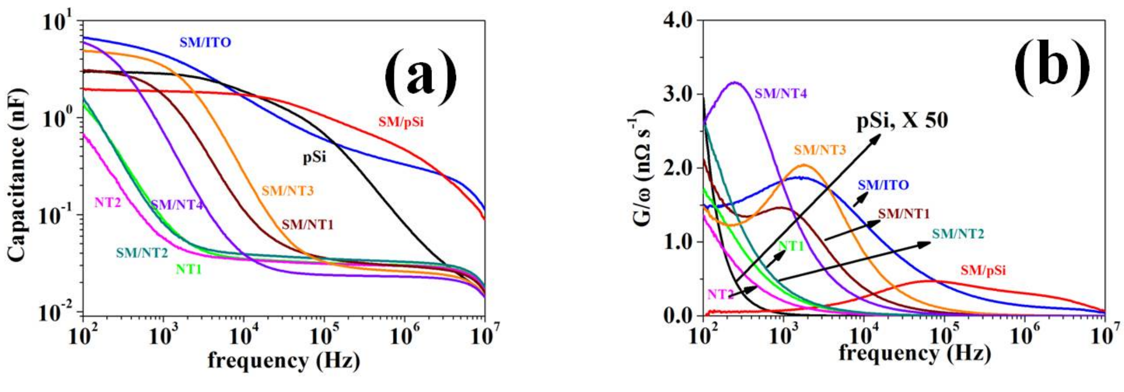

Figure S1. Capacitance *(C vs f)* (**a**) and Conductance (G) over frequency ration *f* vs frequency *f (G/ω vs f)* (**b)** on the full set of the examined structures. The Figure includes the spectra with those typically collected on bare flat p-silicon and on melanin self assembled on ITO (see also ref.18, main text) and flat pSi (multiplied X 50). A quite high reproducibility degree of the spectra has been observed.

S.2 Au/SM/NT2-NT4:more details on EIS analysis before and after a voltage pulse

As detailed in the main text, in *Au/SM/NT2-NT4 structures* the NPs were simulated using two slightly different electrical circuits, depending on the nanotextured silicon surface wetting properties (**Figure S2**). The equivalent circuit fitting the impedance of melanin on hydrophobic short NT silicon features showed an architecture and best fit parameters similar to those observed in bare Au/NT2 structures (Figure S2, c), thus evidencing a low effectiveness of melanin contribution. Moreover, on Au/SM/NT4 i.e. melanin on short hydrophilic nanotextured structures (Figure S2, (**d**)), the Ershler circuit has been found suitable for best fitting, evidencing the presence of a small contribution due to an inhomogenously adsorbed melanin and the partial charge transfer process at Au/SM interface.

The circuit impedance best fittings the NPs read outs for melanin on short NT templates (A*u/SM/NT2-NT4)* after the application of the voltage pulse (V_p=15V, 1s), returned the presence, in the equivalent circuit, of three components in both cases (Figure S2, (**e**)), similarly to those encountered melanin-based structure on long NT templates. The analysis evidences that both structures show signal retention capabilities as can be inferred from the NPs collected after one hour from the end of the pulse and corresponding behavior of the best fit circuital parameters.

Figure S2. Nyquist plots evolutions for SM/NT2 (**a**) and SM/NT4(**b**), at representative time intervals from the end of the voltage pulse. (**c-e**) Equivalent circuits for best fitting of impedance data before (**c,d**) and after (**e**) the end of the pulse. (**f-m**) Variation of the main best fit parameters (C,R) after the end of the voltage pulse referring to the HF (**f-g**) and LF (**h-m**) sections of the equivalent circuits for Au/SM/NT2 (**f,h,l**) and Au/SM/NT4(**g,i,m**).

