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# Light-enhanced Electrochemical Energy Storage of Synthetic Melanin on Conductive Glass Substrates

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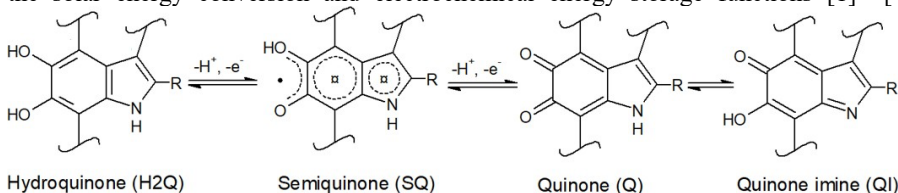
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## ABSTRACT

Eumelanin is a redox active, quinone-based biopigment, featuring a broad band absorption in the UV-Vis region. The combination of the redox and optical properties makes eumelanin an interesting candidate to explore light-assisted storage technologies. Electrodes of melanin on indium tin oxide (ITO) current collectors were investigated for their morphological and voltammetric characteristics in aqueous electrolytes. Under solar light, we observed that the capacity and the capacitance of the melanin electrodes significantly increase with respect to the dark conditions (by 63% and 73%, respectively).

## INTRODUCTION

In order to face possible energy shortages caused by the increasing world population, it is relevant to develop sustainable and efficient solar energy storage technologies, combining the solar energy conversion and electrochemical energy storage functions [1]– [4].



**Scheme 1.** Hydroquinone (H2Q), semiquinone (SQ) and quinone (Q) redox forms of the building blocks of eumelanin: 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA). R is -H in DHI whereas R is the -COOH group in DHICA. The quinone imine form (QI) is the tautomer of Q.

Nature is resourceful of environmentally benign and redox active materials, e.g. organic quinone-based species that can be assembled into energy storage devices [5]–[17]. Eumelanin is a quinone-based biopigment ubiquitous in flora and fauna. It has interesting

physicochemical features, such as UV-Vis absorption, photoconductivity, hydration-dependent electrical conductivity, metal binding affinity (chelation) [18]–[20]. In eumelanin, different redox states coexist in the two building blocks 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole carboxylic acid (DHICA) making up the biopigment (Scheme 1). Eumelanin-based electrodes have been employed in energy storage devices, such as supercapacitors and batteries. Photovoltaic cells including eumelanin have been reported in the literature [7], [21]–[24]. The broad band optical absorption of eumelanin can be explained by chemical disorder (co-existing chromophores) and geometric disorder models [25], [26].

In this work, we report on the capacity and capacitance of DHI-melanin and DHI/DHICA-melanin on ITO current collectors (indium tin oxide) in aqueous electrolytes, as enhanced by solar light illumination [27], [28]. Synthetic, chemically controlled melanins, noted as DHI-melanin and DHICA-melanin, were obtained from the polymerization of the building blocks DHI or DHICA, respectively. DHI/DHICA-melanin (weight/weight 7/3), polymerized from both building blocks, was used to model the behaviour of natural melanin [29]. The transparent ITO current collector permitted rear illumination, expected to lead to higher solar light absorption, in turn leading to faster and higher electrochemical response, under solar light illumination, with respect to carbon paper current collectors. Scanning Electron Microscopy (SEM) images shed light onto the morphology of the material. Cyclic voltammetry of eumelanin, under dark and light conditions, was used to gain insight on the improvement of capacity and capacitance.

