Electrochemical Studies on the Biopigment Eumelanin

Soutenance de Thèse de Doctorat

Presented by
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Polytechnique Montréal, 27/8/2020

- Introduction
- Research Issues and Objectives
- Impact
- Results and Discussion
- Conclusions and Perspectives

Introduction

Energy issues

Energy issues and sustainable energy storage devices

Energy issues

Growing world population
(8.5 billion by 2030)

Sustainability goal

"The ability to meet our needs without compromising the ability of our future generations".

Sustainable electrochemical energy storage devices

- Materials synthesized through "green" chemistry or bio-sourced
- Aqueous solutions
- Abundant and low-cost elements
- Low embedded energy (the energy used to manufacture a material or product)

Irimia-Vladu, *Chem. Soc. Rev.*, 2014.

Tong, et al. *ACS Appl. Energy Mater.*, 2019.

International Energy Agency, 2019.

Why eumelanin is a candidate for electrode material of sustainable electrochemical energy storage?

Why redox properties (electrochemical properties) of eumelanin?

- Ubiquitous in nature (bio-sourced, abundant)
- Quinone-based redox activity gives energy storage properties.
- Biological significance: understanding how eumelanin functions *in vivo*.

Basic elements for this presentation

- Basic knowledge of eumelanin
- The technique cyclic voltammetry
- Comparison of quinone-based energy storage materials (the best achieved so far)

Di Mauro, Eduardo, et al. *MRS Commun.,* 2017.

Basic knowledge of eumelanin

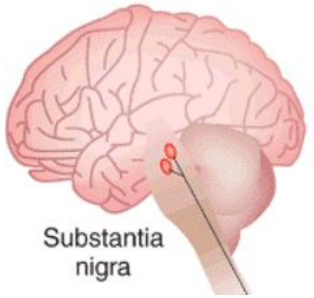
- What is eumelanin
- Polymerization sites
- Supramolecular structures
- Hydration dependence vs. redox activities
- Optical absorption
- Metal chelation

What is eumelanin?

Melanin

- Biopigment that can be found in human body, mammals, plants, fungi.
- Subcategories: eumelanin (brown-black), pheomelanin (yellow-red), neuromelanin

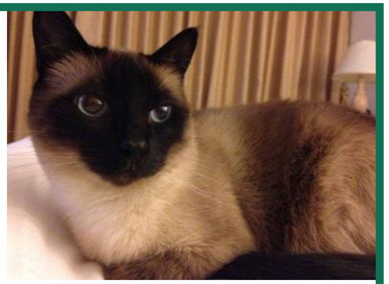
Neuromelanin



Mainly present in *Substantia nigra* in human brain

Eumelanin

- The most common form of melanin in human body and other mammals
- Functions: broadband optical absorption, antioxidant behavior, metal chelation, redox activity, etc.
- Types of eumelanin: Sepia melanin, DOPA(dihydroxyphenylalanine)-melanin, polydopamine, chemically controlled eumelanins (synthetic DHI- and DHICA-melanin, etc.)



Sepia melanin extracted from cuttlefish

Bush *et al.*, *Proc Natl Acad Sci*, 2006.

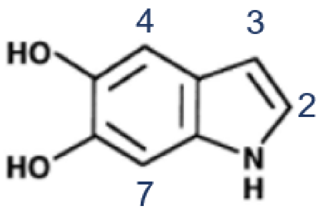
Schroeder, et al., *J. Chem. Neuroanat.*, 2015.

Rahal *et al.*, *Biomed Res. Int.*, 2014.

Di Mauro, et al., *MRS Commun.*, 2017.

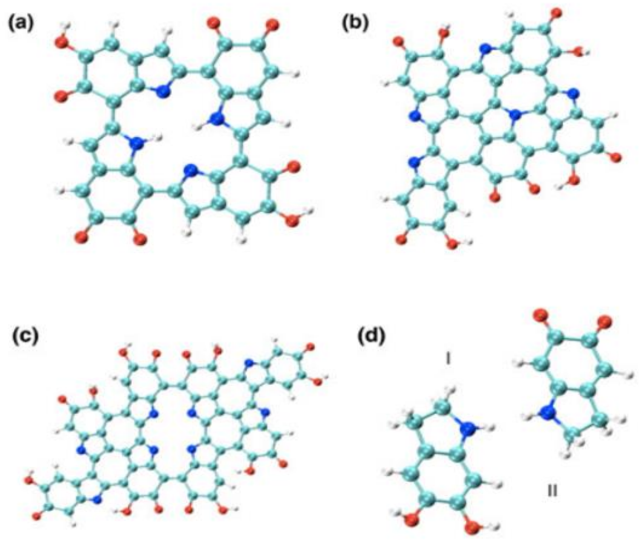
Polymerization sites

DHI (5,6-dihydroxyindole)



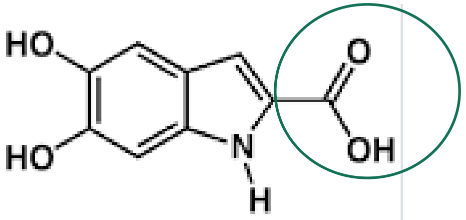
DHI: Multiple polymerization sites.

DHI-melanin: Disordered chemical structure



Dark Blue: nitrogen
Red: oxygen

DHICA (5,6-dihydroxyindole-2-carboxylic acid)

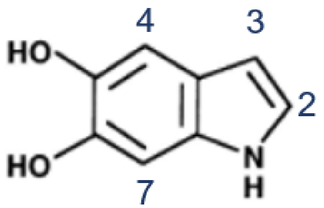


DHICA: Limited number of polymerization sites (Steric hindrance by $-COO^{-}$).
DHICA-melanin: Relatively ordered chemical structure

Panzella et al. *Angew. Chem.*, 2013.

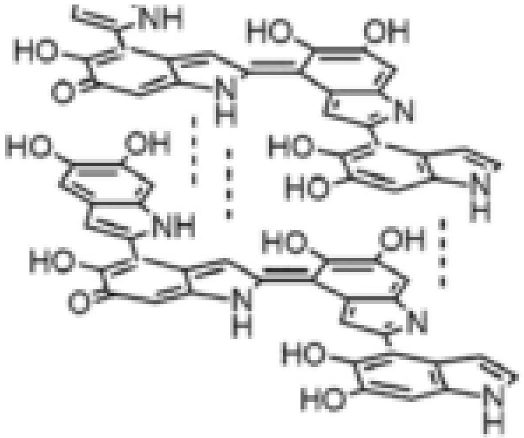
Supramolecular structures

DHI (5,6-dihydroxyindole)



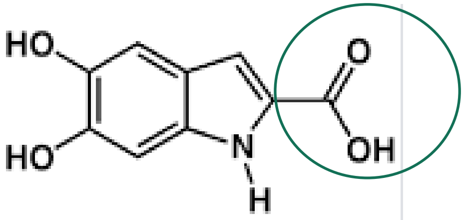
DHI: Multiple polymerization sites.

DHI-melanin: Disordered chemical structure



Layer-by-layer π-π stacking for better electron transport

DHICA (5,6-dihydroxyindole-2-carboxylic acid)



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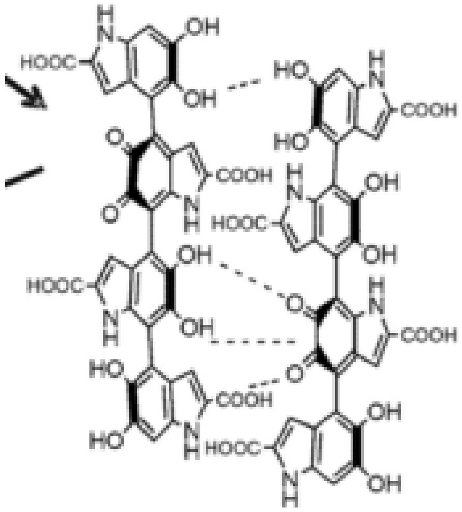

Rod-shaped aggregation to trap radicals

Panzella et al. *Angew. Chem.*, 2013.

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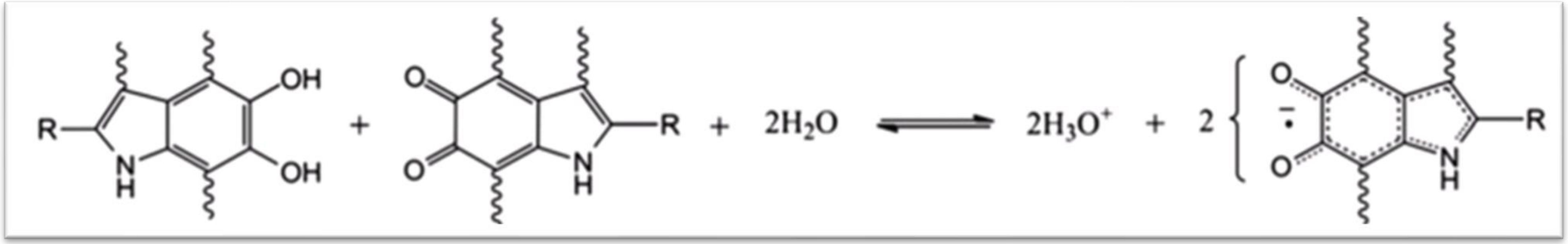
Hydration dependence vs. redox activities

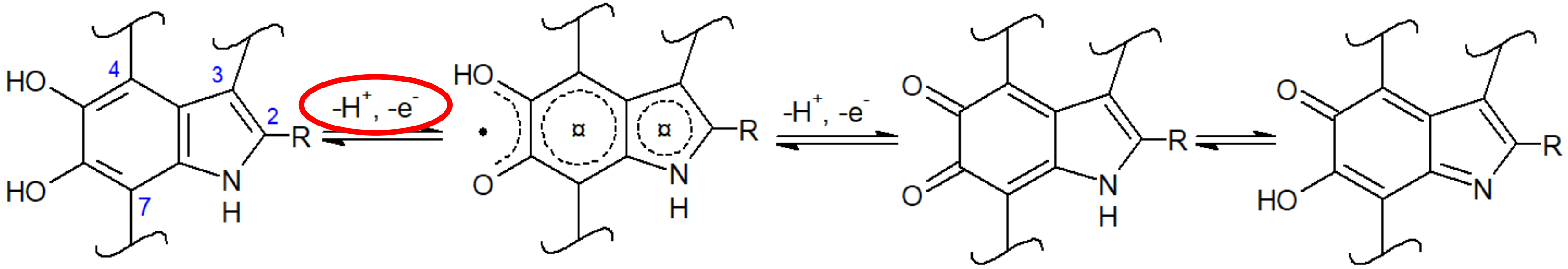
Eumelanin absorbs water



-R is -H
or
-COOH

Hydroquinone (H2Q) Quinone (Q) Semiquinone (SQ)

Redox properties (electron transfer properties)



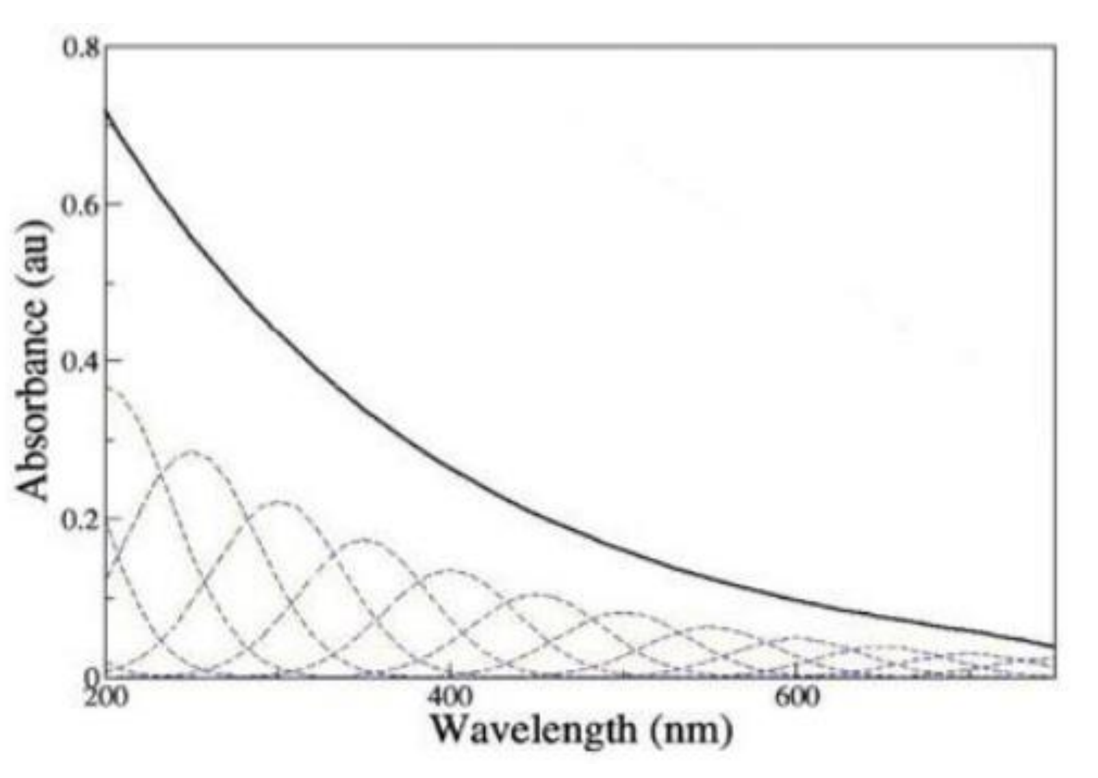
Hydroquinone (H2Q) Semiquinone (SQ) Quinone (Q) Quinone imine (QI)

Reduced form

Oxidized form

Mostert *et al.*, *Proc. Natl. Acad. Sci.*, 2012.
Takeo et al. *J. Phys. Condens. Matter*, 2015.
Wünsche *et al.*, *Chem. Mater.*, 2015.

Broadband optical absorption



Disorder models

- Chemical disorder model: Chemically distinct species (redox forms, number of building blocks in an oligomer, polymerization sites). The absorption spectrum is a convolution of absorption peaks at different wavelengths.

- Geometric disorder model: excitonic coupling of differently packed oligomers.

Meredith, Paul, et al. *Soft Matter.,* 2006.

Tran, et al, *Biophys. J.*, 2005.

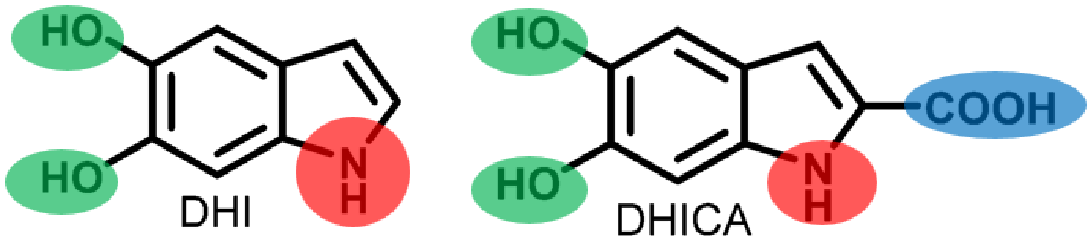
Kaxiras, et al., *Phys. Rev. Lett.*, 2006.

Antidormi, et al. *J. Phys. Chem. C*, 2018.

Chen, et al., *Nat. Commun.*, 2014.