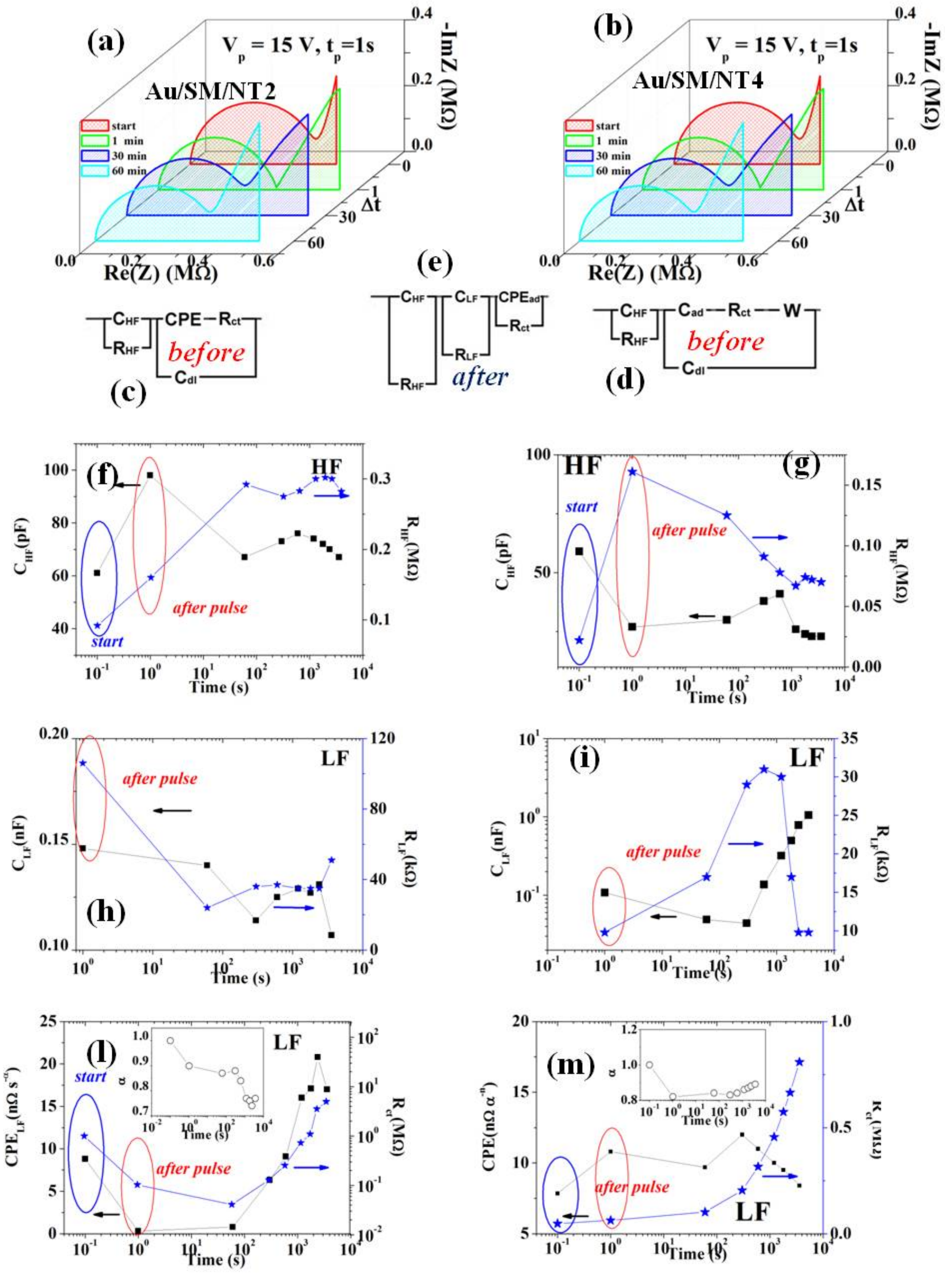

Figure S3. XPS Nitrogen line emission collected on a melanin-like layer on ITO/glass support

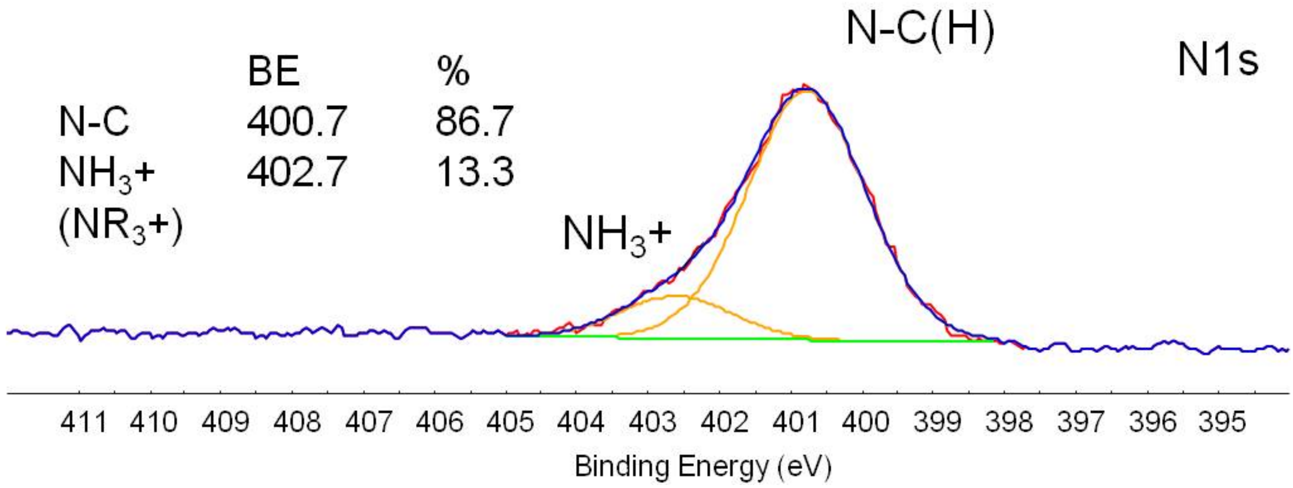

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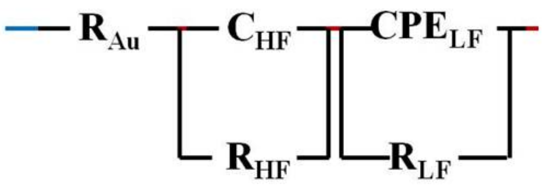
Figure S4. Best fit values for circuital elements for devices on flat and nanotextured silicon support w/o melanin (EIS data from Figure 4a,c main text).

