

Melanin and Light

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Melanin is responsible, in Nature, for photoprotection, for this reason it is expected to be poorly photoreactive. However, the photo-reactivity of melanin and related materials is well documented. Here we discuss some relevant recent examples to demonstrate that, indeed, the actual mechanism of interaction of melanin with light is complex and still not completely understood. Photochemical and photothermal processes are involved, giving a contribution that strongly depends on light wavelength and intensity. Moreover, some interesting experiments demonstrated that photochemical reactivity of melanin related compounds is likely to be indirect, in the sense that the

effect of light is to increase the number of radical species rather than creating photoreactive excited state. These suggestions open-up new perspectives in the interpretation of the role of melanin in photoprotection and in the design of new melanin based photoactive materials for energy conversion, environmental remediation, and nanomedicine. Further complication is given by the role of atmospheric oxygen and humidity in the photoinduced processes. Beside this complexity of behavior makes it difficult a systematic understanding of the interaction of melanin with light, it surely strongly contributes to make the properties of melanin and related materials unique.

Introduction

Melanin, in Nature, is the organic pigment responsible for hair and skin coloration and for photoprotection, hence for defending living organism from the potential damages due to the exposure to sunlight.^[1] Indeed, melanin natural function involves its interaction with light. Another peculiar feature of melanin is that, as shown in Figure 1, it typically exists in living organisms in nanosized form, and it is a peculiar example of natural nanoparticles (NP). The different forms of melanin present in Nature can be classified based on the molecular precursors they are formed from, as schematized in Figure 2.^[2] Importantly, as shown in Figure 1, biomimetic forms of natural melanin can be easily prepared artificially following highly environmentally friendly and simple procedures.^[3] This biomimetic melanin, and in particular polydopamine (PDA), obtained from dopamine, is so similar to the natural one that even human skin cell, keratinocytes, cannot discriminate natural and artificial melanin. Moreover biomimetic melanin NP perform in keratinocytes the same photoprotective action as the natural one, offering the same biocompatibility.^[1]

The unique versatility of the preparation of biomimetic melanin NP combined to their high biocompatibility and their unique optical and electronic properties made melanin-like nanomaterials suitable for application as wide as e.g. environmental remediation, energy conversion and storage, photo-thermal and photochemical catalysis, and nanomedicine.^[4–7]

Many of these applications exploit interaction of natural or biomimetic melanin with light. In this concept paper we

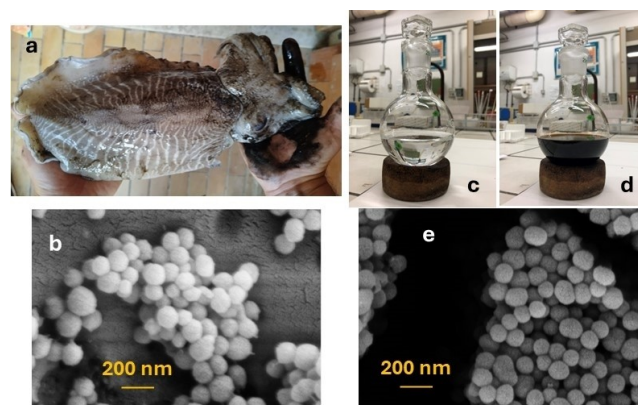


Figure 1. a) Black ink from cuttlefish mainly contains melanin NP, observable at SEM as in b. Similar NP can be prepared starting from a dopamine alkaline solution (c) upon oxidation with atmospheric oxygen (d). SEM image of the polydopamine NP is shown in e. Partially reproduced with permission from ref.^[3]

demonstrate that interaction of melanin with light is indeed very multifaceted and can lead to a variety of photophysical and photochemical processes that can be only in part rationalized but that, at the same time, make melanin a unique multifunctional photoactive material.

Actual chemical composition of both natural and biomimetic melanin is still under discussion and its structure is the result of covalent and supramolecular polymerization. Most consolidated hypothesis suggest the presence in the structure of 5,6-dihydroxyindole (DHI), indole-5,6-quinone (IQ), shown in Figure 3, and their oligomers.^[8,9] Electronic transition are in part localized on these specific chromophores but they can also arise from interchromophoric charge-transfer (CT) interactions.^[10] The multiplicity of electronic transitions is at the basis of the typical broad absorption band ranging from the UV to the NIR region of melanin like materials. Nevertheless, because of their relatively high refractive index, melanin NP also present a relevant, wavelength dependent light scattering.

