

# PHOTOELECTROCHEMICAL PROPERTIES OF MELANIN

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Melanin is to the animal kingdom like chlorophyll to the vegetal kingdom<sup>1</sup>. Melanin collects energy from lower-energy radiation sources, kicks electrons into excited states, initiating a process that would end up producing chemical energy, similar to the way in which photosynthesis supplies energy to plants. However, the precise roles of melanin during this process are unknown. Here we show that the increase in the electron-transfer properties of melanin is independent of the energy of the incident photons. We found in controlled in vivo assays that melanin has the remarkable capability of converting lower-energy radiation towards a more useful form of energy. Furthermore, we found that melanin can break up water molecules and giving up energy suggesting an additional behavior mode for melanin. Our results demonstrate how members of the melanin family are likely to function as transducers, oxidizing water, pushing apart water molecules, as well as recruiting back ions into molecules that are subsequently polarized again. Melanin drives the photon energy of lower-energy radiation sources by quenching electrons and initiating an ionic event independently of their relative energy contention. We anticipate our assay to be a starting point for more sophisticated photoelectrochemical applications. For example, the individual and combined action of multiple photovoltaic applications could be tested, including conducting polymers, for example poly-(phenylenevinylene) (PPV) derivatives or C<sub>60</sub> particles. Furthermore, melanin's energy conversion ability is a major target of solar energy conversion development, and an organic-semiconductor way for photoelectrochemical applications will be relevant for such developments.

Organic active materials electronic circuits, displays, and sensors will enable a future generation of electronic products that may eventually enter the mainstream electronic market. The motivation in using organic active materials come from their ease in tweaking and matching electronic and processing properties by chemical design and synthesis, low cost processing based on low temperature processes, mechanical flexibility, and compatibility with flexible substrates<sup>2</sup>. Within these is the family of organic materials, "*The Melanins*". For the sake of simplicity "melanin" will be used in a generic and unqualified sense, referring primarily to a synthetic, dopa made form of eumelanin. Melanin can be envisaged as an energy transducer with the properties of an amorphous semiconductor; it can absorb many different types of energy and convert it in

another more useful type of energy. In a very enlightening paper, Michael Grätzel<sup>3</sup> looks into the historical background, present status and development prospects for a new generation of photovoltaic cells, the photoelectrochemical cells. Until now, the conversion of sunlight to electrical power has been dominated by solid state junction devices, often made of silicon. But this dominance we foresee will fall by the emergence of these new "melanin-compound" made photovoltaic cells, based on their here reported new photoelectrochemical, conducting, polymer type properties. Melanin offers the prospect of easy fabrication together with other attractive features, such as low cost. This extra special new property of melanin will result in a huge progress in fabricating photoelectrochemical cells and will open up whole new vistas of opportunity. Contrary to expectation, we have proven that some of the made by us new devices have strikingly high conversion efficiencies, which compete with those of conventional devices.

Melanin has proven to be an intractable system to study, in part due to their strong binding with a protein host under in vivo conditions. It is not understood whether this protein host is a left-over from the bio-synthesis, or whether it is crucial for the functionality. Strictly speaking, the term "melanin" should encompass both the chromophore and the associated protein. However, it has become the norm to use the term to refer only to the chromophore (the nominally functional part). The vast majority of studies on the natural system removes (or ignore) the protein and all studies on synthetic melanin involve the chromophore only. Unfortunately, the chromophores themselves are virtually insoluble in most common solvents, and have defied systematic attempts at characterization by standard analytical methods. The predominant strategy in the field is to study the photochemical and photophysical properties of isolated natural models or synthetic analogues without recourse to any consistent structural model.

Dopa-melanin was synthesized from DOPA (dihydroxyphenylalanine) following the auto oxidizing procedure<sup>4</sup>. There is a general agreement that melanin are macromolecules of 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA). The proportion of these two components in the final macromolecule varies depending upon the type of natural melanin or the synthetic route. Recently, melanin have attracted the attention of molecular biophysicists and the soft matter and functional organic materials communities.<sup>5</sup> melanin, possesses an intriguing and rather unique set of physicochemical properties: strong broad band UV and visible absorption; non-radiative conversion of photo-excited electronic states approaching unity (extremely low radiative quantum yield)<sup>6</sup>; powerful anti-oxidant and free radical scavenging ability<sup>7</sup>; and probably most bizarrely of all, electrical conductivity and photoconductivity in the condensed phase<sup>8-9</sup>. In relation to the last two properties, it has even been speculated that melanin may be a bio-organic semiconductors. In figure 1 it is shown the absorbance as a function of wavelength of a typical synthetic eumelanin aqueous (0.0025%/wt) solution<sup>10</sup>.