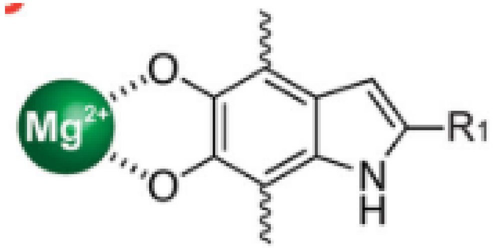
Chelation of multivalent metal ions

Metal cation	Chelation sites		
	Quinone	**-NH- Amine**	**-COOH (DHICA)**
Mg^{2+}	✓	-	✓
Cu^{2+}	✓	✓	✓
Fe^{3+}	✓	✓	✓



Di Mauro et al., *MRS Commun.*, 2017.

Preferential chelation sites



- Multivalent metal ions have preferential chelation sites.
- However, they may be chelated by all the functional groups in certain conditions.

Liu et al., *Pigment Cell Res.*, 2005.

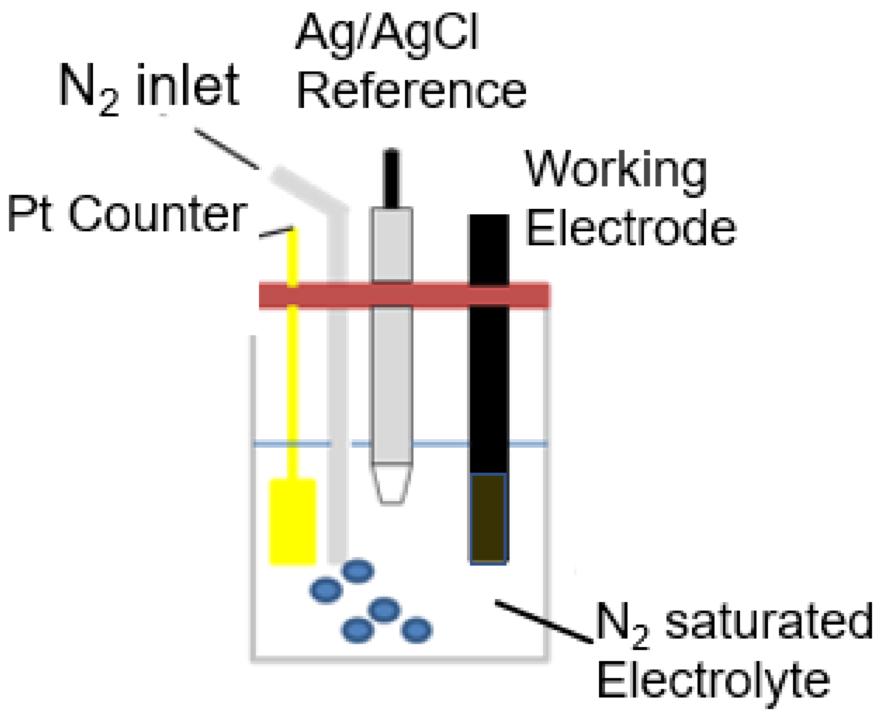
Kim, et al. *Adv. Mater.*, 2014.

The technique
cyclic voltammetry

Potential sweeps in cyclic voltammetry

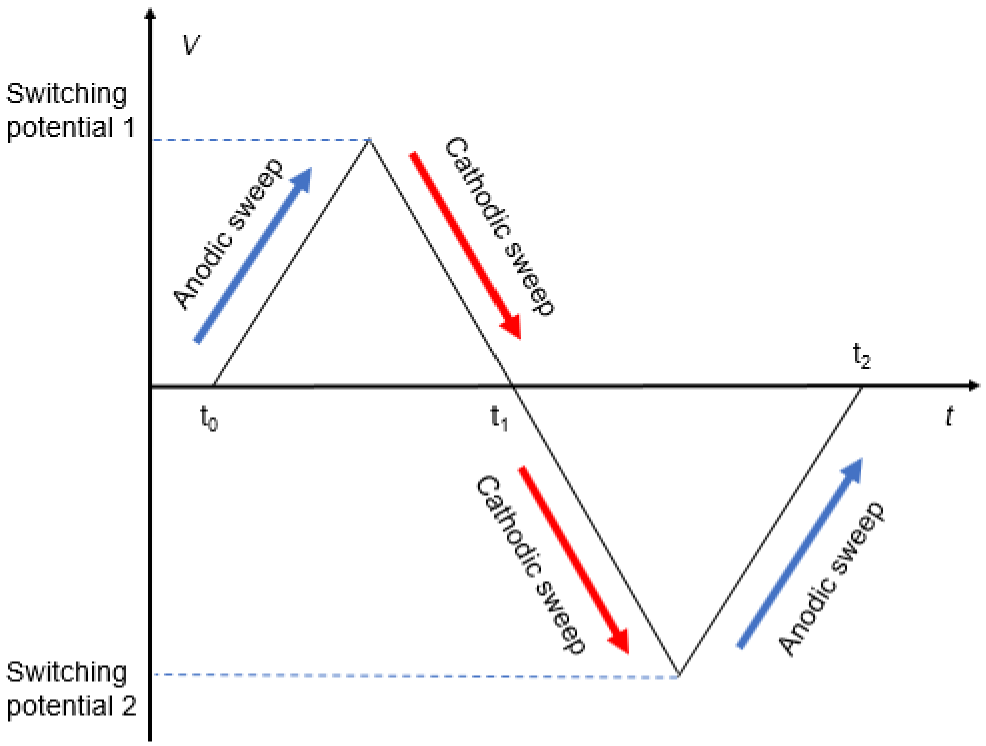
Electrochemical cell

Potential: working vs. reference electrode.
Current: working and counter electrode.



Cyclic voltammetry

Potential is swept linearly vs. time to complete a cycle.

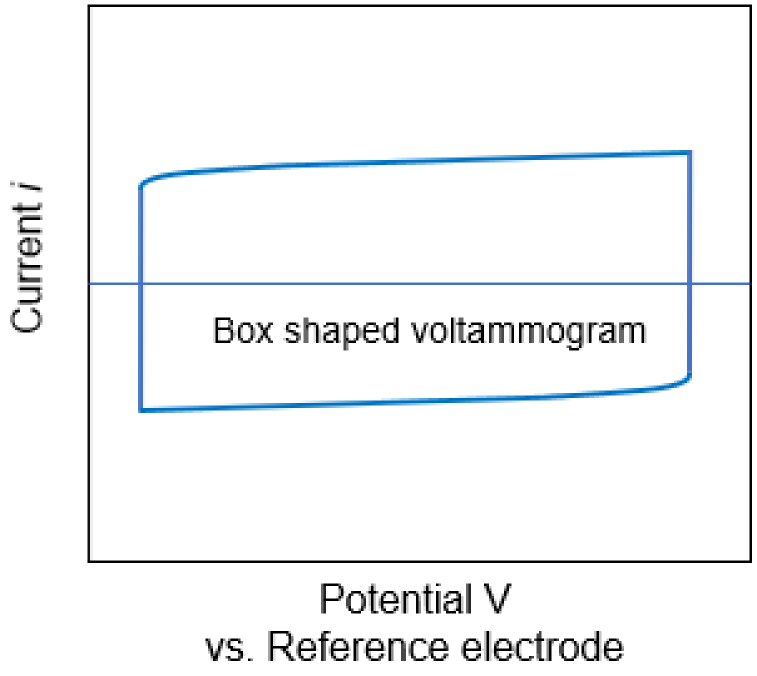


Bard, et al., *Electrochemical Methods: Fundamentals and Applications*, 2001.

Electron transfer generates Faradaic current

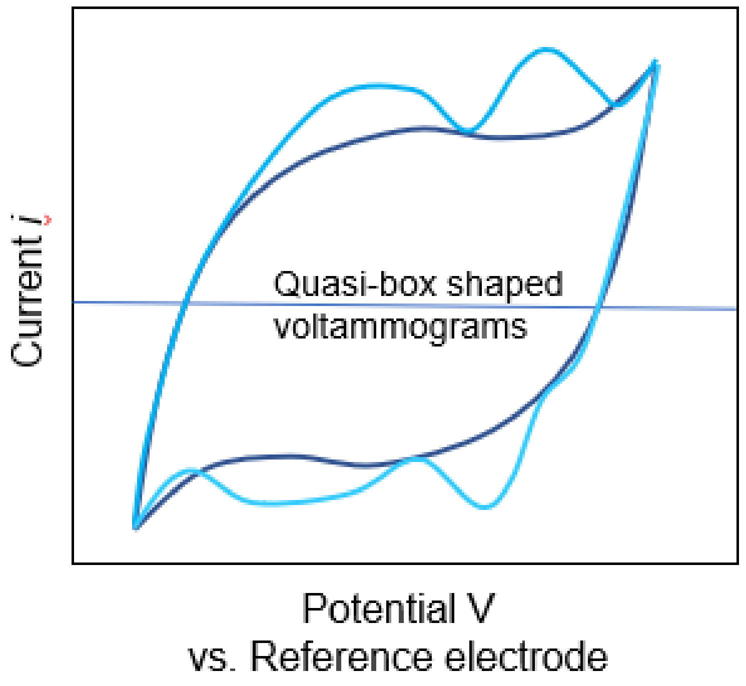
Cyclic voltammograms: *i*-*V* plots.

Double-layer materials



Redox-active materials

Oxidation (peak) currents at oxidation potentials



Pseudocapacitive material

Reduction (peak) currents at reduction potentials

Brousse, et al., *J. Electrochem. Soc.*, 2015.

Energy storage properties

- Energy storage means **charge carrier storage** of the electrochemical system.
- **Capacity** (C): the maximum ability of a material to store charge carriers.
- **Capacitance** (F=C/V): how much charge can be stored for every external voltage exerted on the material.
- **Cycling stability**: how much capacity/capacitance% is left after a number of cycles (usually 50 to 100,000).

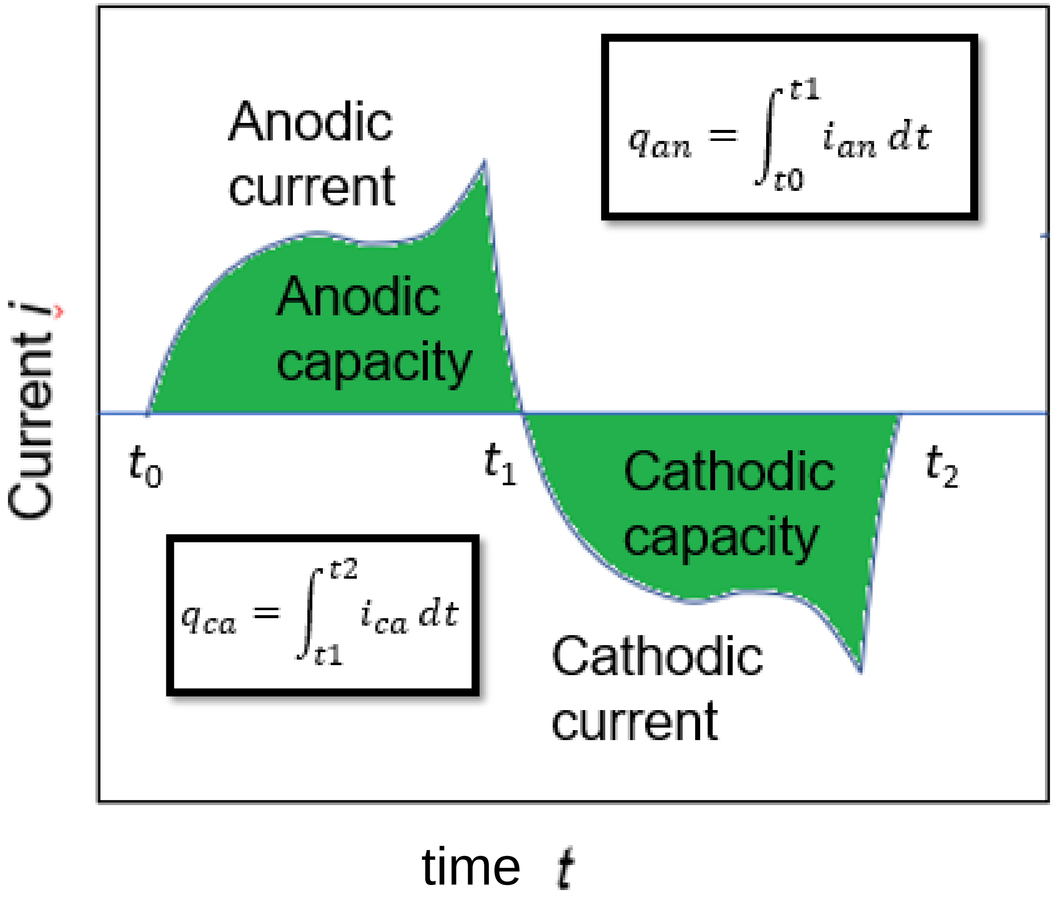
Parameters affecting comparisons among different materials

- Potential range
- Sweeping rate
- Loading of the electrode material
- Metal ions in the electrolyte or present in the materials
- Polymerization states of some materials (specific to this work)

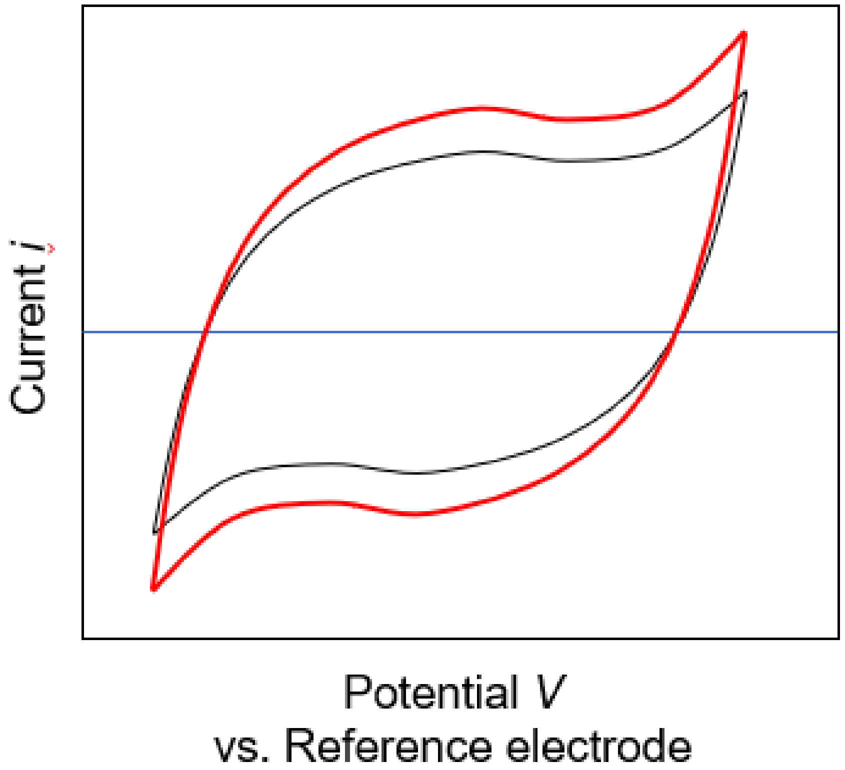
Bard, et al., *Electrochemical Methods: Fundamentals and Applications*, 2001.

Extraction and comparison of capacity from *i-t* plots

Extraction of capacity



Comparison of capacity



At the same condition (sweeping rate and potential range), higher current → higher capacity

Brousse, et al., *J. Electrochem. Soc.*, 2015.