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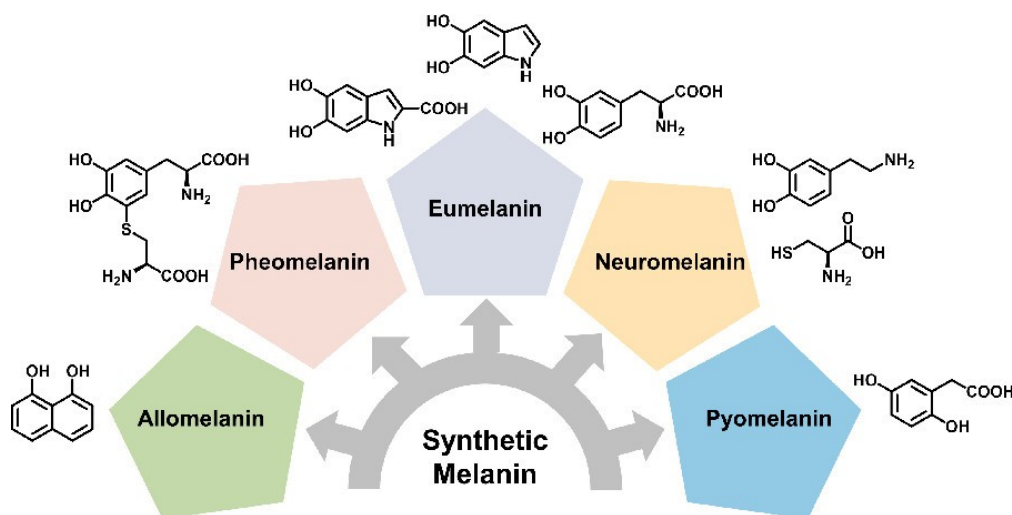


Figure 2. Classification of melanin based on the molecular precursors. Reproduced with permission from ref.^[2]

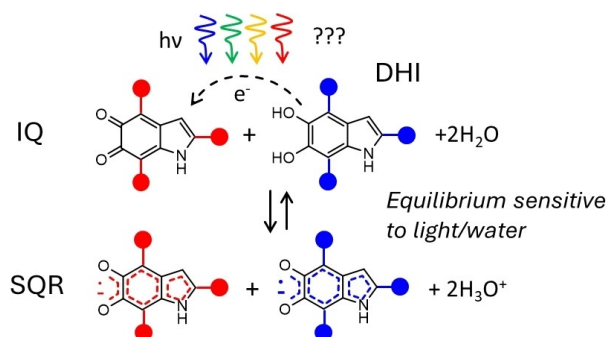


Figure 3. Scheme of the SQR formation process. SQR is in equilibrium with DHI and IQ. Equilibrium is shifted towards the products by water presence and light irradiation.

Because of this, melanin NP were also assembled to provide structural coloration.^[11,12]

The photoprotective action of melanin is based, in part, on its ability of dissipating fast the adsorbed radiative energy without giving any photochemical reaction. Ultrafast transient absorption (UFTA) studies carried out on melanin biomimetic models in fact demonstrate that excited state deactivation is very fast (excited state lifetime $\tau = 1\text{--}2$ ps) in the whole spectral region, ranging from UV to NIR.^[13–15]

Beside the fast deactivation of the excited states, photo-reactivity of natural and biomimetic melanin is well documented,^[16] although different mechanisms have been proposed to explain its origin. According to Li et al.^[16] UVA excitation (320–450 nm, 2.43 ± 0.02 W/cm²) of natural (from cuttlefish) or artificial polydopamine (PDA) or poly-L-DOPA melanin leads to i) oxidation of DHI to IQ by atmospheric



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oxygen; ii) photoinduced formation of endoperoxide; iii) photo-induced decarboxylation with production of diacetylipyrrole and CO₂; iv) photocyclization. According to NASA total solar irradiance is about 0.14 W/cm²,^[17] 8% of which only is in the UV region (200–400 nm) hence UV light irradiance is about 11 mW/cm². According to this information in the experimental conditions chosen by Li et al irradiance was about 220 times more intense than in the case of real solar exposure and hence not comparable with the “natural” sun exposure. In this high irradiance exposure conditions photodegradation occurred in about 10 minutes in all cases with clear formation of CO₂ bubbles detectable by optical microscopy.