## EXPERIMENT

Chemically controlled melanins, i.e. DHI-melanin and (7/3 weight/weight) DHI/DHICA melanin, were synthesized in situ on ITO surfaces by a solid-state polymerization method already reported in the literature [28]. 2 mg/mL solutions of DHI were prepared in ambient conditions and used as precursor. For DHI/DHICA-melanin, 10 mg of powder, including 7 mg of DHI monomer powder and 3 mg of DHICA monomer powder, were dissolved in 5 ml methanol, in ambient conditions, and the solution was used as precursor. Afterwards, the monomer solution (5  $\mu$ l) was drop cast 3 times, sequentially, on the ITO surface (geometric area 1.56 cm<sup>2</sup>). Between each drop casting step, the samples were exposed to NH<sub>3</sub> vapors from NH<sub>3(aq)</sub> (Sigma Aldrich, 28-30% w/v), a polymerization catalyst, for 1 hour. After the third drop cast step, samples were exposed to NH<sub>3</sub> vapors from NH<sub>3(aq)</sub> (Sigma Aldrich, 28-30% w/v) for more than 65 hours, to complete the polymerization reaction. The loading of eumelanin on ITO was ca 20  $\mu$ g cm<sup>-2</sup>. The morphology of the electrodes was examined by scanning electron microscopy (SEM, JEOL JSM7600F), with secondary electron mode, at an acceleration voltage of 5 kV. The morphology of the samples was examined by atomic force microscopy (AFM, D3100). 0.25 M buffer solutions of NaCH<sub>3</sub>COO, pH ca 5, were prepared from NaCH<sub>3</sub>COO (Sigma-Aldrich >99%) and CH<sub>3</sub>COOH (Sigma-Aldrich >99.7%), dissolved in DI water (18.2 M $\Omega$  cm). Electrochemical measurements were performed using a Biologic bipotentiostat (SP-300) in a three-electrode cell, with melanin loaded on ITO as the working electrode, a Pt mesh as the counter electrode and Ag/AgCl<sub>(aq)</sub> in 1 M KCl as the reference electrode. A solar simulator (SLB300A, Sciencetech) was used for electrochemical experiments under light conditions (1 sun, with air mass 1.5 G filter). The experimental configuration was realized by rear (back) illumination.

## RESULTS AND DISCUSSION

We used SEM to characterize the morphology of DHI-melanin and DHI/DHICA-melanin samples loaded on ITO. SEM images show dark and bright regions in both DHI-melanin and DHI/DHICA-melanin samples (Figure 1). DHI-melanin samples are quite homogeneous in terms of coverage (Figure 1a, c). DHI/DHICA-melanin samples are composed of continuous regions and nanosized flakes, probably due to the aggregation of DHICA or DHI-DHICA components (Figure 1b, d) [30].

We performed cyclic voltammetry experiments following the protocol: dark (8 cycles) → light (5 cycles) → dark (5 cycles) → light (5 cycles) in a suitable aqueous electrolyte (Figure 2). The choice of the slightly acidic electrolyte was determined by considering the favourable proton transport properties of eumelanin. [31] Broad redox features, slightly more pronounced under light irradiation, are observable at 0.05 V and -0.1 V vs Ag/AgCl. Apart from such broad features, the voltammograms are characterized by a *quasi* box-shape behaviour, attributable to the pseudocapacitive nature of eumelanin, featuring Faradaic processes [21], [32], [33]. Light enhances the current in the quasi *box*-shaped voltammograms of eumelanin on ITO, suggesting the presence of a photo-enhanced pseudocapacitive behaviour (Table 1). For DHI-melanin, from dark (8<sup>th</sup> cycle) to light (10<sup>th</sup> cycle), the capacity ( $\mu\text{C cm}^{-2}$ , the total electric charge accumulated by melanin per unit of surface) and capacitance ( $\mu\text{F cm}^{-2}$ , the capability of melanin to accumulate electric charge per volt) both increase by about 50%.

