Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2016

## **Electronic supplementary information (ESI)**

## Melanin-based flexible supercapacitors

Prajwal Kumar, Eduardo Di Mauro, Shiming Zhang, Alessandro Pezzella, Francesca Soavi, Clara Santato\* and Fabio Cicoira\*

Prajwal Kumar, Shiming Zhang, Prof. Fabio Cicoira Department of Chemical Engineering Polytechnique Montréal C.P. 6079, Succ. Centre-ville, Montréal, Québec, H3C 3A7 Canada Email: fabio.cicoira@polymtl.ca

Eduardo Di Mauro, Prof.Clara Santato Department of Engineering Physics Polytechnique Montréal C.P. 6079, Succ. Centre-ville, Montréal, Québec, H3C 3A7 Canada Email: clara.santato@polymtl.ca

Prof. Alessandro Pezzella Dipartimento di Scienze Chimiche Università di Napoli Federico II Cupa Nuova Cintia, 21, 80126, Napoli, Italy

Prof. Francesca Soavi Dipartimento di Chimica "Giacomo Ciamician" Università di Bologna Via Selmi, 2, 40126, Bologna, Italy Email: francesca.soavi@unibo.it



**Figure S1** Cyclic voltammograms (first three cycles) of a Mel/CP electrode (33.8  $\mu$ g/cm<sup>2</sup> melanin loading, normalized over the electrode footprint) in NH<sub>4</sub>CH<sub>3</sub>COO<sub>(aq)</sub> at pH 5.5, at 50 mV/s. A broad anodic peak, with irreversible characteristics, is observed during the first cycle of the cyclic voltammetry of Mel/CP.<sup>1</sup>

Three voltammetric cycles, within the interval of electrode potential 0 - 0.6 V vs Ag/AgCl, were initially carried out with the Mel/CP electrodes. These three cycles were carried out prior electrochemical characterization reported in Fig. 1. These cycles likely led to covalent coupling (intramolecular reticulation) of intermediate species formed during the anodic scan.<sup>1</sup>

1. J. Wünsche, Y. Deng, P. Kumar, E. Di Mauro, E. Josberger, J. Sayago, A. Pezzella, F. Soavi, F. Cicoira, M. Rolandi and C. Santato, Chem. Mater., 2015, **27**, 436-442.



**Figure S2** Anodic current at 0 V vs Ag/AgCl vs. scan rate obtained from the cyclic voltammograms of Mel/CP with 33.8  $\mu$ g/cm<sup>2</sup> melanin loading in NH<sub>4</sub>CH<sub>3</sub>COO<sub>(aq)</sub> pH 5.5.



**Figure S3** Cyclic voltammograms at different scan rates of Mel/CP electrodes (33.8  $\mu$ g/cm<sup>2</sup> loading of melanin) in (a) sodium sulfate pH 5.5, (b) phosphate buffer saline pH 7.4 and (c) ammonia buffer pH 10 (see Experimental in main text). Geometric size of samples 0.4 cm<sup>2</sup>. (d) Cyclic voltammograms of Mel/CP electrodes (33.8  $\mu$ g/cm<sup>2</sup> loading of melanin) at 100 mV/s.

The cathodic wave observable below -0.2 V vs Ag/AgCl at pH 10 (Fig. S3d) can be partly attributed to the reduction of  $O_2$ , possibly present in limited amount in our  $N_2$  degassed cell.<sup>2-4</sup> The electrocatalytic effect of hydroquinone species on  $O_2$  reduction in alkaline solutions has already been reported.<sup>[4]</sup> Therefore the measurements performed at pH 10 might lead to an overestimation of the capacitance.

- 2. A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications, 2nd ed*, Wiley, 2000.
- 3. P. Kumar, Z. Yi, S. Zhang, A. Sekar, F. Soavi and F. Cicoira, Appl. Phys. Lett. 2015, 107, 053303.
- 4. A. Sarapuu, K. Vaik, D. J. Schiffrin and K. Tammeveski, J. Electroanal. Chem., 2003, 541, 23-29.