Comparison of energy storage properties

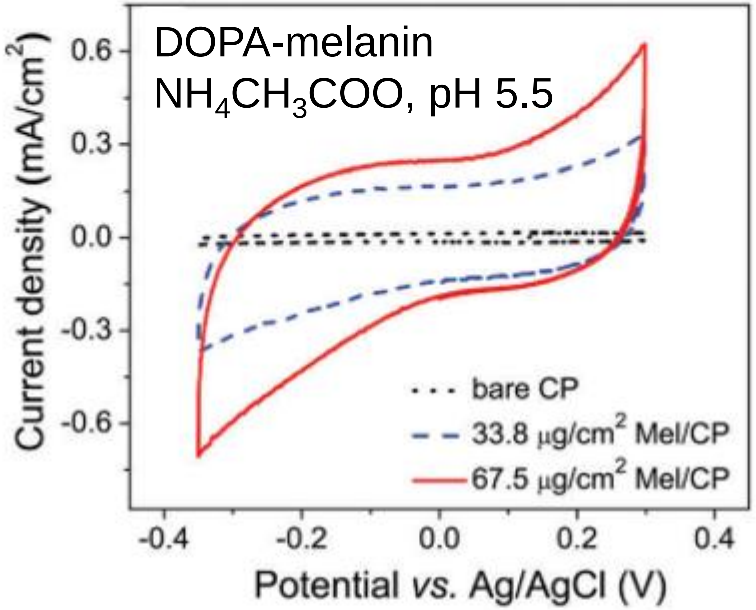
The best energy storage performance of quinone-based material so far?

Capacity (mA h g^{-1}) (battery)	Capacitance (F g^{-1}) (super-capacitor)	Potential range (V vs. Ag/AgCl)	Cycling stability (%) (cycles)	Material	Cation	Ref.
61	-	-0.75 V/0.85 V	100% (50th to 500th)	Sepia melanin	Mg^{2+}	Kim, et al. *Adv. Mater.*, 2014.
-	43	-0.35 V/0.3 V	74% (2nd to 1000th)	DOPA-melanin	NH_4^+	Kumar, et al. *J. Mater. Chem. C*, 2016.
-	1500	0 V/0.65 V	99.5% (13,000 cycles)	Polyaniline−benzoquinone−hydroquinone	H^+	Vonlanthen, et al., *Adv. Mater.*, 2014.

- A quinone-based supercapacitor shows very good cycling stability and capacitance (Vonlanthen’s).
- Eumelanin (in Kim’s work) is reported with very good stability and high potential range for battery.

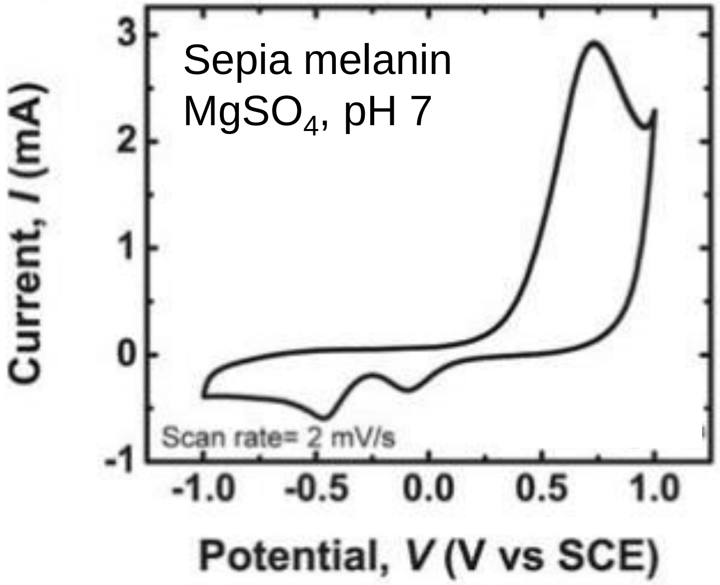
Research Issues and Objectives

Voltammetric potentials of eumelanin are not well-established

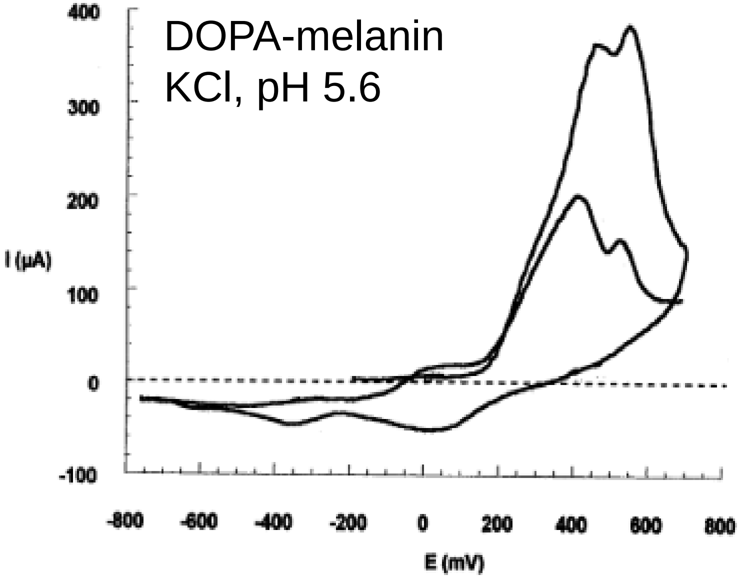


Chemical Heterogeneity

Carbon paper (CP)



Multivalent metal ions



Kumar, et al. *J. Mater. Chem. C,* 2016

Kim, et al. *Adv. Mater.,* 2014.

Serpentini, et al. *Electrochim. Acta,* 2000.

Research Issues

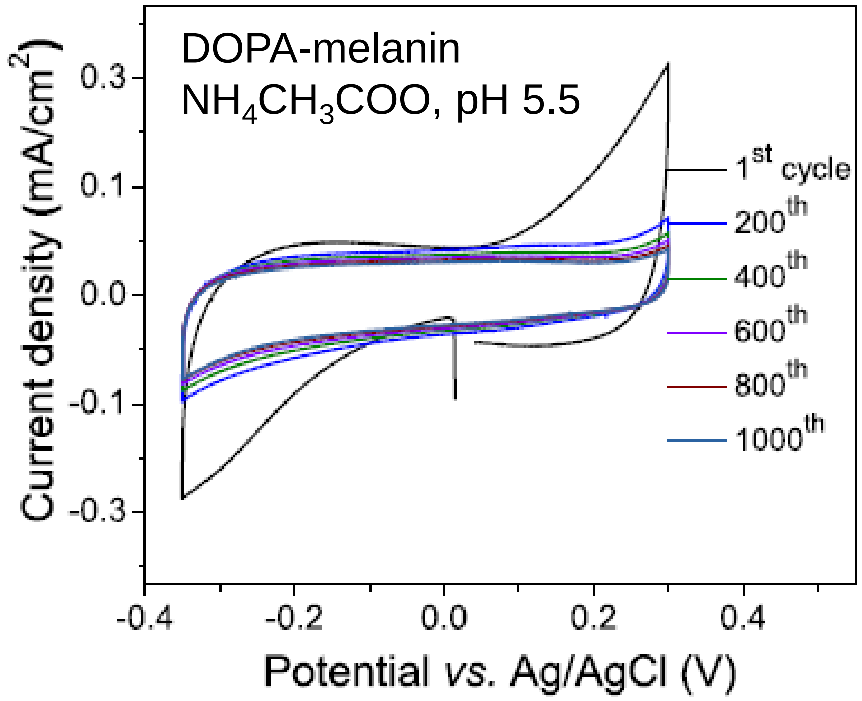
How to gain insight on the electrochemical properties of eumelanin?

Objectives

To explore the electrochemical properties of DHI- and DHICA-melanin and effect of metal ions (Na^+, K^+, Cu^{2+}, Mg^{2+}, Fe^3+, etc.)

Energy storage properties to be improved

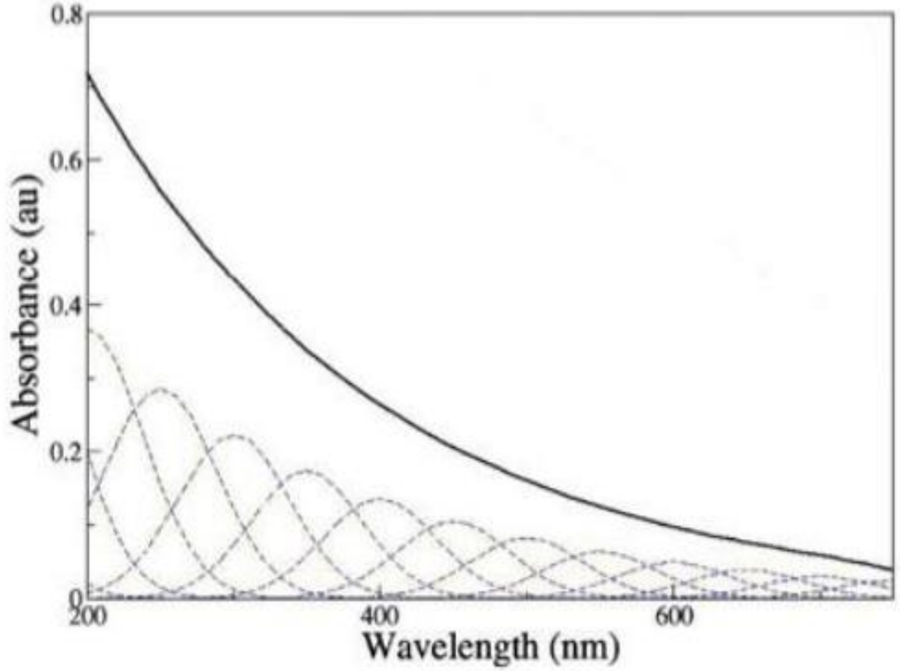
Trade-off (cycling stability vs. capacitance)



- Capacitance: 59 F/g (1st cycle) vs. 43 F/g (1000th cycle)
- Cycling stability: 26% capacitance loss after 1000 cycles.

Kumar, et al. *J. Mater. Chem. C,* 2016

Broadband optical absorption



Such a wide absorption range implies that eumelanin may be able to convert solar light energy into stored energy (larger number of electron transfer events).

Meredith, Paul, et al. *Soft Matter.,* 2006.

Research Issues

How to establish the electrochemical properties of eumelanin?

Based on the optical absorption of eumelanin, can we use solar light to enhance the energy storage properties of eumelanin?

Objectives

To explore the electrochemical properties of DHI- and DHICA-melanin and effect of metal ions (Na^{+}, K^{+}, Cu^{2+}, Mg^{2+}, Fe^{3}+, etc.)

To explore the effect of light on energy storage properties of eumelanin.

Antioxidant/prooxidant properties vs. reductive/oxidative properties of neuromelanin

Oxidative stress

The imbalance between oxidants and antioxidants in favor of the oxidants produced at an elevated rate, potentially leading to damage.

Antioxidant behavior

To delay/prevent the oxidative stress

→ An antioxidant compound can be reductive or by other mechanisms.

Prooxidant behavior

To induce the oxidative stress

→ A prooxidant compound is not necessarily oxidative. Being able to generate a product that is highly oxidative in certain conditions is also called “prooxidant”.

Smith *et al.*, *Free Radic. Biol. Med.*, 2017.

Rahal *et al.*, *Biomed Res. Int.*, 2014.

Winterbourn, *Toxicol. Lett.*, 1995.

Reactions between major chemicals surrounding neuromelanin

ROS (reactive oxygen species): H_2O_2 or $^{\bullet}OH$

Oxidative

Transition metal ions Fe^{3+}, Cu^{2+}

Oxidative

(Neuromelanin) Eumelanin

Reductive

Reduction by eumelanin

$$O_2 \xrightarrow{+\,2e} H_2O_2 \xrightarrow{+\,2e} 2H_2O$$

(0) (-1) (-2)

Synergetic behavior: transition metal ions are reduced by eumelanin and generate $^{\bullet}OH$

$$Fe^{3+} \xrightarrow{+\,e} Fe^{2+}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$

Transition metal ions are chelated by eumelanin

$$\text{Eumelanin} + Fe^{3+} \rightarrow \text{Fe/Eumelanin}$$

Smith *et al.*, *Free Radic. Biol. Med.*, 2017.
Yin *et al.*, *Biomacromolecules*, 2014.
Rahal *et al.*, *Biomed Res. Int.*, 2014.
Zecca *et al.*, *Proc. Natl. Acad. Sci.*, 2004.
Liu et al., *Pigment Cell Res.*, 2005.

Antioxidant vs. prooxidant properties of eumelanin

Antioxidant behavior

delay/prevent the oxidative stress

Prooxidant behavior

induce the oxidative stress

Reduction by eumelanin

$$O_2 \xrightarrow{+\,2e} H_2O_2 \xrightarrow{+\,2e} 2H_2O$$

(0) (-1) (-2)

Prooxidant Antioxidant

Synergetic behavior: transition metal ions are reduced by eumelanin and generate •OH

$$Fe^{3+} \xrightarrow{+\,e} Fe^{2+}$$

Prooxidant

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-}$$

Related to neurodegeneration

Transition metal ions are chelated by eumelanin

$$\text{Eumelanin} + Fe^{3+} \rightarrow \text{Fe/Eumelanin}$$

Antioxidant

Smith *et al.*, *Free Radic. Biol. Med.*, 2017.
Zecca *et al.*, *Proc. Natl. Acad. Sci.*, 2004.
Yin *et al.*, *Biomacromolecules*, 2014.
Liu et al., *Pigment Cell Res.*, 2005.
Winterbourn, *Toxicol. Lett.*, 1995.

Research Issues

How to establish the electrochemical properties of eumelanin?

Based on the optical absorption of eumelanin, can we use solar light to enhance the energy storage properties of eumelanin?

Can we suppress prooxidant properties while maintaining antioxidant properties of eumelanin?

Objectives

To explore the electrochemical properties of DHI- and DHICA-melanin and effect of metal ions (Na^{+}, K^{+}, Cu^{2+}, Mg^{2+}, Fe^{3}+, etc.)

To explore the effect of light on energy storage properties of eumelanin.

To explore the (synergetic) effect of eumelanin, ROS and transition metal ions

Impact

To understand the redox properties of eumelanin

To propose a sustainable method to improve the energy storage properties of eumelanin

To understanding the antioxidant/prooxidant properties vs. redox properties of eumelanin
To put forward a possible method to suppress the prooxidant behavior of eumelanin

Results and Discussions

Fabrication of the working electrodes

Drop-cast

Polymerization of DHI- and DHICA-melanin

Carbon paper

Drop-cast DHI or DHICA (methanol)

0.1 mg cm^{-2}

NH_3 catalyzed polymerization

Synthetic pH 12

In ambient conditions

$$NH_3 + H_2O \rightleftharpoons NH_3H_2O \rightleftharpoons NH_4^+ + OH^-$$

Fabrication from Sepia melanin

Carbon paper

Drop-cast Sepia melanin (DMSO, dimethyl sulfoxide)

Dry

Storage pH 7

In ambient conditions

Pezzella *et al.*, *Mater. Horizons*, 2015.