Our melanin samples have shown very interesting photoelectrochemical properties. The relation between activity-structure of this polymer was noticed as the result of our detailed observations in human retina in vivo, while studying the three main causes of blindness (glaucoma, diabetes, degeneration by age). We noticed the effect in glioma growth and angiogenesis of melanin presence in the ocular liquid, the oxygen content increased up to 34 % which did not come from ATP. We were initially trying to control angiogenesis by studying the proangiogenic and antiangiogenic factors and it is well known that one of the most antiangiogenic factors is a high level of oxygen<sup>11</sup>. Oxygen has a very important presence, and their quantity an activity is determinant in the evolution of these diseases. The explanation about their biological activity and presence in the ocular liquid can not be separated from melanin presence. Because there is not a clear understanding of how UV and visible radiation interacts with melanin's macromolecule to generate properties such as the monotonic broadband absorbance<sup>12</sup>. In an attempt to gain new insight into the dynamics of energy dissipation in melanin under physiological conditions, Forest and Simon<sup>13</sup> undertook a wavelength dependent photo acoustic study. They found (as per radiative quantum yield measurements) that the majority of absorbed energy is dissipated non-radiatively within a nanosecond of excitation. However, when the melanin was excited with 264 nm radiation c. 30% of the absorbed energy was retained for a period longer than a few hundred nanoseconds. This is an important contribution because it suggests that UV radiation with wavelengths below 300 nm generates a longer lived excited state with a significant yield, which in turn may result in excited state photochemistry, which does not occur under visible light stimulation.

The observations of their biological effects, allow us, to elucidate the protective effects on human retinal tissue of melanin, undoubtedly due to melanin's oxidizing effect on water, liberating oxygen and separating it from protonic-hydrogen. Melanin quenches the photons, and with this energy, breaks the water molecule; absorption of light by this pigment initiates an ionic event and a reaction that increases the level of oxygen 34 % in surrounding tissues and even higher in the ocular liquid. This increased energy event in the human eye is the first step to initiate the vision phenomenon. A great part of the photonic energy is transformed by melanin into chemical energy by means of hydrogen generation which acts as an energy carrier, and throughout the action of NADH and FADH, gives up this energy to the cell, finally the cell uses it to energize some of the main chemical reactions that enable vision. Without this energy; there is no vision at all. Melanin in the ocular fluid has an additional characteristic; it supports the opposite reaction, that is: back binding of hydrogen and oxygen and giving up water and electricity. Melanin in human eye is for animal kingdom what chlorophyll is for vegetal kingdom. Both molecules absorb photons, and initiate an ionic event with large metabolic consequences. The melanin's macromolecule solution retains these properties outside the eye for months, even years, unlike chlorophyll which is very unstable and totally inactive after 20 seconds outside the leaf. Melanin's function to other body structures, has shown to be essential too and its medical applications are huge but out of scope of this article.

We claim that photosynthesis exists not only in vegetables, but in animals too. Meredith<sup>14</sup> question – where has all the excess energy gone? – can be answered even without a satisfactory knowledge of the molecular structure of the pigment granules, by saying “just set up a couple of electrodes” and you’ll get melanin’s photoelectrochemical properties, to co-relate the measured potential to a specific chemical activity.

We proceeded to test the photo electrochemical properties of melanin by manufacturing a prototype cell (figure 2). We started with a very simple cell where the electrolyte was a 1.3% solution of melanin in distilled water, copper and aluminum electrodes 2.5 cm apart, copper wires (covered with silicon) were attached to the electrodes by glued them down, we noticed that any kind of welding affected the melanin’s behavior. The cell started to give up electricity just a few minutes after being ensemble.

The output was similar to that of dye-sensitized solar cells, the output was remarkably stable even under light soaking for more than 10,000 h. see figure 3. We believe that developing these prototypes could have a significant impact on the alternative energy sources research.