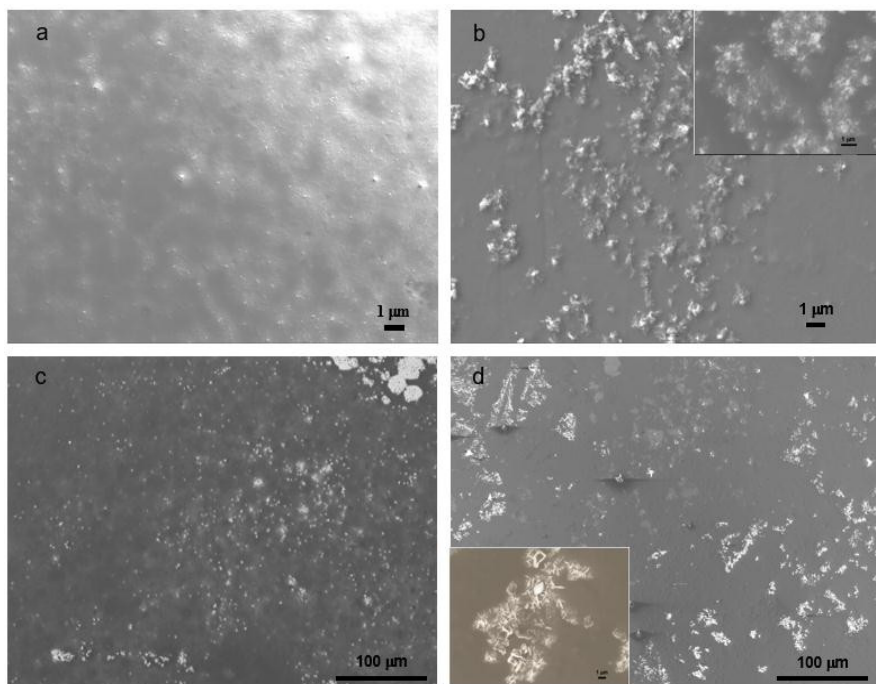


Figure 1. SEM images of (a, c) DHI-melanin and (b, d) DHI/DHICA-melanin on ITO (loading ca  $20 \mu\text{g cm}^{-2}$ ).

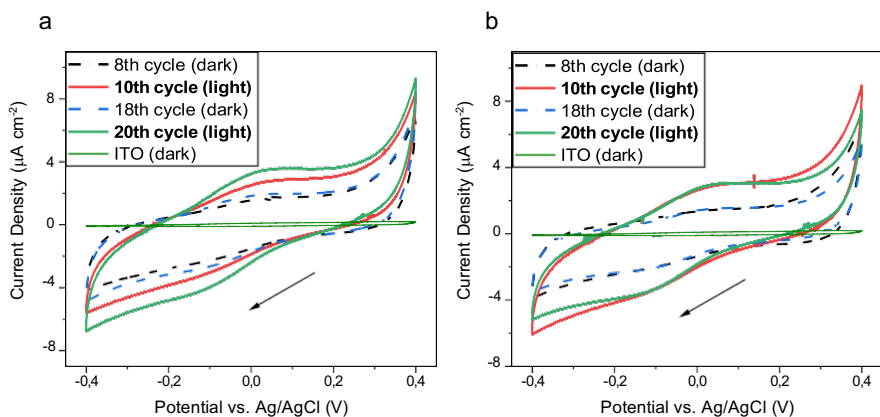


Figure 2. Cyclic voltammeteries of (a) DHI-melanin and (b) DHI/DHICA-melanin on ITO at 5 mV/s in NaCH<sub>3</sub>COO aqueous buffer solution at pH 5. Protocol: dark (8 cycles) → light (5 cycles) → dark (5 cycles) → light (5 cycles). Only the cycle indicated in the legend is shown.

Sample	Condition	Cycle number	Capacity (µC cm <sup>-2</sup> )	Capacitance (µF cm <sup>-2</sup> )
DHI-melanin	Dark	2	245	459
		4	216	409
		6	197	379
		8	188	361
	Light	10	252	495
		12	238	473
	Dark	14	235	432
		16	217	415
		18	211	409
	Light	20	312	617
22		310	619	
DHI/DHICA-melanin	Dark	2	419	554
		4	320	483
		6	215	359
		8	190	353
	Light	10	274	534
		12	267	532
	Dark	14	170	334
		16	156	308
		18	154	306
	Light	20	244	504
22		237	497	

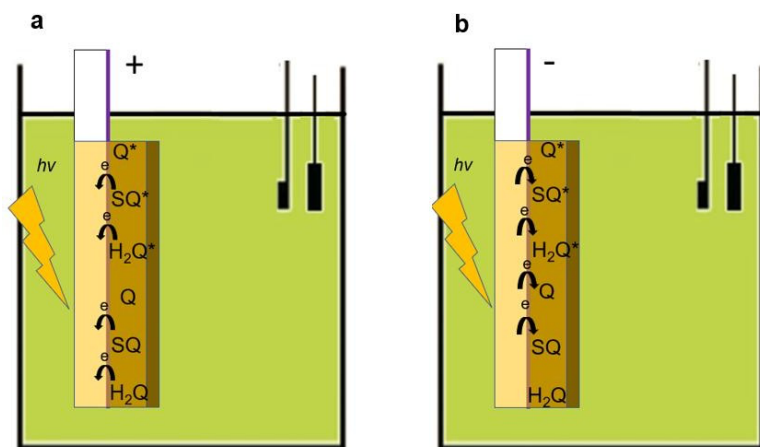
Table 1. Capacity (extracted from integration of current vs. time plots within the cathodic current range, not shown) and capacitance (extracted from linear regression of charge vs. potential plots within the cathodic current range, not shown) of DHI- and DHI/DHICA-melanin on ITO extracted from the cathodic current measured during cyclic voltammetry (Figure 2).