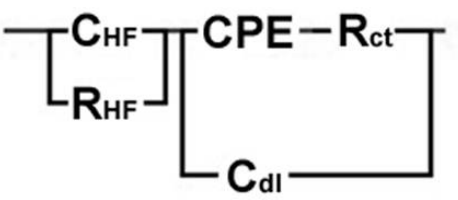
Circuital Elements	*Fitting Parameters*
C_{HF} (nF)	4.7
R_{HF} (KΩ)	31.0
R_{LF} (KΩ)	9.4
CPE (nΩs^{α})	89.5
α	0.7
R_{Au} (KΩ)	0.7

pSi



NT1

Circuital Elements	*Fitting Parameters*
C_{HF}(pF)	138
C_{dl}(pF)	43
R_{ct} (KΩ)	273
R_{HF} (KΩ	167
CPE (nΩ$s^{-\alpha}$)	10.9
α	0.8



NT2

Circuital Elements	*Fitting Parameters*
C_{HF} (pF)	43.4
C_{dl}(pF)	111
R_{HF} (KΩ)	76
R_{ct} (KΩ)	667
CPE (nΩ$s^{-\alpha}$)	20.2
α	0.7

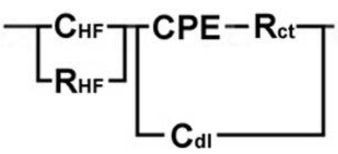
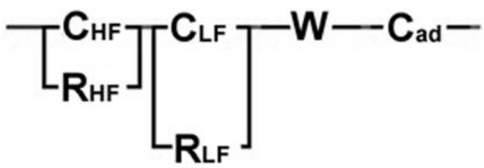


Figure S5. Best fit values for circuital elements for devices on flat support embedding melanin (EIS data from Figure 5a,b main text).

Circuital elements	*Fitting Parameters*
C_{HF}(pF)	1.6
C_{LF}(nF)	22
C_{ad}(nF)	8.8
R_{HF}(kΩ)	24
R_{LF}(kΩ)	344
AW_1($M\Omega s^{-0.5}$)	1.2

SM/ITO/Glass



Circuital Elements	*Fitting parametes*
C_{ad}(nF)	1.8
CPE_1($\mu\Omega s^n$),α	0.3,0.6
CPE_2($n\Omega s^n$), α	0.8,0.8
R_{HF}(MΩ)	0.1
R_{LF}(kΩ)	1.4
AW ($M\Omega s^{-0.5}$)	0.3

SM/pSi

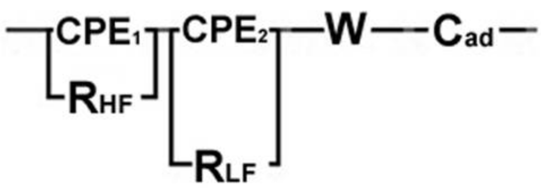


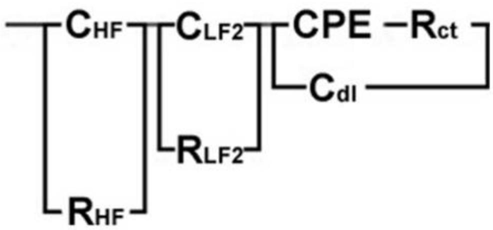
Figure S6. Best fit values for circuital elements for devices on nanotextured silicon support embedding melanin (EIS data from Figure 5c,d main text).

SM/NT3

Circuital Elements	Fitting Parameters
C_{HF} (pF)	323
C_{LF2}(nF)	4.22
C_{dl}(nF)	20.1
R_{HF} (KΩ)	26.4
R_{LF} (KΩ)	458.6
R_{ct} (KΩ)	12.1
CPE(nΩ$s^{-\alpha}$)	108
α	0.73

SM/NT1

Circuital Elements	*Fitting Parameters*
C_{HF} (pF)	35.4
C_{LF2} (nF)	5.6
C_{dl} (pF)	112
R_{HF} (kΩ)	15.4
R_{LF2} (kΩ)	352
R_{ct} (kΩ)	10.6
CPE (nΩs^{α})	235
α	0.7



SM/NT4

Circuital Elements	*Fitting Parameters*
C_{HF} (pF)	59
C_{ad}(nF)	7.8
C_{dl} (pΩ)Cdl	39
R_{HF} (KΩ)	22
R_{ct} (KΩ)	48
AW(MΩ$s^{-0.5}$)	0.64

SM/NT2

Circuital Elements	*Fitting Parameters*
C_{HF} (pF)	61
C_{dl} (pF)	84
R_{HF} (KΩ)	288
R_{ct} (KΩ)	92
CPE (nΩs^{α})	16
α	0.84