As Grätzel<sup>3</sup> says, the pioneering photoelectric experiments were done with liquid not solid state devices, the foundation of modern photoelectrochemistry was laid down by the work of Brattain and Garret<sup>15</sup> and subsequently Gerischer<sup>16</sup> who undertook the first detailed electrochemical and studies of the semiconductor–electrolyte interface. Research on photoelectrochemical cells went through a frantic period after the oil crisis in 1973, which stimulated a worldwide quest for alternative energy sources. Within a few years well over a thousand publications appeared (see ref. 17 for a list). Most of the investigations focused on two types of cells. The first type is the regenerative cell, which converts light to electric power leaving no net chemical change behind. Photons of energy exceeding that of the band gap generate electron–hole pairs, which are separated by the electric field present in the space-charge layer. The negative charge carriers move through the bulk of the semiconductor to the current collector and the external circuit. The positive holes are driven to the surface where they are scavenged by the reduced form of the redox relay molecule (R), oxidizing it:  $h^+ + R = Q$ . The oxidized form Q is reduced back to R by the electrons that re-enter the cell from the external circuit. Much of the work on regenerative cells has focused on electron-doped (n-type) II/VI or III/V semiconductors using electrolytes based on sulphide/polysulphide, vanadium(II)/vanadium(III) or  $I_2/I^-$  redox couples. Conversion efficiencies of up to 19.6% have been reported for multijunction regenerative cells<sup>18</sup>. The second type, photosynthetic cells, operate on a similar principle except that there are two redox systems: one reacting with the holes at the surface of the semiconductor electrode and the second reacting with the electrons entering the counter-electrode. In the example shown, water is oxidized to oxygen at the semiconductor photo anode and reduced to hydrogen at the cathode. The overall reaction is the cleavage of water by sunlight. Titanium dioxide has been the favored semiconductor for

these studies, following its use by Fujishima and Honda for water photolysis<sup>19</sup>. Unfortunately, because of its large band gap, (3–3.2 eV) TiO<sub>2</sub> absorbs only the ultraviolet part of the solar emission and so has low conversion efficiencies. Numerous attempts to shift the spectral response of TiO<sub>2</sub> into the visible, or to develop alternative oxides affording water cleavage by visible light, have so far failed. The width of the band gap is the key about the prospects of photoelectrochemical cells being able to give rise to competitive photovoltaic devices, as those semiconductors with band gaps narrow enough for efficient absorption of visible light. The width of the band gap is a measure of the chemical bond strength. Conducting polymers, for example poly-(phenylenevinylene) (PPV) derivatives or C<sub>60</sub> particles, are attracting great interest as photovoltaic materials<sup>20-25</sup>. Bulk donor-acceptor heterojunctions are formed simply by blending the two organic materials serving as electron donor (p-type conductor) and electron acceptor (n-type conductor). The advantage of these new structures over the flat-junction organic solar cells investigated earlier<sup>20</sup> is the interpenetration of the two materials that conduct positive and negative charge carriers, reducing the size of the individual phase domains to the nanometers range. This overcomes one of the problems of the first generation of organic photovoltaic cells: the unfavorable ratio of exciton diffusion length to optical absorption length. An exciton is a bound electron-hole pair produced by absorption of light; to be useful, this pair must reach the junction and there dissociate into two free charge carriers — but excitons typically diffuse only a few nanometers before recombining. Light is absorbed (and generates excitons) throughout the composite material. But in the composite, the distance the exciton has to travel before reaching the interface is at most a few nanometers, which is commensurate with its diffusion length. Hence photo-induced charge separation can occur very efficiently. Conversion efficiency from incident photons to current of over 50% has been achieved with a blend containing PPV and methanofullerene derivatives<sup>21</sup>. The overall conversion efficiency from solar to electric power under full sunlight achieved with this cell was 2.5%. Although these results are impressive, the performance of the cell declined rapidly within hours of exposure to sunlight<sup>22</sup>. In contrast, the output of dye-sensitized solar cells is remarkably stable even under light soaking for more than 10,000 h. similar long-term stability will be required for large-scale application of polymer solar cells.

## DISCUSSION

The second order structure array must be a graphite type array, that appear to be composed not of a single chromophore type (whether they be extended polymeric or smaller oligomeric systems), but rather of ensembles containing a range of chemically distinct macromolecules (chemical disorder model). Whatever the situation is this stacked oligomeric 'proto-molecules' consisting of indolequinone units (we claim, they could easily be polyhydroindole, figure 4), arranged<sup>14</sup> as figure 5 that appears to agree with the early X-ray diffraction studies of Thathachari and Blois<sup>26</sup>. Will favor the formation of molecular orbital arrangement, and we foresee that, this arrangement between layers will

accommodate the oxygen in such a way with the nitrogen that will generate a very strong competition between them to produce protons; once a proton is created the absorbed photon will provide the necessary energy to recombine the water molecule with the concomitant product of an electron flow.

We should also not ignore the possibility that once the structure-property problem is properly solved, designing melanin-inspired functional materials becomes a real possibility for applications in organic sensors and optoelectronics.