**Figure S4** Specific capacitance and specific capacity *vs.* scan rate extracted from the cyclic voltammograms shown in Fig. S3 for Mel/CP electrodes (33.8  $\mu$ g/cm<sup>2</sup> melanin loading) in (a) sodium sulfate pH 5.5, (b) phosphate buffer saline at pH 7.4 and (c) ammonia buffer at pH 10.



**Figure S5** Cycling stability of 33.8  $\mu$ g/cm<sup>2</sup> Mel/CP in NH<sub>4</sub>CH<sub>3</sub>COO<sub>(aq)</sub> pH 5.5 at 50 mV/s. (a) 1,000 voltammetric cycles and (b) cyclic voltammograms extracted from (a) every 100 cycles.

The cycling stability of Mel/CP (with 33.8  $\mu$ g/cm<sup>2</sup> loading) in NH<sub>4</sub>CH<sub>3</sub>COO<sub>(aq)</sub> at pH 5.5 was investigated. The values of the capacitance calculated for the 2<sup>nd</sup> cycle and 1,000<sup>th</sup> cycle are 1.98 mF/cm<sup>2</sup> (58.7 F/g) and 1.46 mF/cm<sup>2</sup> (43.3 F/g), i.e. a 26 % loss in the capacitance is observed over cycling.



**Figure S6** Trend of the capacitance density of the Mel/CP supercapacitor (67.5  $\mu$ g/cm<sup>2</sup> Mel/CP) at 2.5 mA/cm<sup>2</sup> (a) during 100,000 cycles (b) during the first 1000 cycles, (c) during the first 200 cycles. Cut off voltages: 0 V to 0.75 V.

The cycling stability of a supercapacitor using electrodes with 67.5  $\mu$ g/cm<sup>2</sup> loading was tested at 2.5 mA/cm<sup>2</sup>. A capacitance retention of 75% was observed during the first 1,000 cycles; afterwards, the capacitance did not dramatically change over the following 10<sup>5</sup> cycles. The results point to the need of a stable and efficient electrical contact between the melanin and the current collector. These results are partly attributable to an aging process in the melanin.<sup>5,6</sup>

5. A. Pezzella, A. Napolitano, M. d'Ischia, G. Prota, R. Seraglia and P. Traldi, *Rapid Commun. Mass Spectrom.*, 1997, 11, 368-372.
6. H. Okuda, K.Yoshino, K. Wakamatsu, S. Ito and T. Sota, *Pigment Cell Melanoma Res.*, 2014, 27 664-667.



**Figure S7** Overlay XPS spectra after charging and discharging steps carried out at the melanin-based positive electrode in micro-supercapacitor configuration, for C1s, O1s and N1s. For experimental details on sample preparation and charging and discharging steps please refer to Table S1 and Experimental section in the main text.



**Figure S8** XPS spectra of the melanin-based positive electrode in micro-supercapacitor configuration, for C1s, O1s, N1s and Au4f after the charging step. For experimental details on sample preparation and the charging step please refer to Table S1 and Experimental section in the main text. The assignment of the individual components used for peak fitting can be found in Table S1.



**Figure S9** XPS spectra of the melanin-based positive electrode in micro-supercapacitor configuration, for C1s, O1s, N1s and Au4f after the discharging step. For experimental details on sample preparation and the charging step please refer to Table S1 and Experimental section in the main text. The assignment of the individual components used for peak fitting can be found in Table S1.



**Figure S10** Cyclic voltammograms of melanin micro-supercapacitors (200  $\mu$ g/cm<sup>2</sup> melanin loading on each electrode) in NH<sub>4</sub>CH<sub>3</sub>COO<sub>(aq)</sub> at pH 5.5: (a) at relatively slow and (b) fast scan rates. (c) Specific capacitance and specific capacity vs. scan rate of CV taking into account the total melanin loading of the two electrodes (32  $\mu$ g).



**Figure S11** Electrochemical Impedance Spectroscopy (EIS) of melanin micro-supercapacitors: (a) Nyquist plots and (b) Bode plots in terms of capacitance normalized to the value obtained at 10 mHz  $(C/C_{10mHz})$  from EIS measurements in the frequency range 100 kHz -  $10^{-4}$  kHz with an AC amplitude of 10 mV, at open circuit potential. The loading at each electrode of area 0.08 cm<sup>2</sup> is ~200 µg/cm<sup>2</sup>. The supercapacitor ESR evaluated by the Z<sub>r</sub> intercept of the Nyquist plot at 100 kHz is 4.5  $\Omega$  cm<sup>2</sup>.