This interesting work unfortunately does not reply to some fundamental questions. i) What is the actual role of oxygen in the process? ii) Is light really necessary in all the transformative processes? iii) What is the effect of the irradiance and wavelength? What is in our opinion surprising in the proposed mechanism is that involvement of atmospheric oxygen normally requires dynamic quenching and long living excited states^[18] while UFTA studies show only the formation of very short living excited states. This suggest, either that oxygen is not necessary for the photoreaction or that it is already adsorbed onto the melanin at the ground state and no diffusion of oxygen molecules to interact with the excited state is necessary.^[18]

On the other hand, the formation of a long lived triplet excited state in melanin in porcine retinal pigment epithelial cells was reported by Wang et al.^[19] Triplet excited state was reported by Chiarelli-Neto to interact with oxygen by producing singlet oxygen (¹O₂).^[20,21] Action spectra and quantum yields of singlet oxygen photogeneration were also reported by Szweczyk et al.^[22] while Zadlo et al. showed the role of photodegradation of pheomelanin in singlet oxygen generation.^[23] Moreover action spectra and quantum yields for melanin radicals photogeneration, oxygen photo-consumption and their role in melanin photo-reactivity were reported by T. Sarna.^[24] Apparently, these results are in contrast with the absence of long-lived species in UFTA experiments but we would like to stress that reported quantum yields for radical production are typically <1% for λ > 250 nm and <0.1% in the visible. As a consequence these process can be hardly detected in UFTA experiments.

Meredith and coworkers identified semiquinone radicals (SQR) as the responsible of photo-reactivity of melanin.^[26] This process is schematized in Figure 3. According to this work indeed the effect of light is not to excite the SQR creating reactive excited states but to increase the formation of SQR by photoinduced electron transfer (PeT) from electron donor DHI to IQ units. This hypothesis is in perfect agreement with our results about the formation of polydopamine through supramolecular donor dihydroxybenzenic unit and IQ.^[10] In fact, also in these adduct PeT was responsible for the appearance of a broad absorption band in the VIS-NIR region. According to Meredith and coworkers SQR formation occurs both through a “dark” mechanism and a light activated one. In both cases deprotonation processes are involved. Hence, since experiments were carried out in the solid state, presence of water was

needed for the protonation. The authors quantified the photo-response of melanin by measuring photo-EPR signal and photocurrent. Both resulted to be activated by irradiation but also dependent on the water content. The mechanism proposed by Meredith and coworkers for the photo-reactivity of melanin-like materials is surely very interesting and unusual. It also gives rise to new questions to which the author replied only in part: i) Electron transfer is a short distance process so is very close proximity between IQ and DHI required, or in other words, are only IQ and DHI preassembled pairs photoreactive? ii) How can charge separated species be stabilized without any fast recombination? iii) What is the actual effect of the light wavelength of the process, or in other words, is excitation localized on the chromophores or are CT interaction involved? iv) According to Figure 3 different kind of SQR can be formed, how does this affect the photoinduced reactivity?

Light induced formation of SQR was also suggested by Nothling and Stenzel to explain the activity of polydopamine as a visible-light responsive photosensitiser (PS) for polymerization.^[25] In this work, as shown in Figure 4, the photogenerated SQR reacts with diphenyliodonium hexafluorophosphate (IOD) producing radicals that initiate polymerization of model vinyl monomers. It is interesting to observe that light-induced formation of SQR is quite slow, requiring some minutes irradiation, and reversible. We would like to stress that, from a photochemical point of view, this behavior is very interesting since it demonstrates that it is possible to induce charge separation with light, and charge separated states are stable enough to accumulate under steady state irradiation. This may find important application in light energy conversion but, on the other hand, accumulation of activated melanin is potentially dangerous in biological systems where it can produce e.g. DNA mutations.^[27]

The idea that the effect of light on PDA is related to the presence of water was exploited by Weil and Graczykowski to produce PDA membrane based photoactuators.^[28] According to these authors, irradiation of the PDA membrane with a red (660 nm) laser light leads to a fast (140 μs) contraction because of the photoinduced desorption of water molecules. The authors conclude that contraction is due to pure photothermal effect since a similar effect can be obtained simply by heating