Importantly, the improvement of the storage properties observed under light irradiation persists in the dark (e.g. cycle 15 vs cycle 8: capacity increases by 25% and capacitance by 30%). The second series of experiments under light irradiation (from 19<sup>th</sup> to 24<sup>th</sup>) gives even more encouraging results: ca 50% increase of capacity and capacitance, from dark to light conditions (18<sup>th</sup> to 20<sup>th</sup> cycle). In the case of DHI/DHICA-melanin, from dark to light (8<sup>th</sup> to 10<sup>th</sup> cycle), the capacity increases by 63% whereas the capacitance increases by ca 73%. From the 18<sup>th</sup> cycle in the dark to the 20<sup>th</sup> under light irradiation, the capacity increases by 58% and the capacitance increases by 64%. Bare ITO does not contribute to the overall current (Figure 2).

Condition	Cycle	DHI-melanin		DHI/DHICA-melanin	
		Capacity loss	Capacitance loss	Capacity loss	Capacitance loss
Dark	2 to 5	25%	27%	13%	12%
	5 to 8	8%	3%	8%	7%
Light	10 to 13	6%	2%	4%	-
Dark	15 to 18	5%	-	4%	2%
Light	20 to 23	4%	3%	3%	-

Table 2. Capacity and capacitance losses during cycling for DHI- and DHI/DHICA-melanin on ITO (extracted from Table 1).

Interesting observations can be proposed with respect to the stability of the melanin samples on ITO. On the one hand, there are capacity and capacitance losses during cycling, possibly due to a limited compatibility of eumelanin on ITO surface (Table 2). From the 15<sup>th</sup> to the 18<sup>th</sup> cycle, for DHI-melanin, the capacity decreases by 5%, whereas the capacitance is maintained. For DHI/DHICA-melanin, the capacity decreases only by ca 4%, whereas the capacitance decreases only by 2%. On the other hand, our experiments suggest that the cycling stability of both melanins is acceptable after exposure to solar light. Surprisingly, the capacitance of DHI/DHICA-melanin is maintained during light irradiation.



Scheme 2. Melanin photo-electrodes (a) positively biased and (b) negatively biased investigated in this work.

We explain the increased response of DHI- and DHI/DHICA-melanin under irradiation conditions by the action of the light that increases the number of charge carriers stored in the melanin (Scheme 2). In the dark, the positively biased melanin electrodes (with redox species largely present in the SQ and Q redox forms) experience electron transfers from SQ to ITO to produce Q. When the light is absorbed by the melanin, it excites electrons from the ground electronic state to the excited state, from where electrons are, in principle, easily transferred to ITO. Therefore, the total capacity of the melanin is enhanced under irradiation by the higher number of electron transfer events, due to photoinduced transfers from the excited states taking place in parallel to the transfers due to the applied electrochemical potential. On the other hand, the negatively biased melanin electrode (with redox species largely present in the H<sub>2</sub>Q and SQ redox forms) in the dark, experiences electron transfers from ITO to SQ to produce H<sub>2</sub>Q. When the light is absorbed by the melanin, the electrons are promoted to excited state and easily transferred from ITO, e.g., to SQ to produce H<sub>2</sub>Q [34].

## CONCLUSION

In conclusion, we reported on the use of chemically controlled melanins (DHI- and DHI/DHICA-melanins) deposited on transparent Indium Tin Oxide (ITO) electrode current collectors as sustainable organic redox materials where the electrode capacity and capacitance are improved under solar light. The broad band absorption and the redox properties offer the possibility to enhance the storage properties of melanin electrodes under solar light. We observed that the solar light improves the capacitance, capacity (by 63% and 73%, respectively, with DHI/DHICA-melanin) and stability of the melanin electrodes. Work is in progress to understand if there is an effect of the solar light on the structure of eumelanin on ITO to better explain the beneficial effects of the solar illumination on the storage performance and the good eumelanin stability on ITO.