**Figure S12** (a) Capacitance of melanin micro-supercapacitors (200  $\mu$ g/cm<sup>2</sup> loading at each electrode, NH<sub>4</sub>CH<sub>3</sub>COO<sub>(aq)</sub> pH 5.5) from galvanostatic discharges at 0.625, 1.25, 6.25, 12.50 and 25 mA/cm<sup>2</sup>. Cut off voltages of 0 V to 0.75 V. (b) Ragone plot extracted from the galvanostatic discharge cycles at the above mentioned current densities taking into account that the total area of the two electrodes is 0.16 cm<sup>2</sup> and the corresponding total volume is about 2×10<sup>-4</sup> cm<sup>3</sup>.



**Figure S13** Trend of the capacitance density of the melanin micro-supercapacitors (200  $\mu$ g/cm<sup>2</sup> loading at each electrode, NH<sub>4</sub>CH<sub>3</sub>COO<sub>(aq)</sub> pH 5.5 electrolyte) during the first 20,000 galvanostatic charge–discharge cycles at 1.25 mA/cm<sup>2</sup>. Cut off voltages: 0 V to 0.75 V; area of each electrode: 0.08 cm<sup>2</sup>. We observed 61% retention in the capacitance from the 500<sup>th</sup> cycle to the 20,000<sup>th</sup> cycle.



**Figure S14** Cyclic voltammograms of flexible melanin micro-supercapacitors in  $NH_4CH_3COO_{(aq)}$  pH 5.5, at a scan rate of 50 mV/s, without bending (black curve) and with 50% bending (red curve). The voltammograms indicate that the micro-supercapacitor is significantly stable at least up to 50% bending (as defined in the figure caption of Scheme S2). See also supporting video file.



**Figure S15** Cyclic voltammograms of carbon Super C-65 and melanin/ Super C-65 (4/1 weight ratio) electrodes in  $NH_4CH_3COO_{(aq)}$  pH 5.5, at a scan rate of 50 mV/s. Pt foil and Ag/AgCl<sub>(aq)</sub> were used as counter and reference electrodes. The voltammograms show the higher capacitance of melanin/ Super C-65 compared to carbon Super C-65.

 Table S1 Electrode materials derived from natural sources for supercapacitors (please refer to references cited right below this Table).

Electrode material	Surface area (m <sup>2</sup> /g)	Highest Processing Temperature ('C)	Electrolyte	Electrode capacitance (F/g)	Stability (Capacitance retention over cycling)	Ref
PEDOT/Lignin	NA	RT	0.1 M HClO <sub>4</sub> / acetonitrile	170 (GCD) <sup>a</sup>	83% after 1000 cycles	7
Ppy/Lignin- sulfonate	NA	RT	0.1 HClO <sub>4</sub>	1000 (GCD)	NA	8
Ppy/Lignosulfo- nate, anthra- quinone sulfonate	NA	RT (electro- polymerization)	0.1 M HClO <sub>4</sub>	250-500 (GCD)	88-98% after 200 cycles	9
Carbon derived from cellulose, potato starch, eucalyptus wood saw starch	2100- 2900	Hydrothermal carbonization at 250-300 and activation 700- 800	1 M TEABF <sub>4</sub> in acetonitrile	236 (CV) <sup>b</sup>	NA	10
Lignin confined on reduced graphene oxide	NA	RT	0.1 M HClO <sub>4</sub>	432 (CV) 203 (GCD)	96% after 3000 cycles	11
Carbon-derived from cellulose	346	1000	5 M KCl	89 (CV) 107 (GCD)	90% after 2000 cycles	12
Porous carbon foams (from banana peel)	1650	1000	6 М КОН	206 (GCD)	98% after 1000 cycles	13
Biochar derived from corn cob (wrapped in a Au wire)	543.7	900	0.5M H <sub>2</sub> SO <sub>4</sub>	221 (GCD)	97% after 5000 cycles	14
CNTs/DNA hydrogel/ PANI	NA	RT	1M Na <sub>2</sub> SO <sub>4,</sub> 1M H <sub>2</sub> SO <sub>4</sub>	146° (CGD)	90% after 1000 cycles	15
Carbon derived from chicken feathers	1839	800	1M H <sub>2</sub> SO <sub>4</sub>	302 (GCD)	84% after 5000 cycles	16
Carbon derived from dead neem and Ashoka leaves	1230	1000	1 M H <sub>2</sub> SO <sub>4</sub>	400 (GCD)	NA	17
Carbon derived from chitosan	2200	800	0.5 M K <sub>2</sub> SO <sub>4</sub>	231 (GCD)	99% after 3000 cycles	18