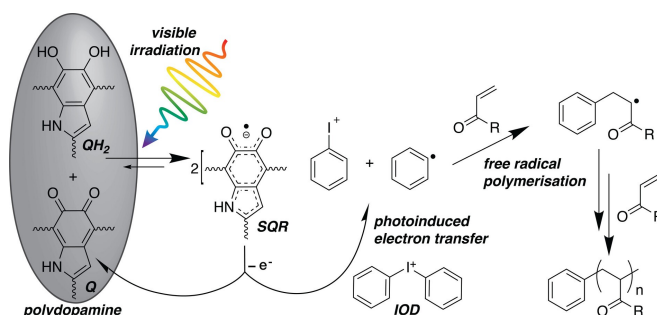


Figure 4. Proposed mechanism of PDA photoredox catalysis for photo-sensitised free radical polymerisation. Visible light absorption by PDA increases SQR production. SQR undergoes PeT by reducing IOD, causing homolysis into its cationic/radical fragments and initiating polymerization of vinyl monomers. Reproduced with permission from ref.^[25]

the membrane. It is interesting observing that, according to this model, water is released in the environment upon melanin irradiation while considering the SQR formation upon irradiation water is necessary (and hence expected to be adsorbed) for the photoproduct deprotonation.

Exposure of PDA films to more focalized and intense blue irradiation leads to a different chemical modification reported by Messersmith and coworkers as graphitization. The degree of graphitization was quantified by these authors by Raman spectroscopy while XPS was used to identify the functional groups revealing an increase of the fraction of the sp² carbon atoms with respect to the sp³ ones with a corresponding decrease of the amount of C–N/C–O/C=O groups. Graphitization was reported to improve the mechanical strength of the PDA film preserving its multifunctionality. It is important noticing that irradiation in the conditions reported by the authors induced also a strong temperature increase because of the intense photothermal effect.^[29] Moreover graphitization led to an increase of the absorption of the film in the Vis-NIR region as observed at weaker irradiation for human skin in the case of Immediate darkening.^[30] Indeed, the authors identified the process as a pure photothermal one although they stated that thermal annealing over 1000 K in the furnace of the PDA films yielded no graphitization. In our opinion the overall process is, indeed, a combination of photochemical and photophysical processes.^[31] Same opinion was proposed by Olejnik and coworkers who performed laser induced graphitization of PDA on titania nanotubes.^[32]

Broad band absorption, high biocompatibility and fast excited state non radiative deactivation make melanin derivatives ideal platform for photothermal application in nanomedicine, as in the case of cancer photothermal therapy PTT.^[33,34]

Biological tissues present in fact two windows NIR 1 and NIR 2 with enhanced transparency.^[35] Additionally, melanin materials produce efficient photoacoustic signal which can be exploited to image them in the tissues.^[36,37] PTT exploits hyperthermia produced by irradiating a photothermal agent (PTA) accumulated into the tumor. One limitation is hence that it works on large tumors which can be reached by NIR light irradiation but not on disseminated metastatic tumors. Hence combination of PTT with chemotherapy was considered. In this application photothermal effect was also reported to enhance the release of the chemotherapeutic agent.^[34] Nevertheless this mechanism was never investigated in detail. It's worth noticing that any possible photochemical action of melanin materials in phototherapy was, as far as we know, never considered in a systematic way. Mostly this is due to the fact that for phototherapy NIR excitation (typically 808 nm) is used and photo-reactivity of melanin like materials at this excitation wavelength was never systematically investigated.^[34] Nevertheless, photo-reactivity cannot be ruled out especially when fast pulsed excitation is used leading to possible two-photon absorption processes and hence to the production of high energy excited states similarly to what happens upon UVA excitation.

Photodynamic therapy (PDT) is a quite consolidated method for cancer phototherapy. This technique is based on the

photoexcitation of a specific molecule, the PS, which in the presence of oxygen produces ROS (Reactive Oxygen Species) damaging the cancer tissue in different ways. Although melanin related species were widely employed in the design of nano-platforms for PDT, they normally have a role different from the PS. According to the demonstrated photoactivity of PDA as PS in photopolymerization, in our opinion, a complete redesign of PDA based nanoplatform for PDT should be considered.