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Figure 1. Absorbance as a function of wavelength of a typical synthetic eumelanin aqueous solution (0.0025%/wt). The same data is shown on a log-linear plot in the inset demonstrating the excellent fit of the raw data to an exponential form.

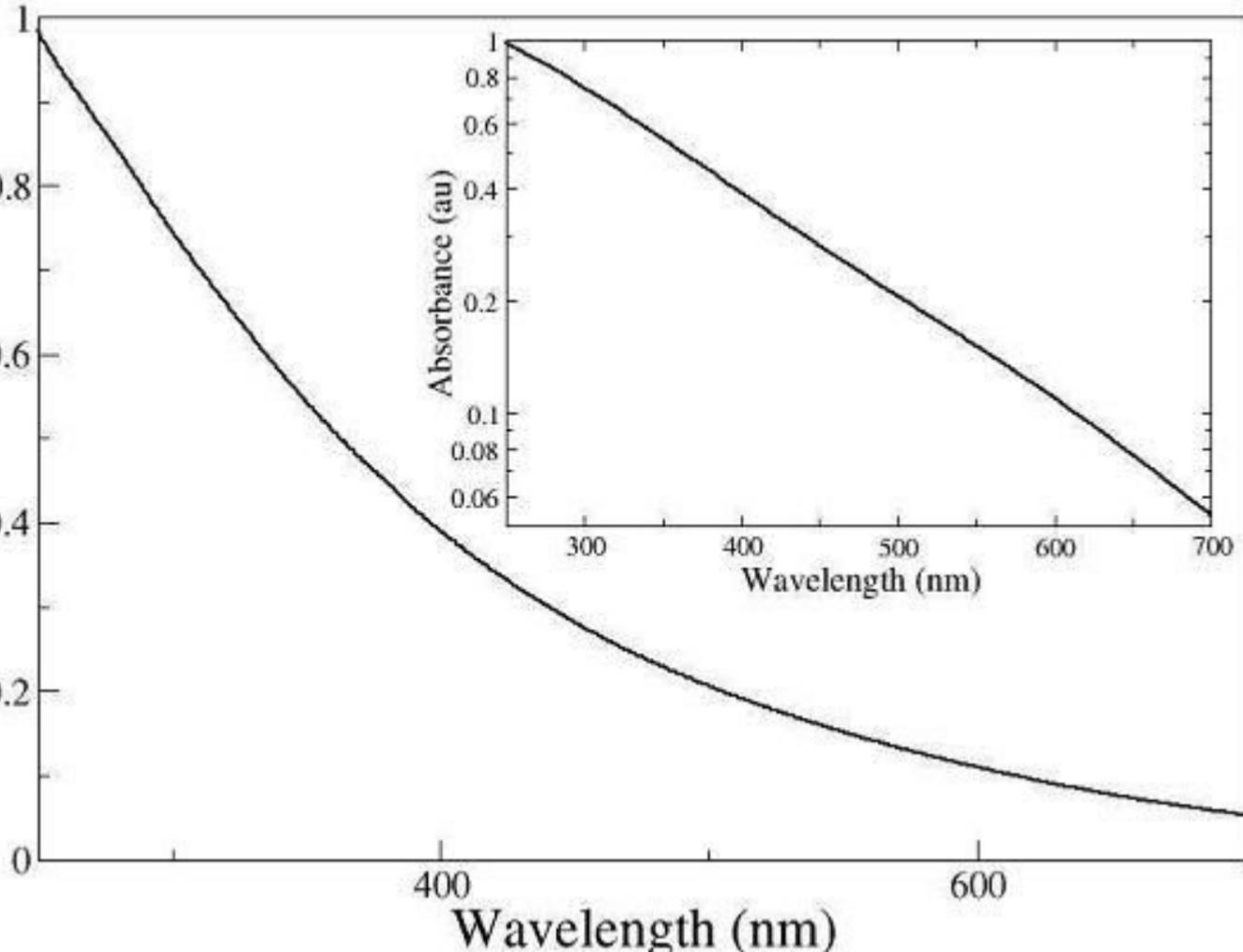
Figure 2. Melanin photoelectrochemical cell and its energy output

Figure 3. A LED which has been working for more than 10,000 h.

Figure 4. Polyhydroxindole

Figure 5. Stacked oligomeric 'proto-molecules' consisting of indolequinone units.

Absorbance (au)



Wavelength (nm)



Nature Precedings : <http://dx.doi.org/10.1016/j.npre.2007.1312.1> ; Posted 12 Nov 2007



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