Carbon derived from bacterial cellulose (BC)	491	900	BC-H <sub>3</sub> PO <sub>4</sub> , PVA- H <sub>3</sub> PO <sub>4</sub> gel	241 (GCD)	93% after 10000 cycles	19
Carbon from spruce and corn cob hydrolyzed, PTFE and acetylene black	2300	Hydrothermal carbonization at 250-300 activation at 700	0.5 M H <sub>2</sub> SO <sub>4</sub>	291 (CV)	NA	20
Carbon from sodium alginate, PVDF	273	600	1 M H <sub>2</sub> SO <sub>4</sub>	198 (CV)	85% after 10000 cycles	21
Carbon from Lessonia Nigrescens seaweed	800	600 -900	1 M H <sub>2</sub> SO <sub>4</sub>	264 (GCD)	capacitance loss 11% after 10000 cycles	22
Carbon from horseweed	1500	1050	6 М КОН	184 (GCD)	97.6 % after 1000 cycles	23
Carbon from gelatin	440	700	6 М КОН	220 (GCD)	NA	24
Carbon microtubes from willow catkins	1000	700	6 М КОН	306 (GCD)	NA	25
Carbon from rice husks	1886	850	3 M KCl	210 (GCD)	NA	26
Carbon from firewood	1100	900	0.5 M H <sub>2</sub> SO <sub>4</sub>	140 (CV)	NA	27
Carbon from pistachio shells	1100	780	0.5 M H <sub>2</sub> SO <sub>4</sub>	120 (CV)	NA	28
Carbon from firewood	1064	780	$0.5 \text{ M H}_2\text{SO}_4$	180 (CV)	NA	28
Carbon from banana fibers	1100	800	1 M Na <sub>2</sub> SO <sub>4</sub>	75 (GCD)	95% after 500 cycles	29
Carbon from waste coffee beans	1000	900	1 M H <sub>2</sub> SO <sub>4</sub>	368 (GCD)	95% after 10000 cycles	30
Carbon from sugar cane bagasse	1800	900	1 M H <sub>2</sub> SO <sub>4</sub>	300 (GCD)	77-83% after 5000 cycles	31
Carbon from cassava peel waste	1350	800	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	264 (GCD)	NA	32

Carbon from sunflower seed shell	2500	900	30 wt% KOH	311 (GCD)	NA	33
Carbon from argan seed shell	2100	800	0.5 M H <sub>2</sub> SO <sub>4</sub>	358 (CV)	NA	34
Carbon from sucrose	2340	1200	1 M H <sub>2</sub> SO <sub>4</sub>	280 (GCD)	100% after 10000 cycles	35
Melanin	NA	RT	7.5 M NH <sub>4</sub> CH <sub>3</sub> COO pH 5.5	167 (CV)	75% after 1000 cycles (GCD)	This study

<sup>a</sup> GCD, Galvanostatic charge discharge. <sup>b</sup> CV, Cyclic Voltammetry. The two acronyms indicate the techniques used to deduce the electrode capacitance. <sup>c</sup> The capacitance value is for the supercapacitor and not the electrode.

Table S1 includes a number of reports on supercapacitors making use of electrodes obtained from natural materials. It is clear from Table S1 that, quite often, the natural materials are pyrolyzed or are mixed to conducting polymers to obtain the "real" electrode material. The natural materials, the surface area of the electrode material (when available), the highest processing temperature, the electrolyte where the supercapacitor behavior was characterized and the value of the electrode capacitance (obtained by cyclic voltammetry, CV, or galvanostatic charge discharge, GCD) are reported.