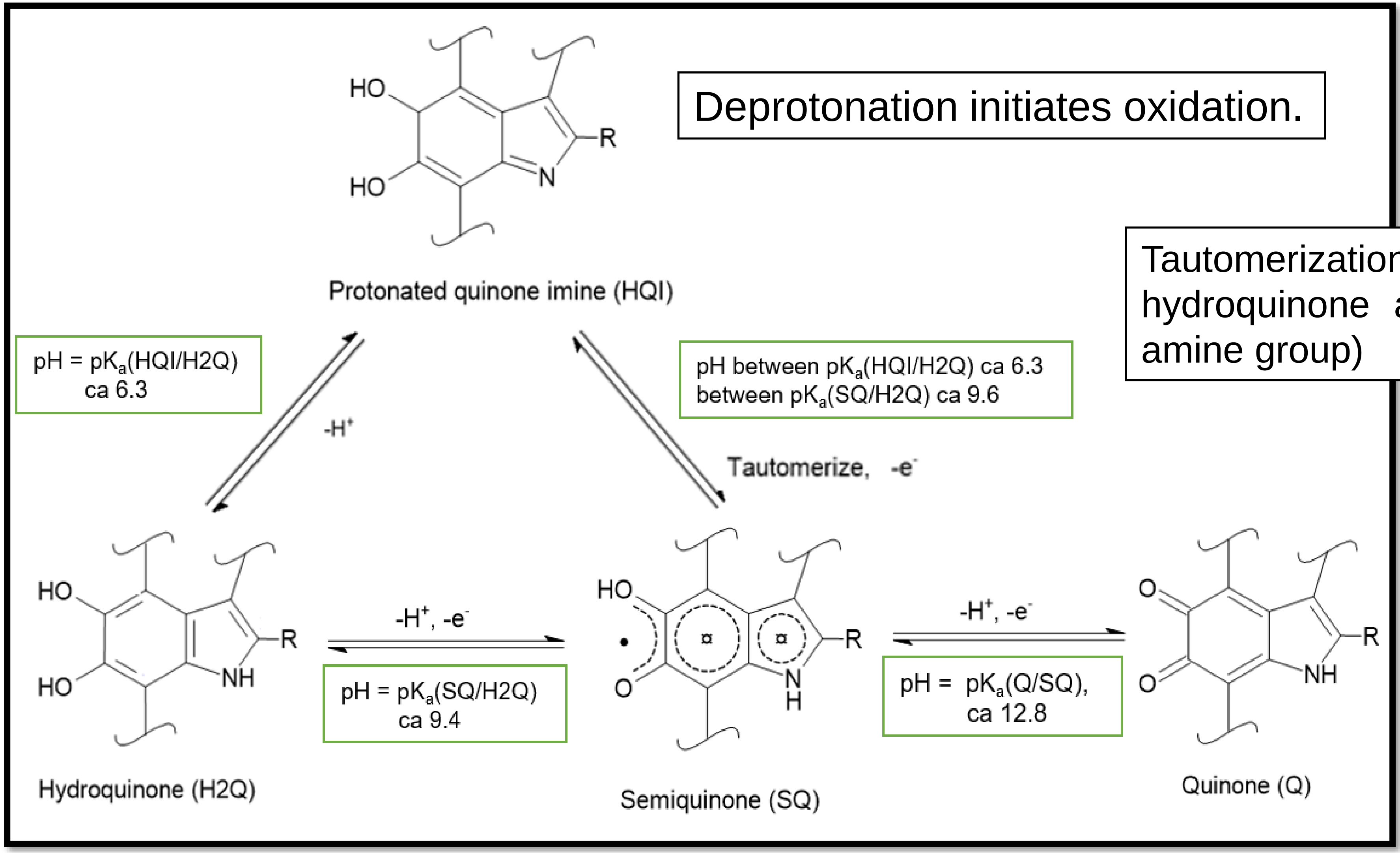
D'Ischia, et al., *Adv. Heterocycl. Chem.* 2005.

Basic hypothesis to understand the proton-assisted electron transfer processes of eumelanin

- pH-controlled redox properties
- Redox properties in cyclic voltammograms
- Polymerization based on redox activities
- Hypothesis: shift of pK_a values during polymerization

Redox properties of eumelanin are controlled by ***environmental pH***.

Deprotonation initiates oxidation.



Tautomerization (H^+ detaches from hydroquinone and attaches on the amine group)

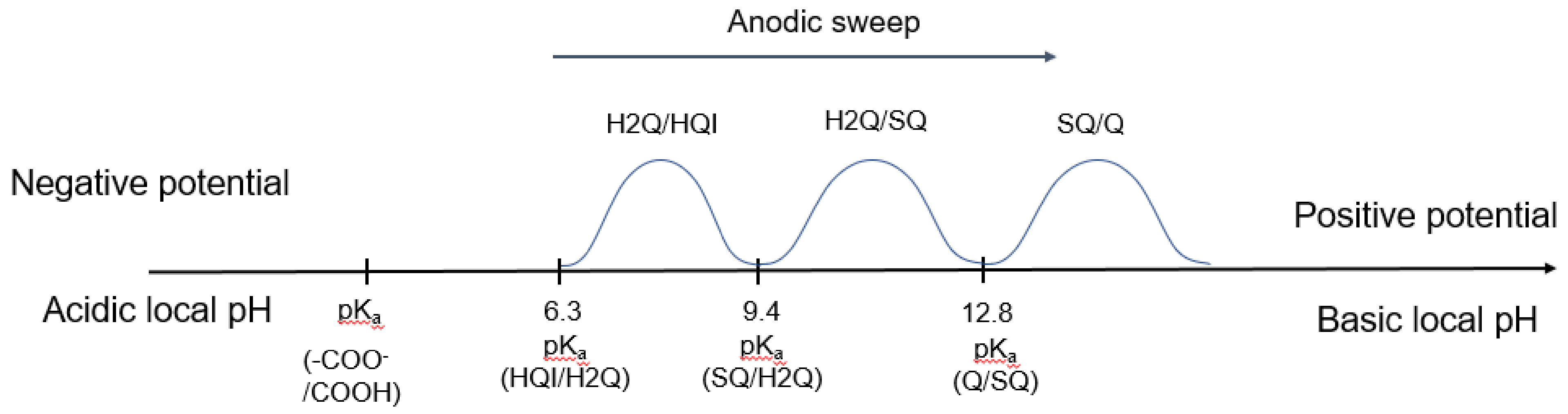
Szpoganicz, et al., *J. Inorg. Biochem.*, 2002.

Charkoudian et al., *Inorg. Chem.*, 2006.

Applied potential induces local pH with electrostatic force

Local pH controls the redox properties

- Local pH: the pH value in a small space surrounding the interface of electrode/electrolyte.
- Bulk pH: The pH of the electrolyte.



$$\begin{cases} E_{ox(onset)}\,(pH_{bulk}) = E_{ox(onset)}\,(pH_{bulk} = 0) - 0.059\ pH_{bulk} \\ E_{ox(onset)}\,(pH_{bulk}) = 0 \text{ when } pH_{bulk} = pK_a \end{cases}$$

vs. NHE (normal hydrogen electrode)

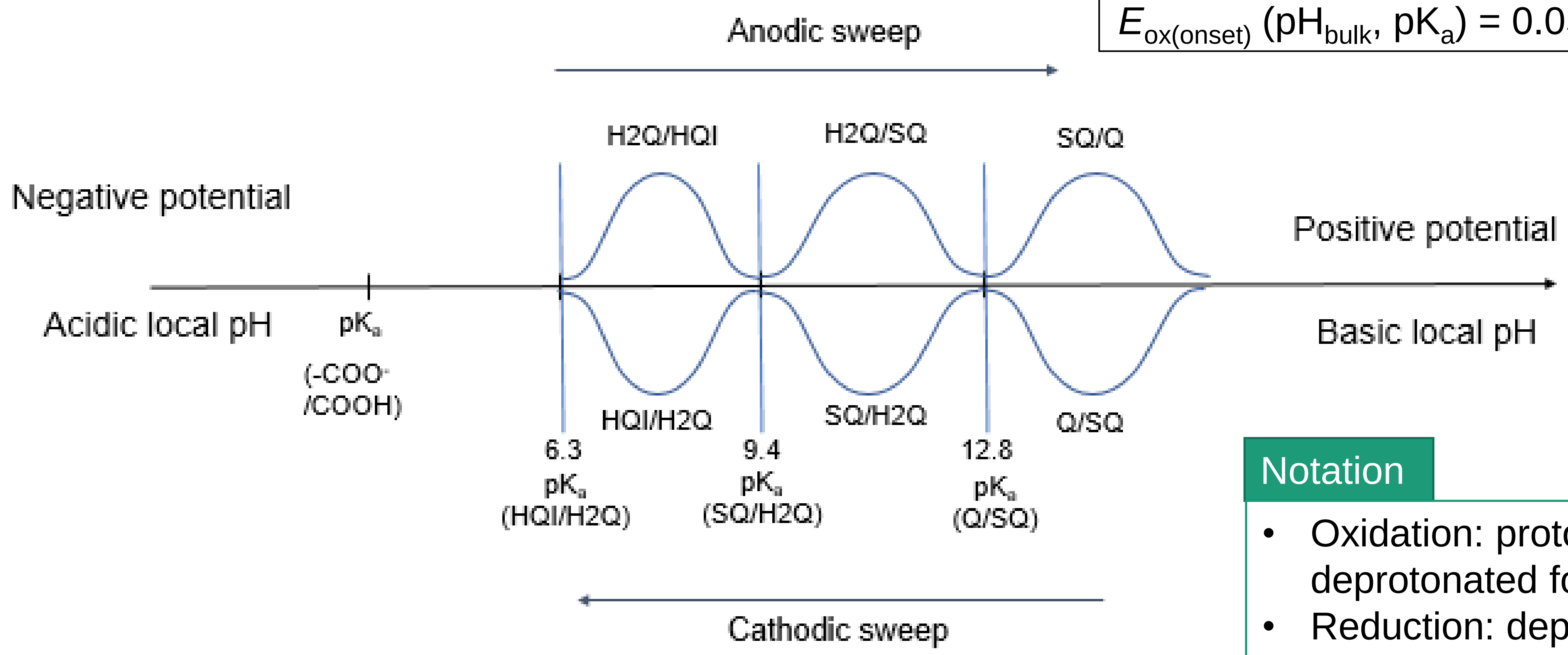
$$\boxed{E_{ox(onset)}\,(pH_{bulk}, pK_a) = 0.059\,(pK_a - pH_{bulk})}$$

$$E_{ox(onset)}\,(pH_{bulk}, pK_a) = 0.059\,(pH_{local} - pH_{bulk})$$

At 0 V vs. NHE: local pH = bulk pH

Reduction processes during cathodic sweep

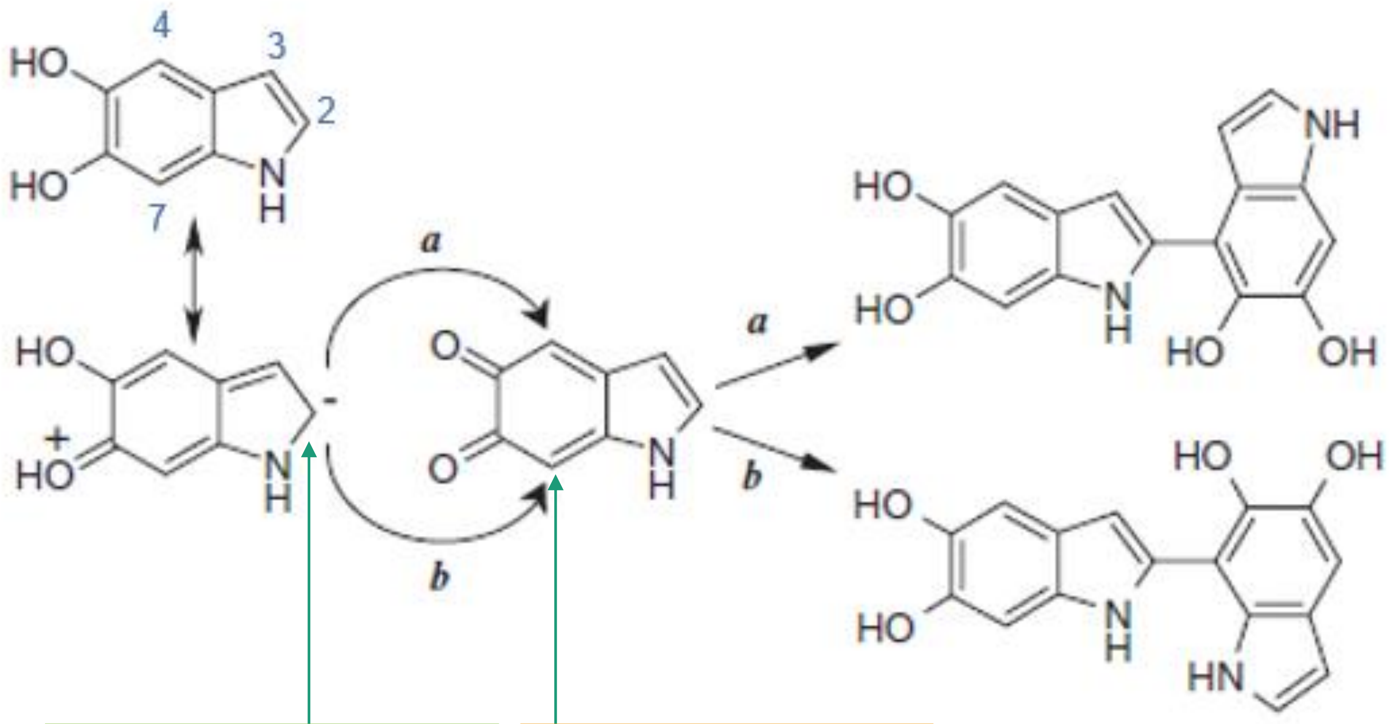
$$E_{ox(onset)}\,(pH_{bulk}, pK_a) = 0.059\,(pK_a - pH_{bulk})$$



Notation

- Oxidation: protonated form/ deprotonated form
- Reduction: deprotonated form/ protonated form
- pK_a (deprotonated form/ protonated form)

Redox activities of eumelanin initiates its polymerization



H2Q generates sites that donate electron pairs

Q generates sites that accept electron pairs

Eumelanin is prone to be (further) polymerized in hydrated conditions due to the coexisting redox forms H2Q and Q.

Oxidative polymerization

Polymerization due to higher amount of oxidative form Q of eumelanin

Reductive polymerization

Polymerization due to higher amount of reductive form H2Q of eumelanin

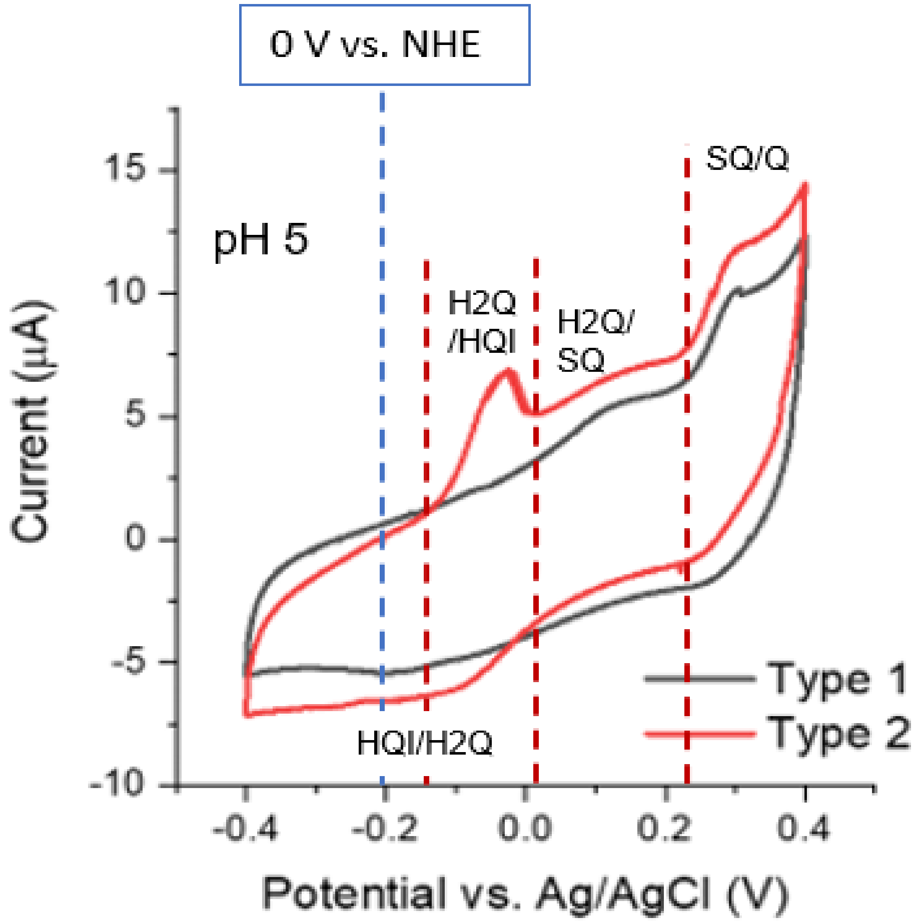
D'Ischia, et al., *Adv. Heterocycl. Chem.*, 2005.