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## REFERENCES

- [1] International Energy Agency, "World Energy Outlook 2017," 2017.
- [2] N. Armaroli and V. Balzani, *Powering planet Earth: energy solutions for the future*. John Wiley and Sons: New York City, USA, 2012.
- [3] A. S. Arico, P. Bruce, B. Scrosati, J.-M. Tarascon, and W. Van Schalkwijk, "Nanostructured materials for advanced energy conversion and storage devices," in *Materials For Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group*; World Scientific: Singapore, Singapore, 2011, pp. 148–159.
- [4] N. Vlachopoulos and A. Hagfeldt, "Photobatteries and Photocapacitors," in *Molecular Devices for Solar Energy Conversion and Storage*, Springer: New York City, USA, 2018, pp. 281–325.
- [5] Y. Zhou *et al.*, "Polyanthraquinone-based nanostructured electrode material capable of high-performance pseudocapacitive energy storage in aprotic electrolyte," *Nano Energy*, vol. 15, pp. 654–661, 2015.
- [6] Z. Song *et al.*, "A quinone-based oligomeric lithium salt for superior Li-organic batteries," *Energy Environ. Sci.*, vol. 7, no. 12, pp. 4077–4086, 2014.
- [7] Y. J. Kim, W. Wu, S.-E. Chun, J. F. Whitacre, and C. J. Bettinger, "Biologically derived melanin electrodes in aqueous sodium-ion energy storage devices.," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 110, no. 52, pp. 20912–7, 2013.
- [8] Y. Liang, Z. Tao, and J. Chen, "Organic electrode materials for rechargeable lithium batteries," *Adv. Energy Mater.*, vol. 2, no. 7, pp. 742–769, 2012.
- [9] D. Vonlanthen, P. Lazarev, K. A. See, F. Wudl, and A. J. Heeger, "A Stable Polyaniline-Benzoquinone-Hydroquinone Supercapacitor," *Adv. Mater.*, vol. 26, no. 30, pp. 5095–5100, 2014.
- [10] C.-Y. Gao, L. Zhao, and M.-X. Wang, "Stabilization of a reactive polynuclear silver carbide cluster through the encapsulation within a supramolecular cage.," *J. Am. Chem. Soc.*, vol. 134, no. 2, pp. 824–7, Jan. 2012.
- [11] Y. Liang *et al.*, "Universal quinone electrodes for long cycle life aqueous rechargeable batteries," *Nat. Mater.*, vol. 16, pp. 841–850, 2017.
- [12] T. Janoschka *et al.*, "An aqueous, polymer-based redox-flow battery using non-corrosive, safe, and low-cost materials," *Nature*, vol. 527, no. 7576, pp. 78–81, 2015.
- [13] M. R. Gerhardt, C. J. Galvin, B. Huskinson, M. P. Marshak, C. Suh, and X. Chen, "A metal-free organic-inorganic aqueous flow battery," *Nature*, vol. 505, pp. 195–198, 2014.
- [14] K. Naoi, S. Suematsu, M. Hanada, and H. Takenouchi, "Enhanced cyclability of  $\pi$ - $\pi$  stacked supramolecular (1, 5-diaminoanthraquinone) oligomer as an electrochemical capacitor material," *J. Electrochem. Soc.*, vol. 149, no. 4, pp. 472–477, 2002.
- [15] T. Sun, Z. Li, H. Wang, D. Bao, F. Meng, and X. Zhang, "A Biodegradable Polydopamine-Derived Electrode Material for High-Capacity and Long-Life Lithium-Ion and Sodium-Ion Batteries," *Angew. Chemie*, vol. 128, no. 36, pp. 10820–10824, 2016.
- [16] Z. Song and H. Zhou, "Towards sustainable and versatile energy storage devices: An overview of organic electrode materials," *Energy Environ. Sci.*, vol. 6, no. 8, pp. 2280–2301, 2013.