Table S1 shows that natural materials have already been used for the fabrication of supercapacitor electrodes. *Nevertheless, unlike these natural materials, our melanin can be simply deposited by solution processing at room temperature and does not require any thermal treatment or further mixing.* Consequently, our melanin exhibits a great advantage over natural materials investigated to date. All in all, the biocompatibility and biodegradability featured by melanin, together with its easy availability, make it an extremely attractive material for environmentally and human friendly energy storage solutions. The main novelty of our work is the discovery of a new *natural* material for supercapacitor electrodes, besides well-established materials, such as activated carbons, carbon nanotubes, graphene, metal oxides and conducting polymers.

- 7. F. N. Ajjan, N. Casado, T. Rebis, A. Elfwing, N. Solin, D. Mecerreyes and O. Inganäs, J. Mater. Chem. A, 2016, 4, 1838–1847.
- 8. G. Milczarek and O. Inganas, *Science*, 2012, **335**, 1468-1471
- 9. D. H. Nagaraju, T. Rebis, R. Gabrielsson, A. Elfwing, G. Milczarek and O. Inganäs, *Adv. Energy Mater.*, 2014, **4**, 1300443(1-7).
- 10. L. Wei, M. Sevilla, A. B. Fuertes, R. Mokaya and G. Yushin, Adv. Energy Mater. 2011, 1, 356–361.
- 11. S-K. Kim, Y. K. Kim, H. Lee, S.B. Lee and H.S Park, ChemSusChem 2014, 7, 1094 1101.
- 12. L. Jiang, G.W. Nelson, S.O. Han, H. Kim, I.N. Sim and J.S. Foord, *Electrochim. Acta*, 2016, **192**, 251–258.

- 13. Y. Lva, L. Ga, M. Liu, W. Xiong, Z. Xu, D. Zhu and D.S. Wright, *J. Power Sources* 2012, **209**, 152–157.
- 14. M. Genovese, J. Jiang, K. Lian and N. Holm, J. Mater. Chem. A, 2015, 3, 2903–2913.
- 15. J. Hur, K. Im, S. W. Kim, U. J. Kim, J. Lee, S. Hwang, J. Song, S. Kim, S. Hwang and N. Park, *J. Mater. Chem. A*, 2013, **1**, 14460–14466.
- Q. Wang, Q. Cao, X. Wang, B. Jing, H. Kuang and L. Zhou, J. Power Sources, 2013, 225, 101-107.
- 17. M. Biswal, A. Banerjee, M. Deo and S. Ogale, Energy Environ. Sci., 2013, 6, 1249-1259.
- 18. L. Zhu, F. Shen, R. L. Smith, Jr. and X. Qi, *Energy Technol.* 2016, 4, 1 10.
- 19. X. Wang, D. Kong, Y. Zhang, B. Wang, X. Li, T. Qiu, Q. Song, J. Ning, Y. Song and L. Zhi, *Nanoscale*, 2016, **8**, 9146–9150.
- C. Falco, J. M. Sieben, N. Brun, M. Sevilla, T. Mauelen, E. Morallon, D.Cazorla-Amoros and M-M. Titirici, *ChemSusChem* 2013, 6, 374 – 382.
- 21. E. Raymundo-Piñero, F. Leroux and F. Béguin, Adv. Mater. 2006, 18, 1877-1882.
- 22. E. Raymundo-Piñero, M. Cadek and F. Béguin, Adv. Funct. Mater. 2009, 19, 1032-1039.
- 23. L. Yuan, C. Feng, C. Wang, Z. Fu, X. Yang and Y. Tang, J. Mater. Sci., 2016, 51, 3880-3887.
- 24. B. Xu, S. Hou, F. Zhang, G. Cao, M. Chu and Y. Yang, J. Electroanal. Chem. 2014, **712**, 146–150.
- 25. K. Wang, R. Yan, N. Zhao, X.Tian, X. Li, S. Lei, Y. Song, Q. Guo and L. Liu, *Mater. Lett*, 2016, **174**, 249–252.
- 26. Y. Guo, J. Qi, Y. Jiang, S. Yang, Z. Wang and H. Xu, Mater. Chem. Phys., 2003, 80, 704-709.
- 27. F. Wu, R. Tseng, C. Hu and C. Wang, J. Power Sources, 2004, 138, 351-359.
- 28. F. Wu, R. Tseng, C. Hu and C. Wang, J. Power Sources, 2005, 144, 302-309.
- 29. V. Subramanian, C. Luo, A. M. Stephan, K. S. Nahm, S. Thomas and B. Wei, J. Phys. Chem. C, 2007, 111, 7527-7531.
- 30. T. E. Rufford, D. Hulicova-Jurcakova, Z. Zhu and G. Q. Lu, Electrochem. Commun., 2008, 10, 1594-1597.
- T. E. Rufford, D. Hulicova-Jurcakova, K. Khosla, Z. Zhu and G. Q. Lu, J. Power Sources, 2010, 195, 912-918.
- 32. A. E. Ismanto, S. Wang, F. E. Soetaredjo and S. Ismadji, Bioresour. Technol., 2010, 101, 3534-3540.
- 33. X. Li, W. Xing, S. Zhuo, J. Zhou, F. Li, S. Qiao and G. Lu, Bioresour. Technol., 2011, 102, 1118-1123.
- 34. Elmouwahidi, Z. Zapata-Benabithe, F. Carrasco-Marin and C. Moreno-Castilla, Bioresour. Technol., 2012, 111, 185-190.
- 35. C. Wang, M. J. O. Connell, C. K. Chan, ACS Appl. Mater. Interfaces 2015, 7, 8952 8960.