Hypothesis: pK_a shifts towards the environmental pH during polymerization

When the eumelanin is in a new environment, with an appropriate environmental pH, it tends to (further) polymerize. During polymerization, the pK_a value that is close to the environmental pH shifts towards the environmental pH, so that the **polymerization rate decreases** until it reaches a given level.

Data analysis: pK_a vs. potential

Potentials of DHICA-melanin fit the predicted data



$NaCH_3COO$

pK_a values shift towards environmental pH

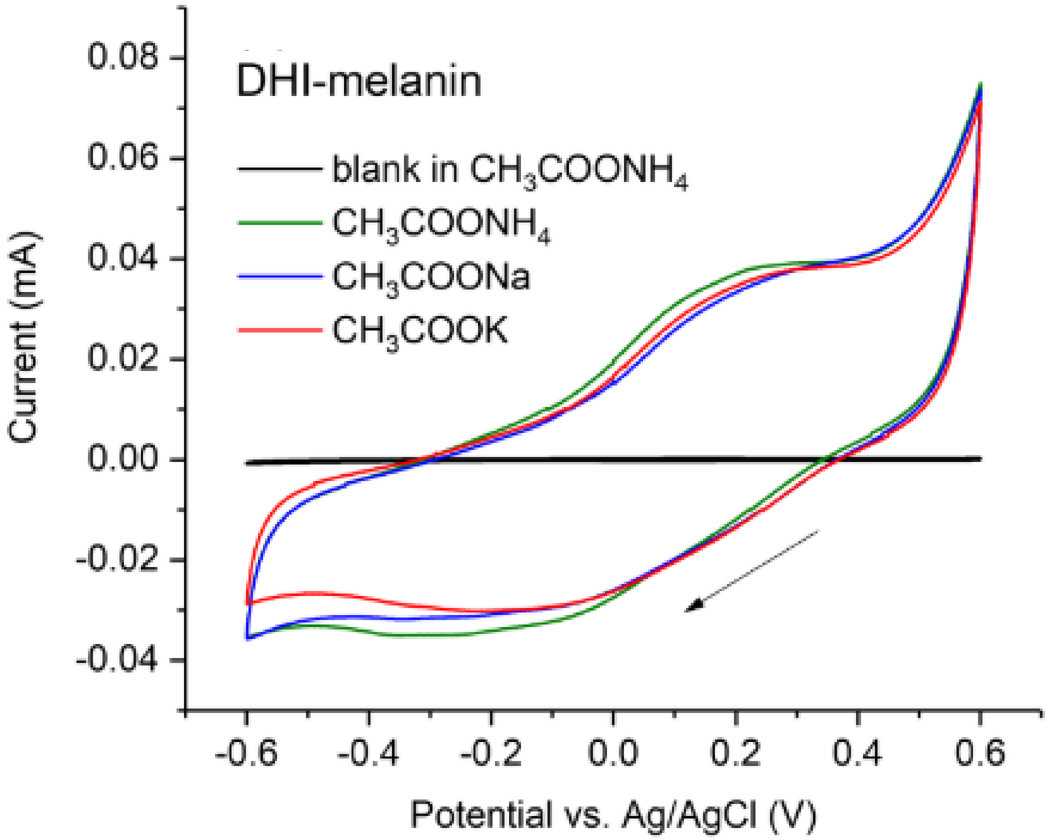
- pK_a(HQI/H2Q) 6.3 $\rightarrow$ between 6 and 7.2 (towards storage pH 7)
- pK_a(SQ/H2Q) 9.4 $\rightarrow$ 8.7 (towards storage pH 7)
- pK_a(Q/SQ) 13.3 $\rightarrow$ 12.1 (towards synthetic pH 12)

With all the parameters fixed, we observe two types of DHICA-melanin.
The structure of Type 1 may block the deprotonation of amine groups.

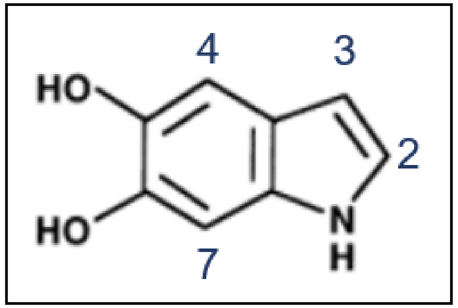
$$E_{ox(onset)}\,(pH_{bulk}, pK_a) = 0.059\,(pK_a - pH_{bulk})$$

Xu, et al., *APL Mater.*, 2017.
Charkoudian et al., *Inorg. Chem.*, 2006.
Szpoganicz, et al., *J. Inorg. Biochem.*, 2002.

DHI-melanin has multiple pK_a due to disordered structures



Broad (convoluted) redox features



Multiple polymerization sites → multiple chemical structures → multiple pK_a

Xu, et al., *APL Mater.*, 2017.

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Polymerization states of the DHI- and DHICA-melanin

Methods for oxidative polymerization

Oxidative polymerization

- pH ≥ ca 6.3
- Oxidant.

Chemical methods in ambient conditions

- pH ≥ ca 6.3
- Oxidants: O_2 and H_2O_2

$$O_2 \longrightarrow H_2O_2 \longrightarrow H_2O$$

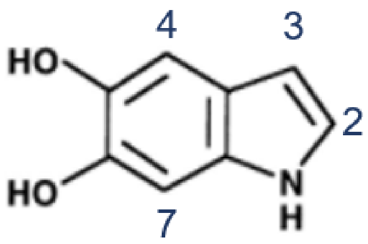
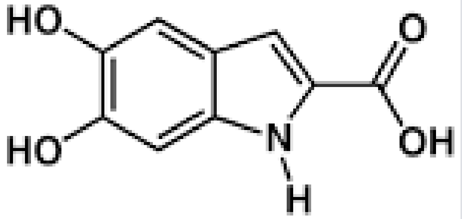
(0) (-1) (-2)

Oxidized by O_2 | Oxidized by H_2O_2

Electrochemical routes

- Local pH ≥ ca 6.3
- The oxidation force given by the applied potential. Ideally no O_2 is present if degassed.

Polymerization states

DHI-melanin	DHICA-melanin
 q: capacity	

Monomeric/oligomeric: $q_{an} > q_{ca}$

Semi-polymerized: $q_{an} \approx q_{ca}$

DHI-melanin	DHICA-melanin	
High q (ca 140 C g^{-1})	Low q (ca 13 C g^{-1})	Presence of SQ/Q

Fully-polymerized: $q_{an} \approx q_{ca}$

DHI-melanin	DHICA-melanin	
Low q (ca 23 C g^{-1})	Low q (ca 13 C g^{-1})	No SQ/Q

π- π stacked structures that favors electron transport

Increase of redox peak current of H2Q/HQI in **Type 2** DHICA-melanin

The capacities are extracted from cathodic currents of eumelanin on carbon paper in potential range -0.4 V/0.4 V at 5 mV/s

Effect of pH on oxidative polymerization rate

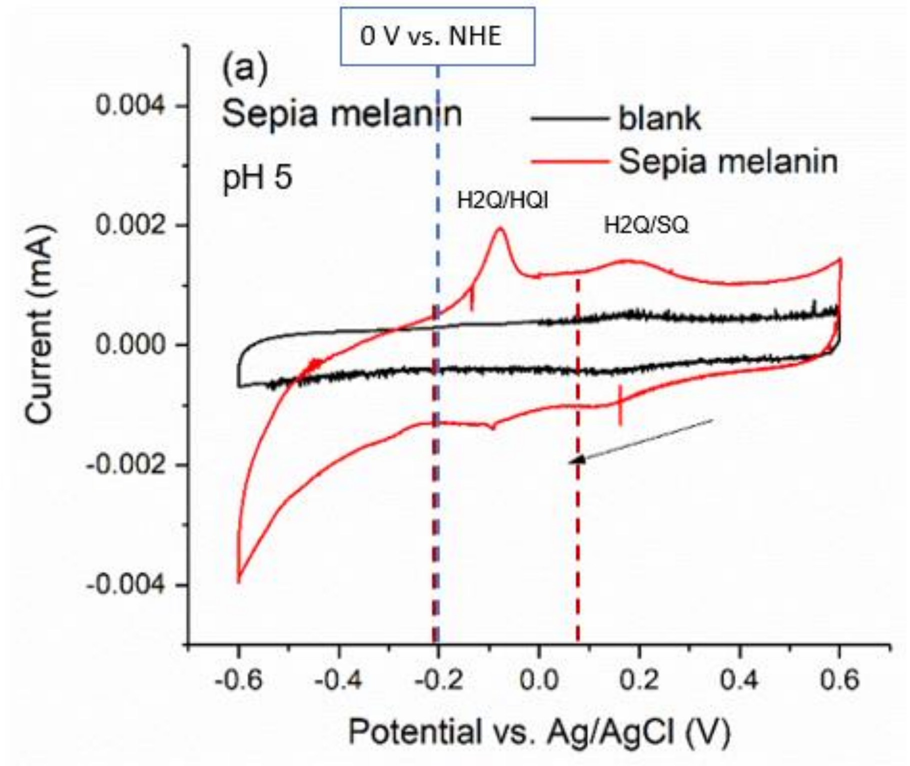
Two Chemical synthesis routes in ambient conditions

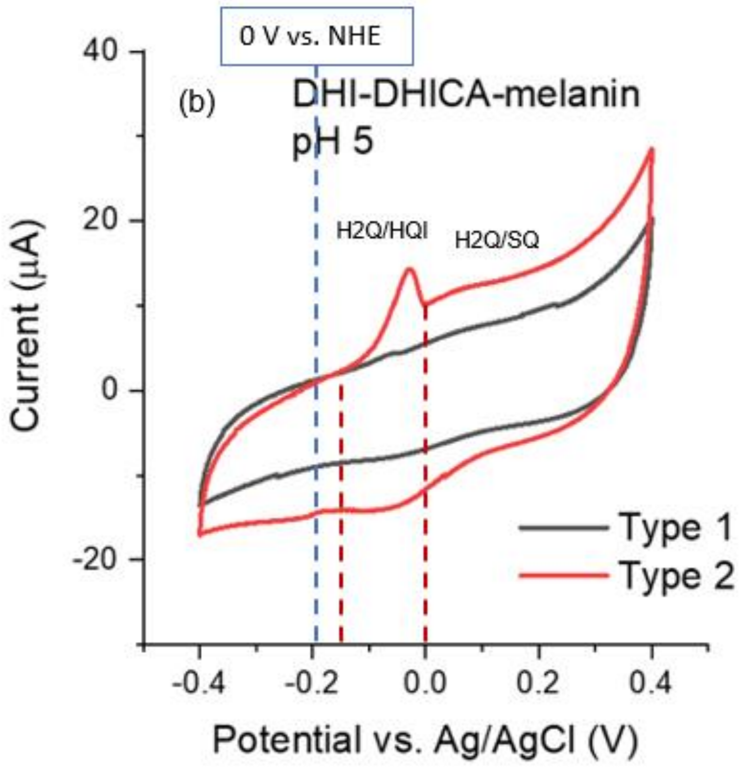
- **pH ca 12**
- Oxidant: O_2 and H_2O_2
- **Fast** (**ca 65 h** from semi- to fully-polymerized DHI-melanin)

- **pH ca 7 (during storage)**
- Oxidant: O_2 and H_2O_2
- **Slow** (**ca 1 year** from semi- to fully-polymerized DHI-melanin)

$NH_3 + H_2O \rightleftharpoons NH_3H_2O \rightleftharpoons NH_4^+ + OH^-$

Disappearance of SQ/Q for fully-polymerized DHICA component



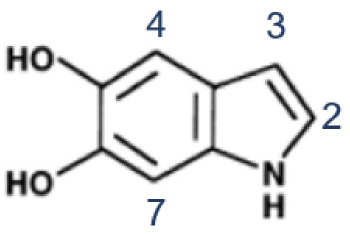


SQ/Q of DHICA disappears due to its oxidative or reductive polymerization with DHI component.

The structure of Type 1 may block the deprotonation of amine groups.

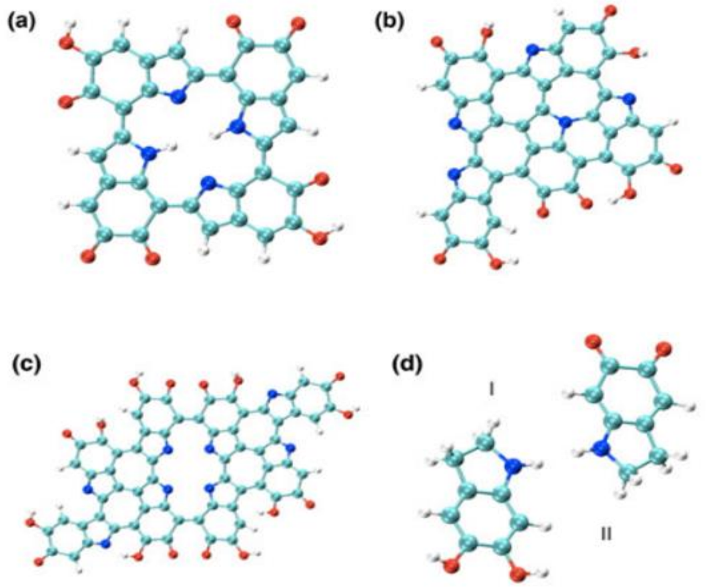
Summary 1: disordered DHI-melanin vs. ordered DHICA-melanin

DHI-melanin



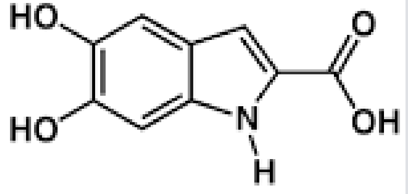
Disordered structure due to multiple polymerization sites

Broad (convoluted) redox features



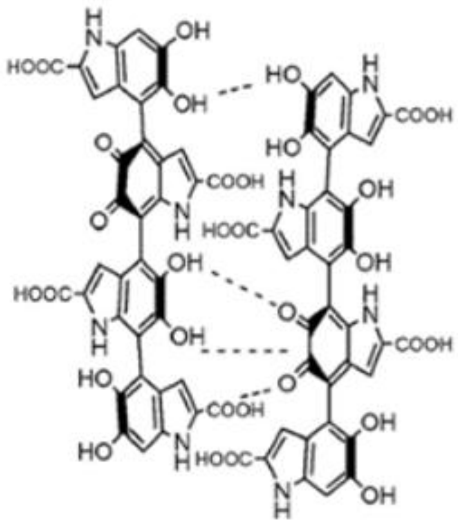
Chen, et al., *Nat. Commun.*, 2014.