- [17] A. Mukhopadhyay, Y. Jiao, R. Katahira, P. N. Ciesielski, M. Himmel, and H. Zhu, "Heavy Metal-Free Tannin from Bark for Sustainable Energy Storage," *Nano Lett.*, vol. 17, no. 12, pp. 7897–7907, 2017.
- [18] E. Di Mauro, R. Xu, G. Soliveri, and C. Santato, "Natural melanin pigments and their interfaces with metal ions and oxides : emerging concepts and technologies," *MRS Commun.*, vol. 7, no. 2, pp. 141–151, 2017.
- [19] M. Jastrzebska, A. Kocot, and L. Tajber, "Photoconductivity of synthetic dopa-melanin polymer," *J. Photochem. Photobiol. B Biol.*, vol. 66, no. 3, pp. 201–206, 2002.
- [20] P. Meredith, C. J. Bettinger, M. Irimia-Vladu, A. B. Mostert, and P. E. Schwenn, "Electronic and optoelectronic materials and devices inspired by nature," *Rep. Prog. Phys.*, vol. 76, no. 3, p. 034501, 2013.
- [21] P. Kumar *et al.*, "Melanin-based flexible supercapacitors," *J. Mater. Chem. C*, vol. 4, no. 40, pp. 9516–9525, 2016.
- [22] Y. J. Kim, W. Wu, S. E. Chun, J. F. Whitacre, and C. J. Bettinger, "Catechol-mediated reversible binding of multivalent cations in eumelanin half-cells," *Adv. Mater.*, vol. 26, no. 38, pp. 6572–6579, 2014.
- [23] G. Mula, L. Manca, S. Setzu, and A. Pezzella, "Photovoltaic properties of PSi impregnated with eumelanin," *Nanoscale Res. Lett.*, vol. 7, pp. 1–21, 2012.
- [24] A. Antidormi, C. Melis, E. Canadell, and L. Colombo, "Assessing the Performance of Eumelanin/Si Interface for Photovoltaic Applications," *J. Phys. Chem. C*, vol. 121, no. 21, pp. 11576–11584, 2017.
- [25] M. L. Tran, B. J. Powell, and P. Meredith, "Chemical and Structural Disorder in Eumelanins - A Possible Explanation for Broad Band Absorbance," *Biophys. J.*, vol. 90, no. 3, p. 28, 2005.
- [26] C. Chen, C. Chuang, J. Cao, V. Ball, D. Ruch, and M. J. Buehler, "Excitonic effects from geometric order and disorder explain broadband optical absorption in eumelanin.," *Nat. Commun.*, vol. 5, p. 3859, 2014.
- [27] L. K. Povlich, J. Le, J. Kim, and D. C. Martin, "Poly(5,6-dimethoxyindole-2-carboxylic acid) (PDMICA): A Melanin-Like Polymer with Unique Electrochromic and Structural Properties," *Macromolecules*, vol. 43, pp. 3770–3774, 2010.
- [28] A. Pezzella *et al.*, "Stem cell-compatible eumelanin biointerface fabricated by chemically controlled solid state polymerization," *Mater. Horiz.*, vol. 2, no. 2, pp. 212–220, 2015.
- [29] A. Pezzella, M. D'Ischia, A. Napolitano, A. Palumbo, and G. Prota, "An Integrated Approach to the Structure of Sepia Melanin . Evidence for a High Proportion of Degraded 5 , 6-Dihydroxyindole-2- carboxylic Acid Units in the Pigment Backbone," *Tetrahedron*, vol. 53, no. 24, pp. 8281–8286, 1997.
- [30] L. Panzella *et al.*, "Atypical structural and  $\pi$ -electron features of a melanin polymer that lead to superior free-radical-scavenging properties," *Angew. Chemie - Int. Ed.*, vol. 52, no. 48, pp. 12684–12687, 2013.
- [31] J. Wünsche *et al.*, "Protonic and electronic transport in hydrated thin films of the pigment eumelanin," *Chem. Mater.*, vol. 27, no. 2, pp. 436–442, 2015.
- [32] R. Xu, A. Gouda, M. F. Caso, F. Soavi, and C. Santato, "Melanin: A Greener Route To Enhance Energy Storage under Solar Light," *ACS Omega*, vol. 4, no. 7, pp. 12244–12251, 2019.
- [33] T. Brousse, D. Bélanger, and J. W. Long, "To Be or Not To Be Pseudocapacitive?," *J. Electrochem. Soc.*, vol. 162, no. 5, pp. A5185–A5189, 2015.
- [34] A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications, 2nd edition*. John Wiley and Sons: New York City, USA, 2000.