			Atomic %				
		Identification	Charging		Discharging		
	BE (eV)		Total over 100%	Each element normalized to 100%	Total over 100%	Each element normalized to 100%	
Au(4f7/2)	84.1	Au <sup>0</sup>	0.2	100.0			
	84.2				0.2	100.0	
	284.6	C=C and C-C	34.4	54.8	42.2	66.5	
	285.4	C-N	6.0	9.6	4.5	7.1	
C(1s)	286.2	C-0	10.8	17.2	8.3	13.1	
	287.4	C=O	5.2	8.3	3.2	5.1	
	288.9	O-C=O	5.4	8.7	4.9	7.6	
	291.3	$\pi \rightarrow \pi^*$ of C=C	0.8	1.3	0.4	0.6	
N(1s)	399.5	Amine N-H	1.1	27.7	0.9	32.1	
	400.4	Aromatic C-N	2.1	54.8	1.6	53.6	
	402.0	C-N <sup>+</sup> and/or N <sup>+</sup>	0.7	17.5	0.4	14.4	
	531.7	C=O (aromatic)	10.6	32.0	8.5	25.4	
O(1s)	532.5	C-O (aliphatic), C=O (aliphatic), Si-O	16.4	49.3	19.3	57.7	
	533.5	O**-C=O (aliphatic and aromatic), C-O aromatic	6.2	18.7	5.6	16.9	

**Table S2** Identification of chemical bonding from high resolution XPS scans in melanin-based electrodes after charging and discharging steps, in micro-supercapacitor configuration.

\*\*indicates that the identification pertains to this atom

Samples were prepared by initially drop casting a mixture of conductive carbon Super C-65 with a melanin suspension in DMSO, with a weight ratio 1/4. The electrode area was 0.08 cm<sup>2</sup>. We prepared two types of samples, i.e. after charging and discharging steps carried out galvanostatically in the electrolyte  $NH_4CH_3COO_{(aq)}$  pH 5.5. To prepare the samples after charging, a micro-supercapacitor pre-oxidized by cyclic voltammetry was galvanostatically charged at 0.25 mA/cm<sup>2</sup> for 15 minutes. To prepare the samples after discharging, a micro-supercapacitor pre-oxidized by cyclic voltammetry was galvanostatically charged at 0.25 mA/cm<sup>2</sup> for 15 minutes, followed by galvanostatic discharge at -0.25 mA/cm<sup>2</sup> for 15 minutes. Samples were rinsed gently in water and placed under vacuum (at 30 mbar) for 1 hr prior to the XPS analysis.



Scheme S1 Micro-supercapacitor geometry.



Scheme S2 Micro-supercapacitor bending. The bending percentage is defined as  $[(L-L')/L] \times 100\%$ . L and L' are the initial length and the length under bending, respectively.