DHICA-melanin



Relatively **ordered** structure due to limited polymerization sites

$E_{ox(onset)}$ (pH$_{bulk}$, pK$_a$) = 0.059 (pK$_a$ – pH$_{bulk}$)

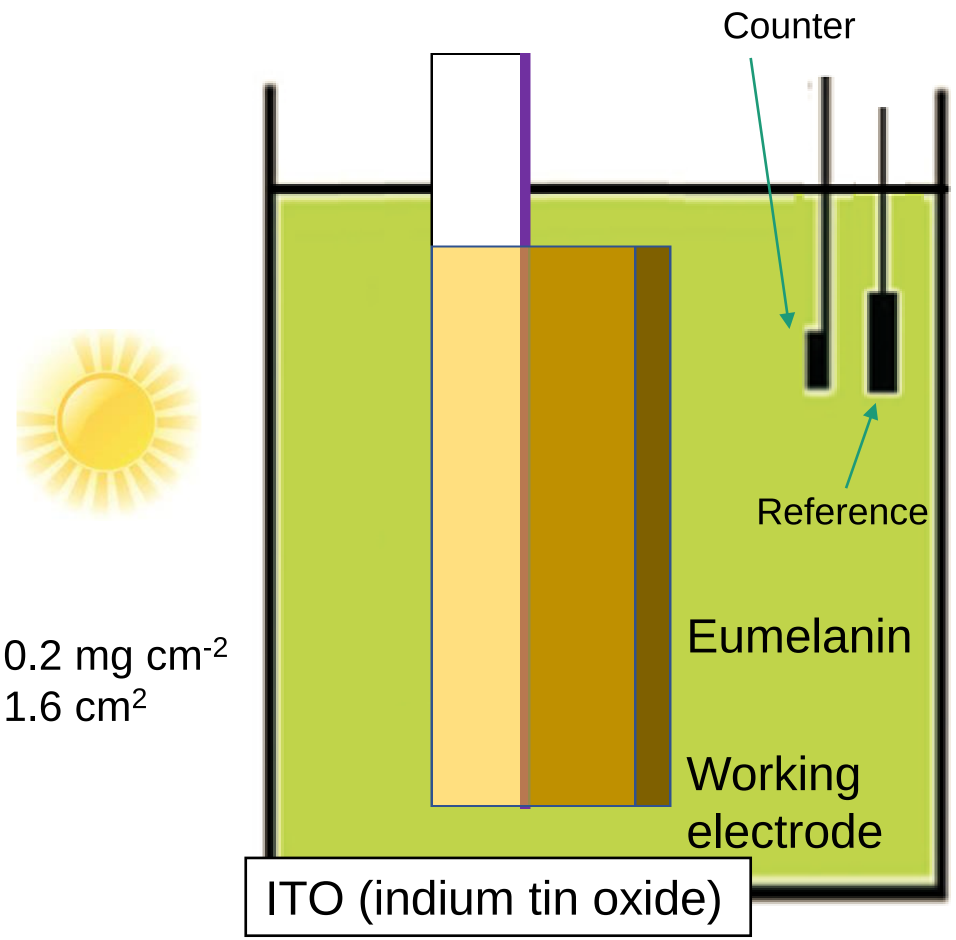


Monomer-like behavior demonstrated by SQ/Q in not fully-polymerized DHICA-melanin

Panzella, et al. *Angew. Chem.*, 2013.

Light-enhanced energy storage

Back-scattering configuration using transparent current collector

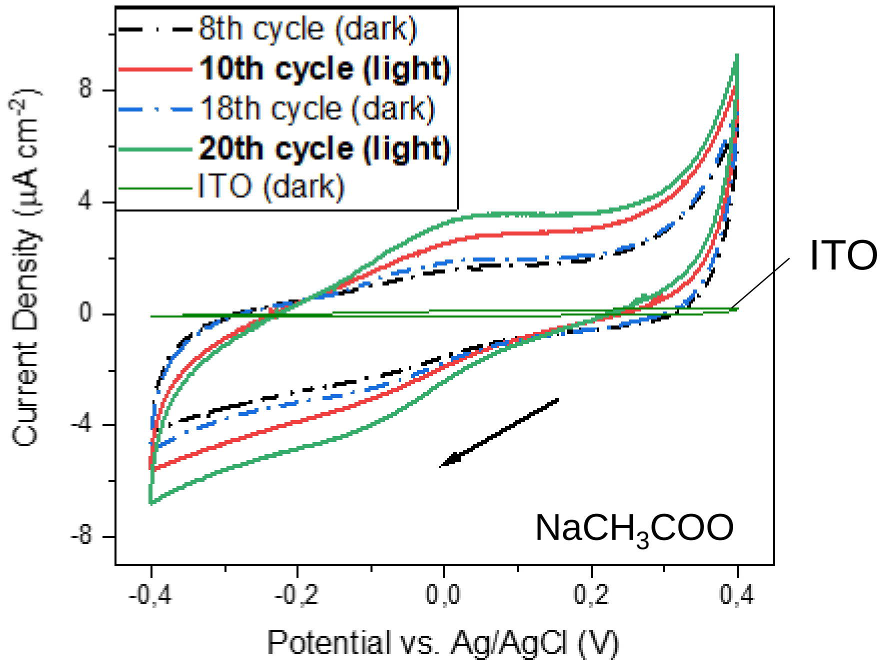
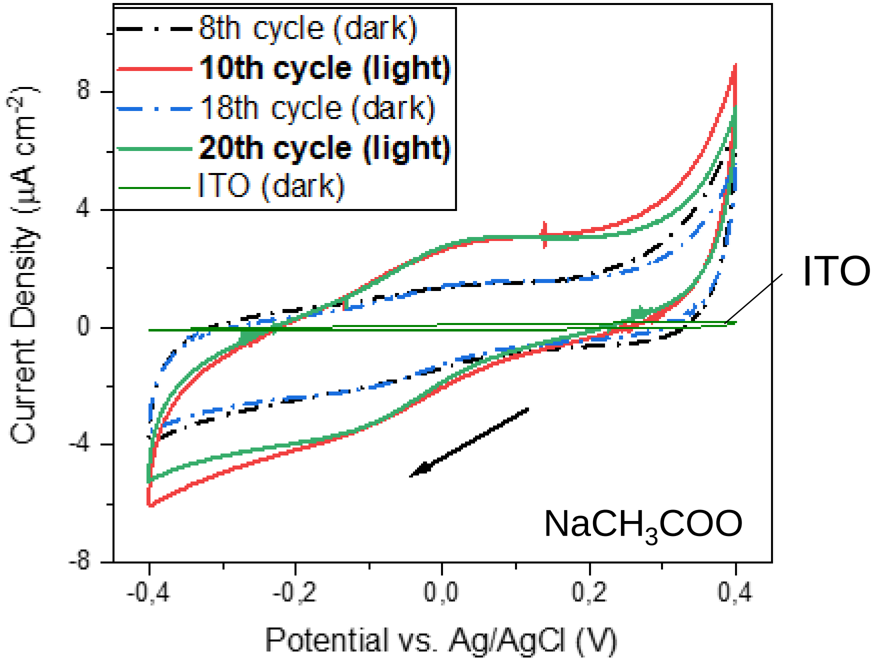


0.2 mg cm^{-2}
1.6 cm^{2}

- Absorbs most light → high enhancement
- Poor cycling stability

Povlich, et al. *Macromolecules*, 2010.

Light-enhanced capacity/capacitance

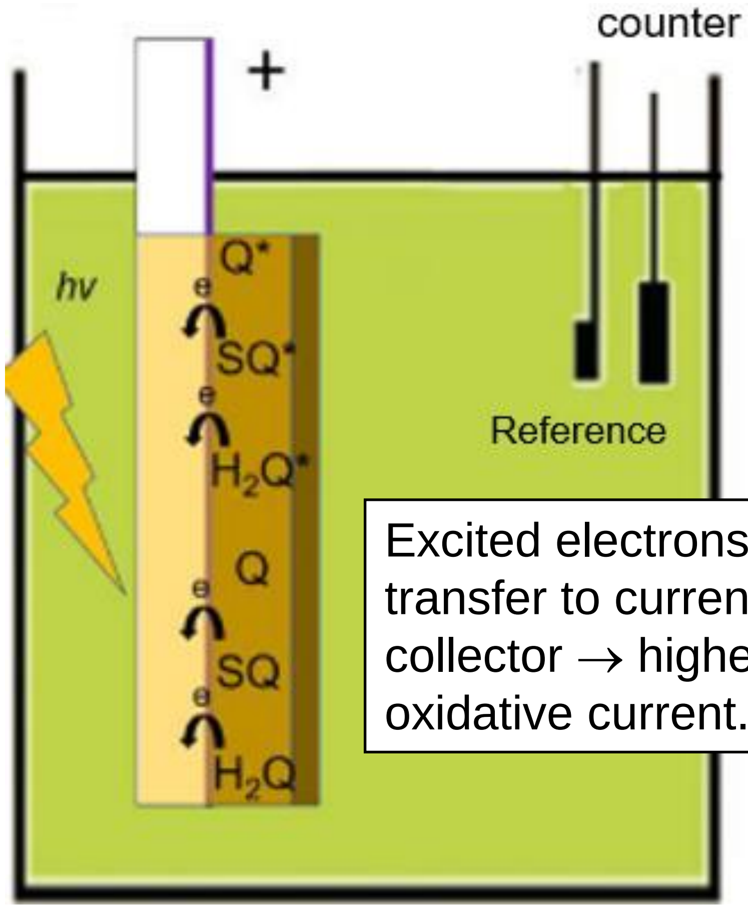
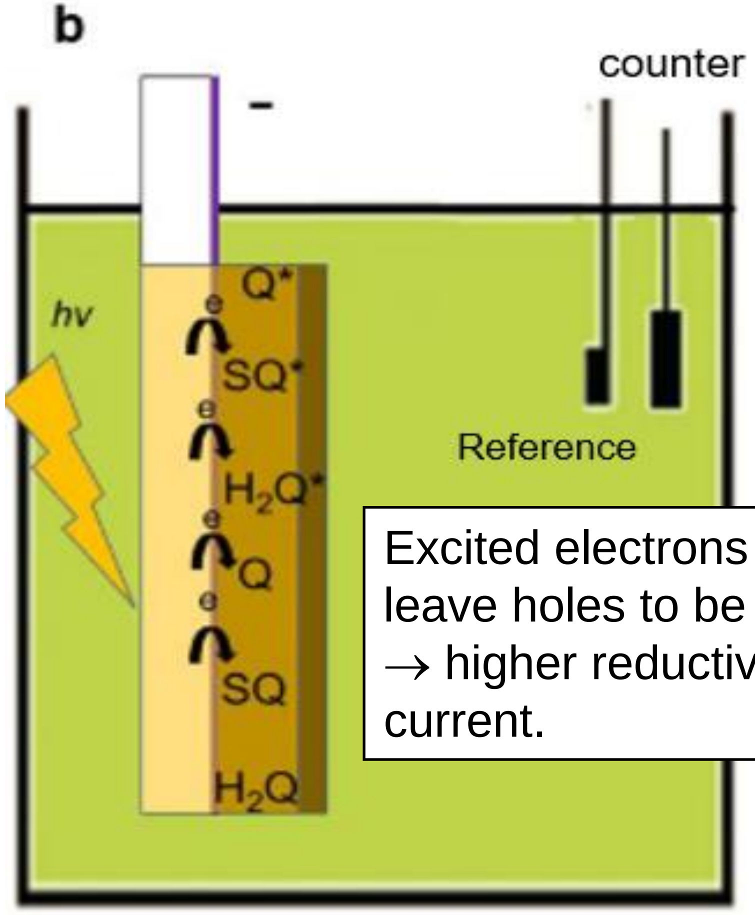
DHI-melanin	DHI-DHICA-melanin (7:3)
	

10^{th} cycle vs. 8^{th} cycle:

DHI-melanin	DHI-DHICA-melanin (7:3)
Capacity +50% Capacitance +50%	Capacity: +73% Capacitance: +63%

Xu, et al. *MRS Adv.*, 2020.

Light-enhanced electron transfer

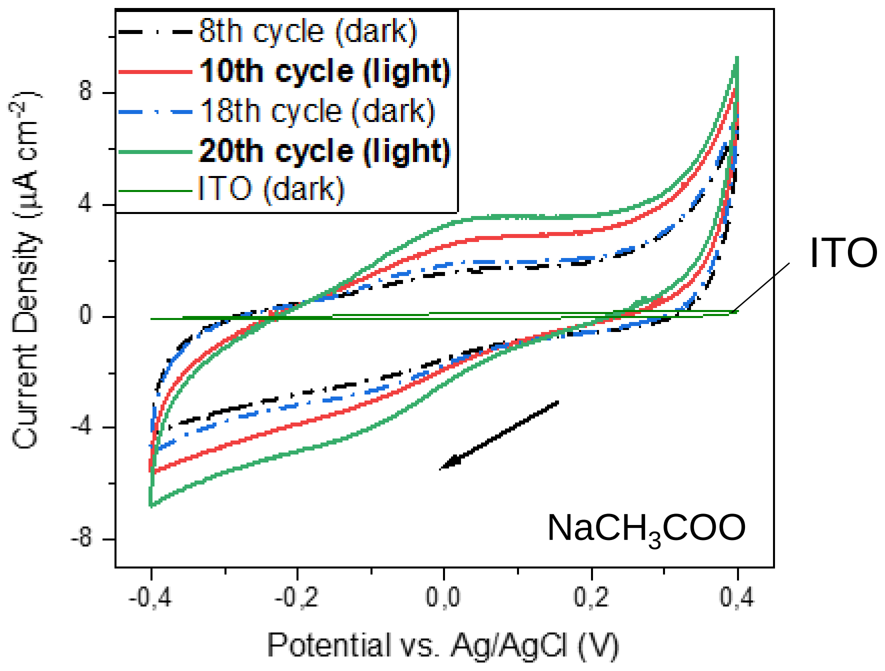
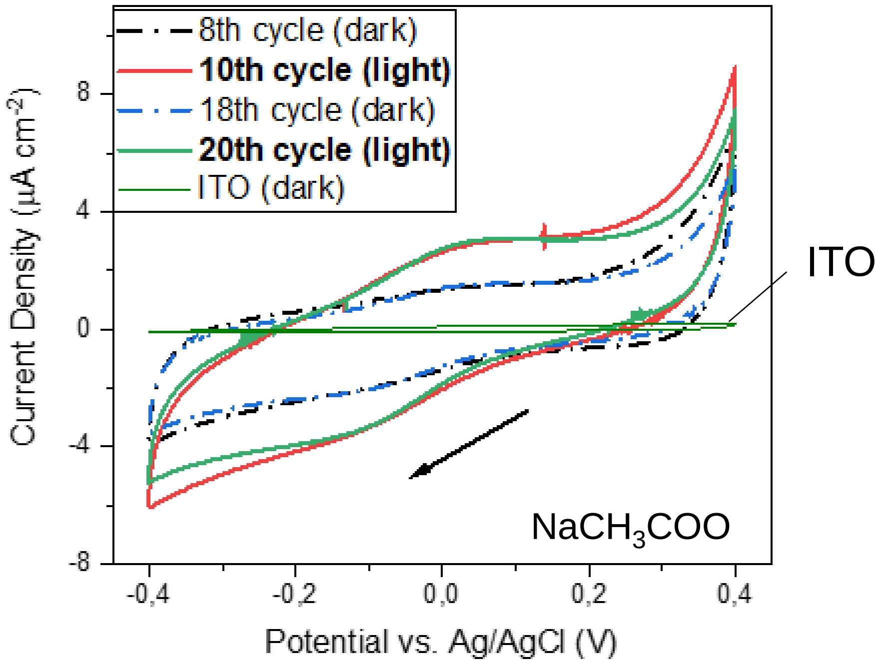
Higher anodic capacity at positively biased electrode	Higher cathodic capacity at negatively biased electrode
	

Excited electrons transfer to current collector → higher oxidative current.