Finally, melanin derivatives have been often applied for fluorescence imaging. Nevertheless, according to our recent results PDA NP are not fluorescent while only smaller fragments of PDA are. Although this was in part already known it is not completely clear what is the fluorescence of these materials originated from.^[38]

Summary and Outlook

Reported examples clearly demonstrate the multiplicity of effects that light irradiation can produce on melanin. The complexity of the response of natural and biomimetic melanin to light exposure surely makes this material unique for the design of new photoactive agent for application in light energy conversion and storage, photochemical and photothermal catalysis and nanomedicine. Nevertheless, we believe this complexity deserves a systematic study which is still missing.

Photochemical or Photothermal?

Distinguishing photochemical and photothermal process is fundamental for the design of photo-responsive agents based on melanin. We strongly believe that the behavior of these melanin-based materials upon irradiation is often a synergic combination of photochemical and photothermal processes that should be analyzed separately for an optimal design. Discrimination can be based on irradiance dependent experiments as for other materials.^[39] Differently an unpredictable effect of light intensity, of the use of continuous or pulsed excitation, and of the excitation wavelength can be observed.

Which Photochemistry?

What is the mechanism of chemical response of melanin related materials to light? Formation of SQR is surely an intriguing possibility demonstrated by very convincing technique but is this process the only one? Indeed, in most cases the increase of SQR concentration upon light irradiation looks quite modest. Is this compatible with the level of photo-reactivity of these materials? What is really intriguing with this mechanism is that light irradiation would lead to an increase of the production of SQR which are ground state molecules with a very long lifetime. This may explain the effect on photoinduced process of diffusing molecules like oxygen which can interact only with long living species. Nevertheless, a question still needs a reply:

what is the effect of the irradiation on the SQR themselves?
How does this depend on the wavelength?

Oxygen, Water and pH?

If the effect of oxygen on the photoinduced process of melanin related materials can be in part explained, the role of humidity may seem to be even contradictory. For the reaction scheme of Figure 3 water consumption seems to increase upon light irradiation while in the case of the example of Figure 5 water is released upon irradiation. The reason of this apparent contradiction is that in the former case a photochemical process is considered while the second was interpreted as purely photo-thermal. On the other hand, this also makes even more necessary the capability of distinguishing photochemical from photothermal processes. Regarding pH, according to Figure 3 alkaline environment is expected to increase the rate of SQR formation upon irradiation. Nevertheless, although alkaline pH has been reported to lead to melanin degradation^[14] the combined effect of pH and irradiation has not been investigated yet.

In conclusion, we believe scientific literature demonstrated that interaction of natural and biomimetic melanin materials with light presents unique features and that these materials offer unprecedented possibilities for application in important fields such as energy conversion and storage and nanomedicine. Nevertheless, the complexity of the interaction of these materials with light still give origin to many questions we tried to summarize here. Replying to these questions would represent, in our opinion, a real breakthrough that would give scientists the key to fully exploit the incredible applicative potentiality of melanin related species.

Acknowledgements

The authors thank the project "Network 4 Energy Sustainable Transition-NEST" (European Union-NextGenerationEU - PE000021) and Ministero Italiano Università e Ricerca (MIUR) PRIN 2022 PNRR, PP20224N3WK (NANOTHERM). Open Access publishing facilitated by Università degli Studi di Bologna, as part of the Wiley - CRUI-CARE agreement.

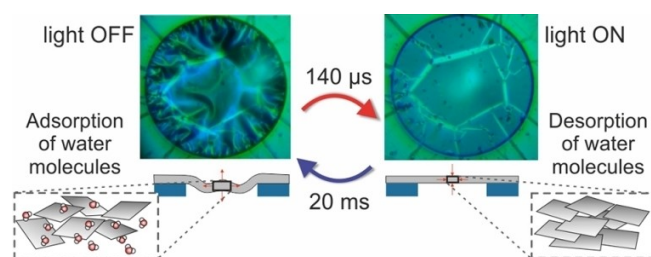


Figure 5. Optical images of PDA membrane contraction/expansion due to light-, heat- or moisture-induced desorption/adsorption of water molecules. The insets show the proposed microscopic lamellar-like structure that can adsorb (left) or desorb (right) water molecules from the atmosphere. Reproduced with permission from ref.^[28]

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Nanoparticles · Polydopamine · Biocompatibility · Photochemistry · Photothermal

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Manuscript received: February 1, 2024

Accepted manuscript online: September 17, 2024

Version of record online: October 31, 2024