Excited electrons leave holes to be filled → higher reductive current.

Xu, et al. *MRS Adv.*, 2020.

Persistent enhancement in DHI-melanin

DHI-melanin	DHI-DHICA-melanin (7:3)
	

20th cycle vs. 10th cycle:

Persistent enhancement despite poor cycling stability

DHICA does not favor the persistent enhancement.

Xu, et al. *MRS Adv.*, 2020.

Light-induced polymerization for persistent enhancement of energy storage properties of DHI-melanin

Positively biased eumelanin	Negatively biased eumelanin
Excited electrons transfer to current collector → Higher oxidative current	Excited electrons leave holes to be filled → Higher reductive current
→ Higher amount of oxidative form of eumelanin Q generated → **Oxidative polymerization**	→ Higher amount of reductive form of eumelanin H2Q generated → **Reductive polymerization**

The polymerization increases the degree of delocalization of π-electrons.

Summary 2: light-enhanced of energy storage properties of DHI-melanin

Light-enhanced energy storage properties

(Compare to dark) Increase of capacity up to ca 73%, capacitance up to ca 63% of eumelanin on ITO.

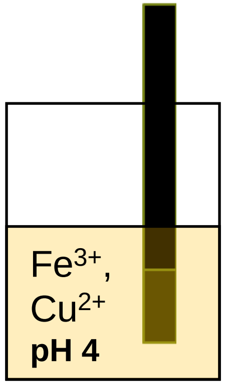
Light induced polymerization

Light → excited states → More Q at positive potential / More H2Q at negative potential → Further polymerization and persistent enhancement of energy storage properties

Effect of multivalent metal ions M^{n+}

Morphology of Fe/Cu/eumelanins

Pre-immersion



Fe^{3+}:Cu^{2+}:eumelanin
0.2:0.002:1 mol:mol:mol

24 h

$Fe_2(SO_4)_3$
$Cu_2(CH_3COO)_2$

Contrast of brightness

Backscattered electron mode of SEM: high atomic number Fe^{3+} and Cu^{2+} shows brightness with respect to carbon element (dark)

pH controlled chelation

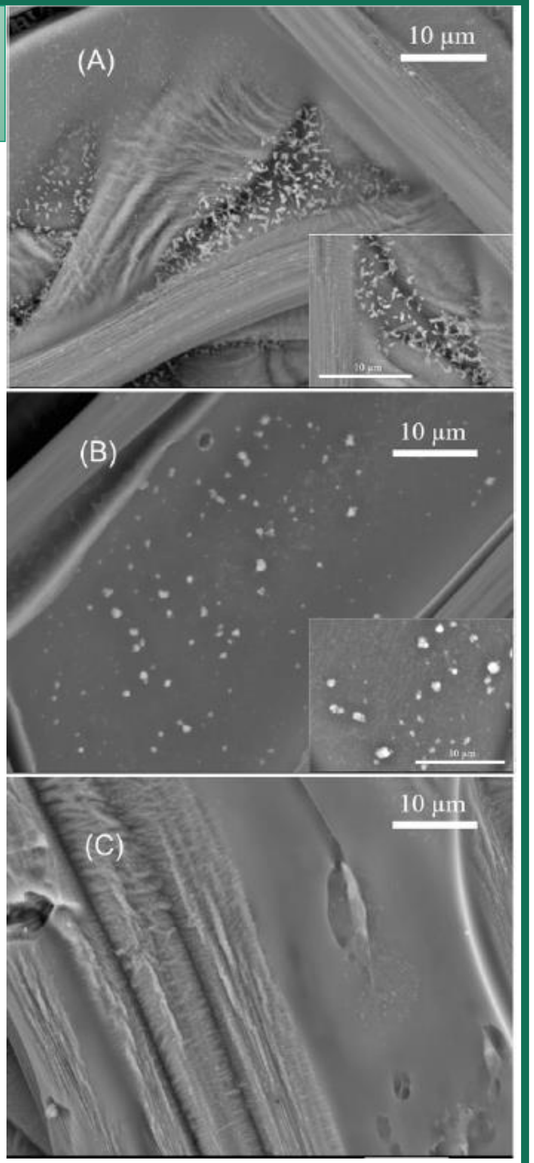
Chelation occurs only after deprotonation of -COOH (pK_a ca 3). It requires that pH > pK_a.

SEM (scanning electron microscope)

DHICA-melanin

DHI-DHICA-melanin

DHI-melanin



Xu, et al. *Front. Bioeng. Biotech.*, 2019.

Effect of multivalent metal ions M^{n+} on electrochemical properties

Cathodic shift(s)

Lower pK_a values of the functional groups

Anodic shift of SQ/Q and/or H2Q/SQ

Functionalization of the electron-withdrawing group $–COO^-$ on the molecules can increase the redox potentials of the materials.
The degree of electron-withdrawing increases due to the chelation on $–COO^-$.

Oxidative polymerization

Transition metal ions Fe^{3+}, Cu^{2+} | Oxidative | $Cu^{2+} \rightleftharpoons Cu^+ + e^-$

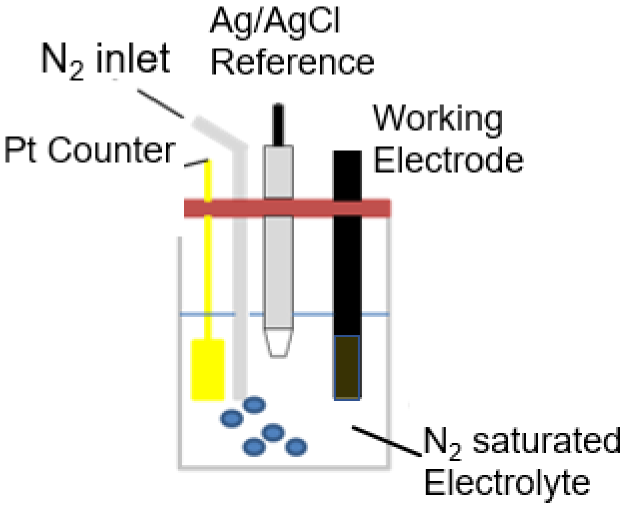
Effect of Cu^{2+} and Fe^{3+} during voltammetry in electrolyte - methodology

2 Cycles → Add metal ions → 2 cycles

Fe^{3+} or Cu^{2+}

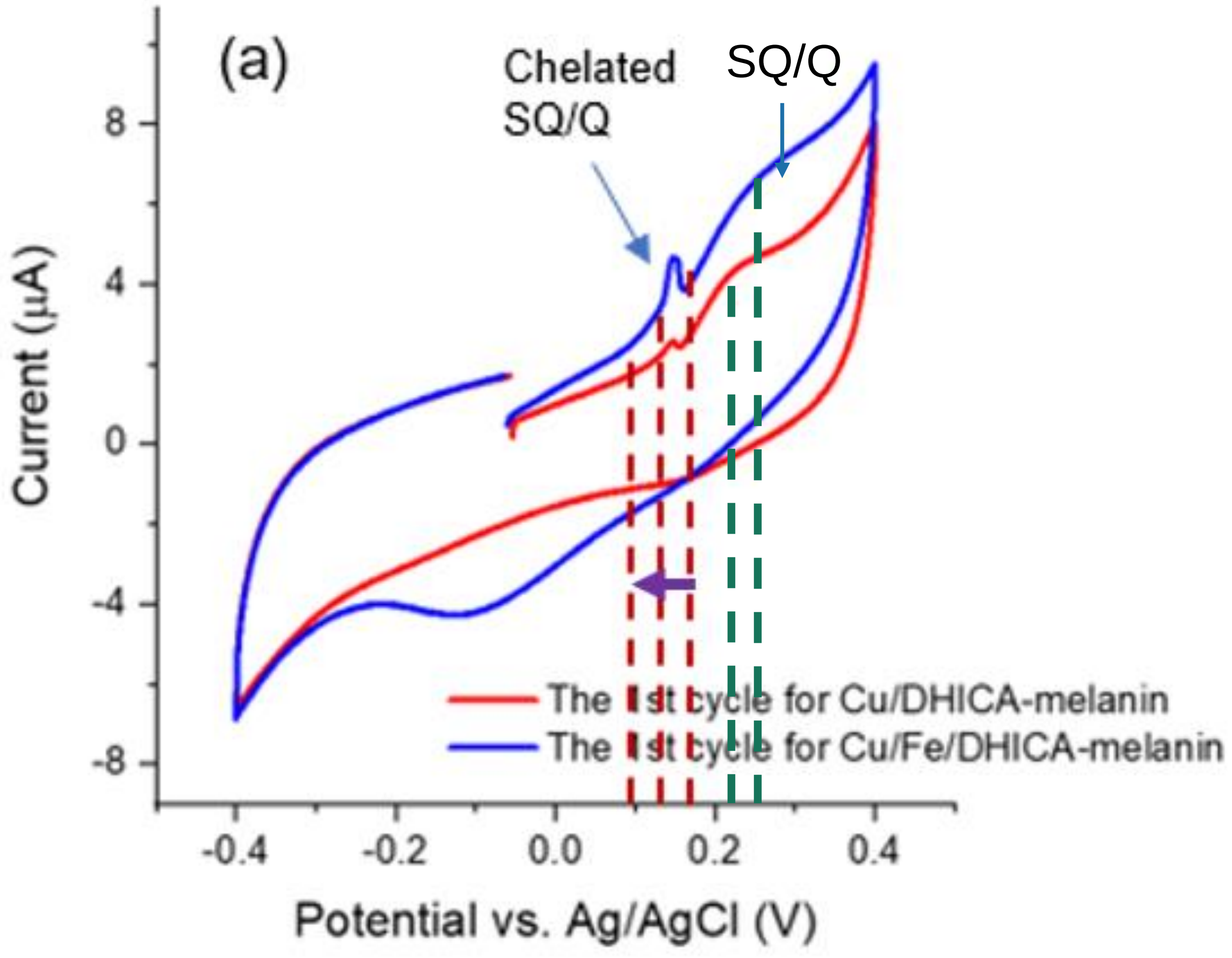
(Cu^{2+}:Fe^{3+}:eumelanin 0.002:0.2:1 mol:mol:mol)

- $Fe_2(SO_4)_3$
- $Cu_2(CH_3COO)_2$



145 mM KCH_3SO_4, 10 mM NaCl, 2 mM $MgCl_2$, 10 mM $NaCH_3COO$, buffered with CH_3COOH at pH 7

Effect of Cu^{2+} and Fe^{3+} during voltammetry in electrolyte



Fe^{3+} and Cu^{2+}-chelated-quinone groups

Adsorption peak with cathodic shift of SQ/Q (onset oxidation potential from ca 0.17 V to ca 0.1 V vs. Ag/AgCl).

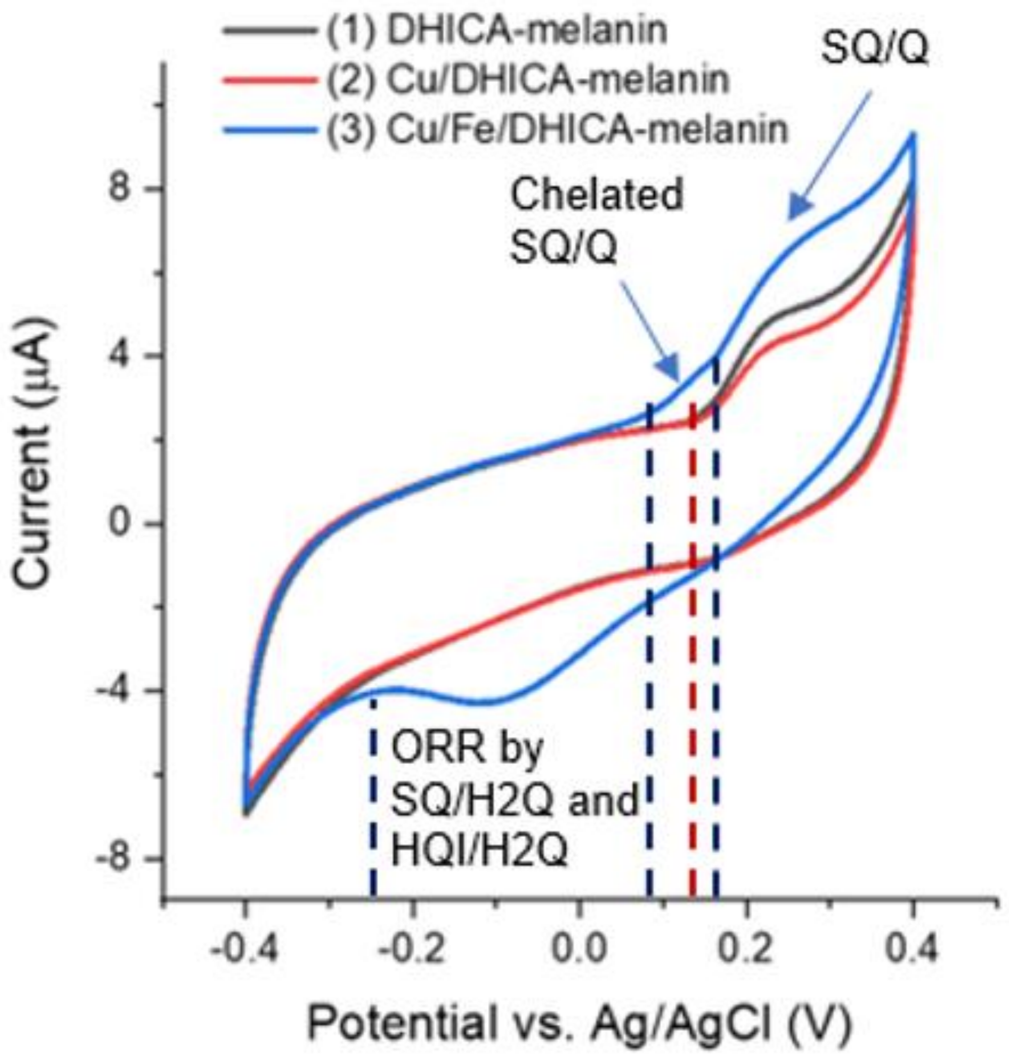
Fe^{3+}-chelated- $–COO^-$

Anodic shift of oxidation peak SQ/Q (ca 0.22 V to 0.26 V vs. Ag/AgCl).

145 mM KCH_3SO_4, 10 mM NaCl,
2 mM $MgCl_2$, 10 mM $NaCH_3COO$, pH 7

Xu, et al. *Front. Bioeng. Biotech.*, 2019.

Effect of Cu^{2+} and Fe^{3+} during voltammetry in electrolyte



Possible oxidative polymerization
Cu^{2+} lowers peak SQ/Q

145 mM KCH_3SO_4, 10 mM NaCl,
2 mM $MgCl_2$, 10 mM $NaCH_3COO$, pH 7

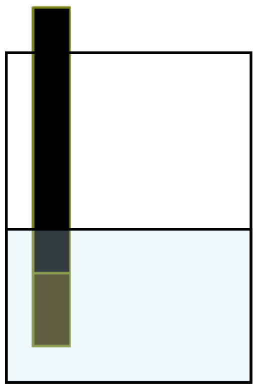
Xu, et al. *Front. Bioeng. Biotech.*, 2019.

Effect of ROS
(reactive oxygen species)

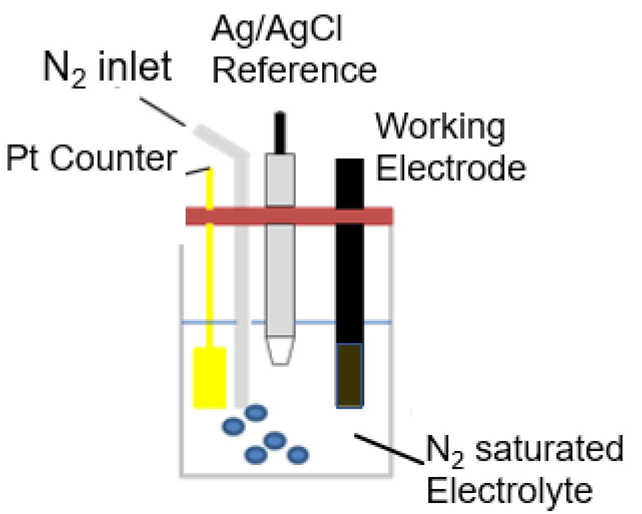
Effect of H_2O_2 or $^{\bullet}OH$ - methodology

Electrodes are exposed to ROS (in another beaker) between measurements

5 min



1.5 mM H_2O_2
or $^{\bullet}OH$



For $^{\bullet}OH$: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$

H_2O_2: Fe^{2+}: eumelanin 50 mol: 0.2 mol:1 mol

$FeSO_4$

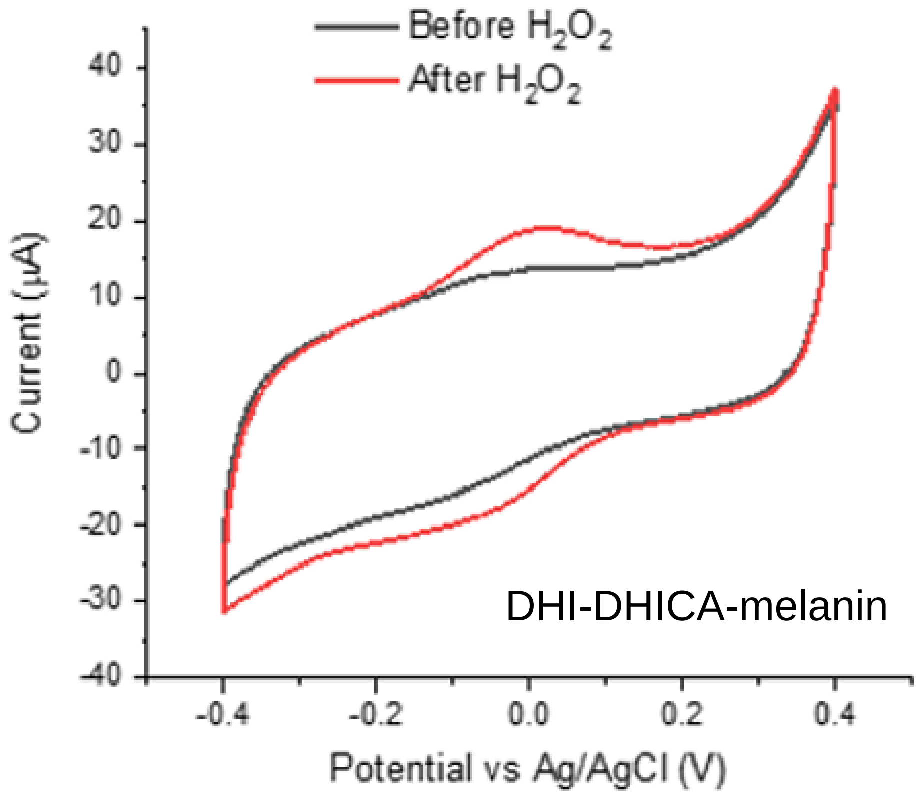
145 mM KCH_3SO_4, 10 mM NaCl,
2 mM $MgCl_2$, 10 mM $NaCH_3COO$, pH 7

Chen, et al., *J. Neurophysiol.*, 2001

Effect of ROS: 1) more quinone/carbonyl groups

XPS (X-ray photoelectron spectroscopy)

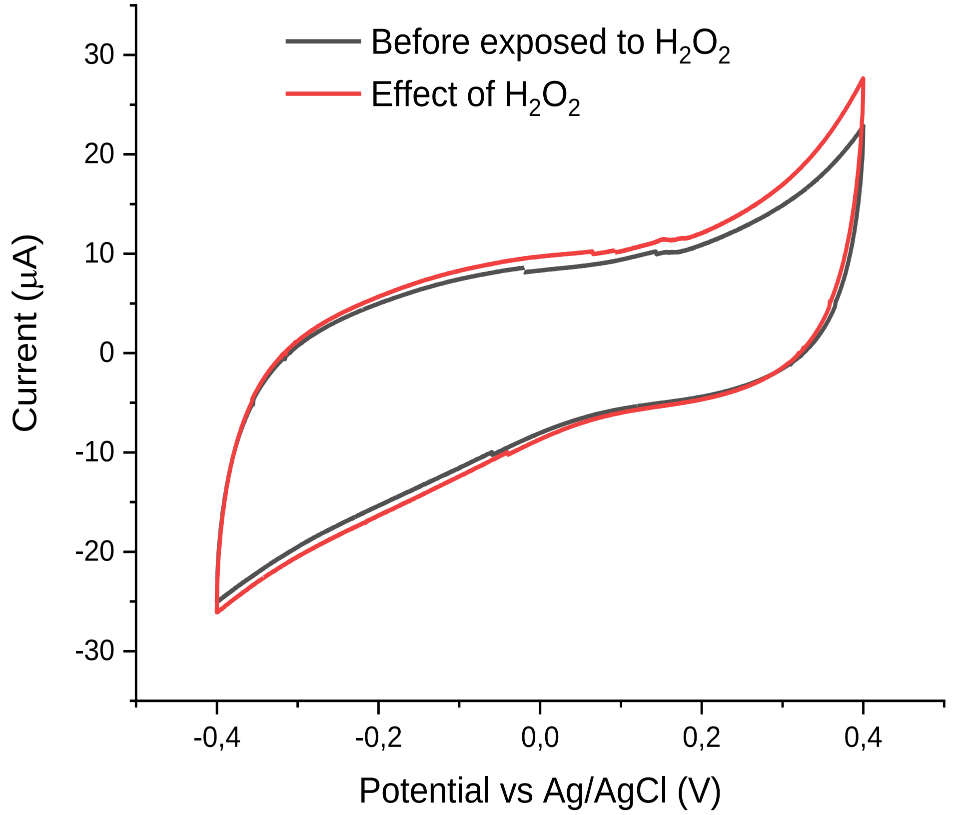
Orbital of the atom	Binding Energy (eV)	Identifi-cation	After vs. before (%)
C 1s	284.6	C=C	-37%
	286.5	C-O	+27%
	287.7	C=O	+17%
O 1s	531.3	C=O	+13%
	542.3	C-OH aliphatic	+23%
	533.6	C-OH aromatic	+33%



Xu, et al. *Front. Bioeng. Biotech.*, 2019.

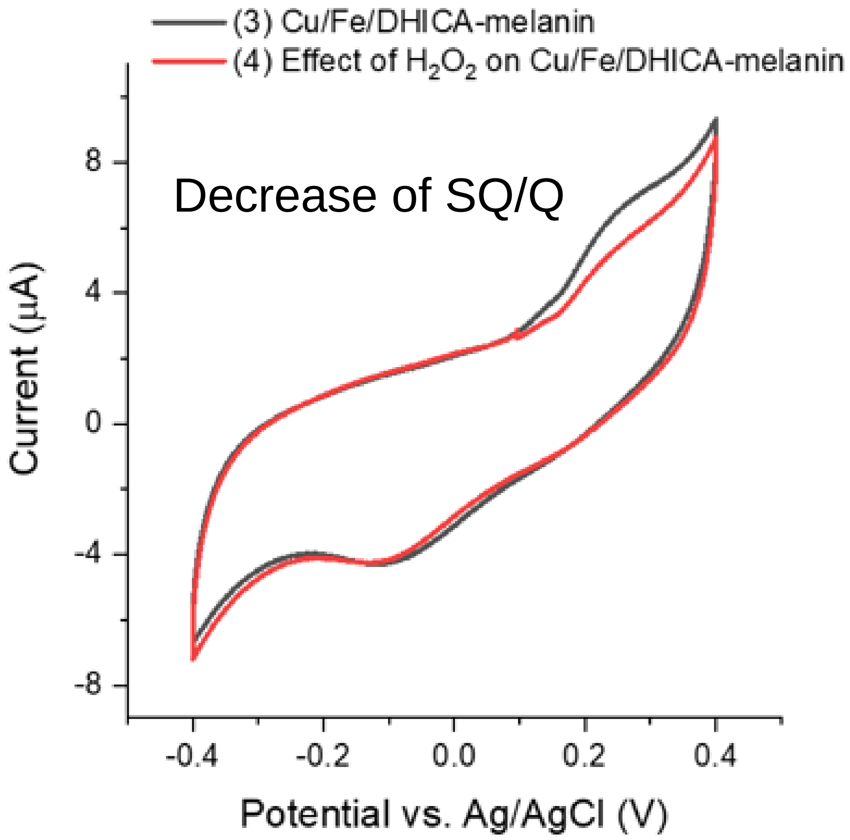
Effect of ROS: 2) further polymerization

DHI-melanin



Little effect on DHI-melanin because the sample is fully-polymerized

DHICA-melanin



Semi-polymerized DHICA-melanin

Xu, et al. *Front. Bioeng. Biotech.*, 2019.

Summary 3: prooxidant properties

DHI-melanin	DHICA-melanin
• Multiple polymerization sites • Polymerizes fast by oxidative polymerization • Very reductive	• Limited polymerization sites • Polymerizes slowly by oxidative polymerization • Less reductive
Strong prooxidant behavior (generate H_2O_2 in ambient conditions)	Weak prooxidant behavior (does not generate much H_2O_2)
↓	↓
The sample we use is fully-polymerized DHI-melanin	The sample we use is semi-polymerized DHICA-melanin

Panzella, et al. *Angew. Chem.*, 2013.

Novellino, et al., *Chem. Res. Toxicol.*, 1999.

Summary 3: antioxidant properties

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DHI-melanin

- **π-π stacked structures**
- Multiple polymerization sites
- Polymerizes fast by oxidative polymerization
- Very reductive

- Strong prooxidant behavior (generate H_2O_2)

- Strong antioxidant behavior by being reductive before being fully-polymerized

Panzella, et al. *Angew. Chem.*, 2013.

DHICA-melanin

- **Rod-shaped structures**
- Limited polymerization sites
- Polymerize slowly by oxidative polymerization
- Less reductive

- Very weak prooxidant behavior (does not generate much H_2O_2)

- Strong antioxidant behavior by trapping ROS in rod-shaped structures after being semi-polymerized

Novellino, et al., *Chem. Res. Toxicol.*, 1999.

Conclusions and Perspectives

Conclusions and perspectives

- ✓ Redox activities of eumelanin controlled by environmental pH.
- ✓ Effect of local pH in cyclic voltammograms of eumelanin.
- ✓ Polymerization of eumelanin based on redox activities. pH-controlled reaction rate of the polymerization.
- ✓ Effect of multivalent metal ions on redox properties of eumelanin.
- ✓ Light-enhanced energy storage properties of eumelanin.
- ✓ Different mechanisms of antioxidant/prooxidant properties of DHI-melanin and DHICA-melanin.

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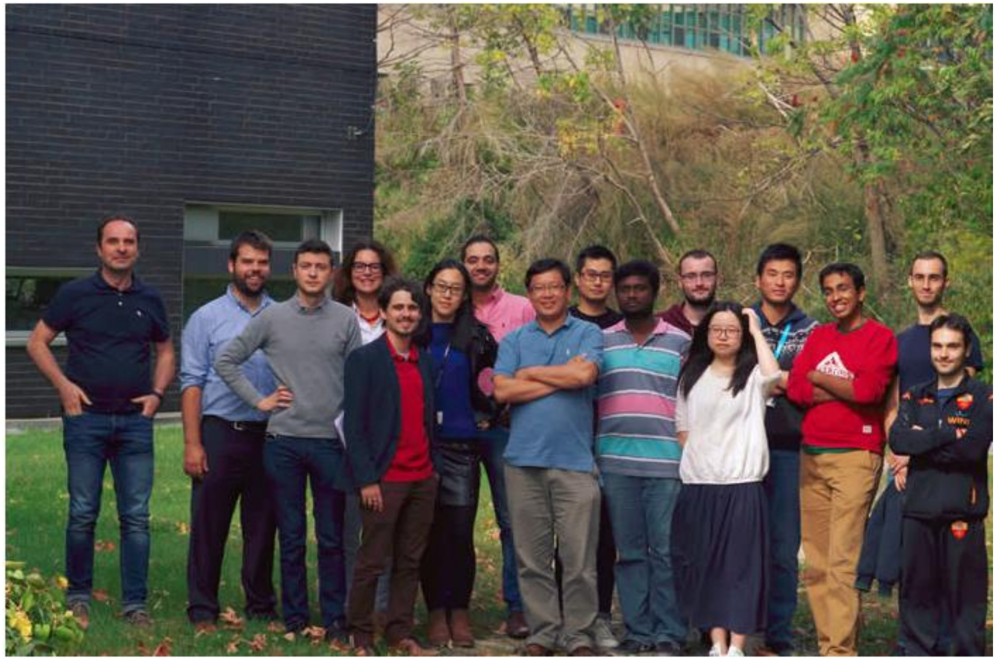

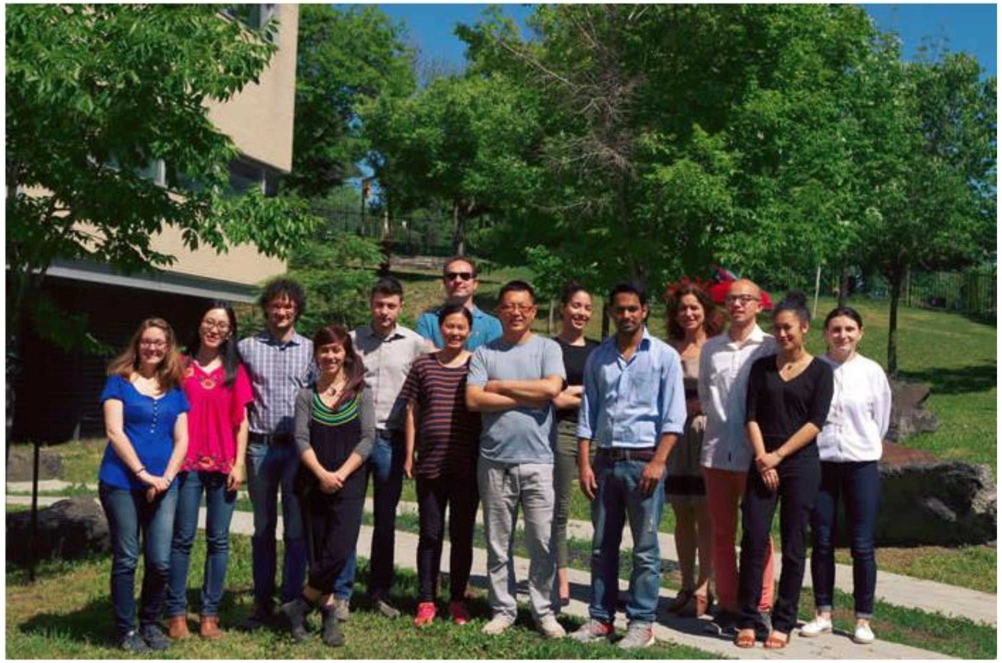

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Prof. **William SKENE** , Member

Prof. **Young Jo KIM**, External Member

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