Electrochemical behaviour of ZnO/flavonoid pairs

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Abstract

The last years are witnesses of continuous raise in the price of traditional fuels. This fact, joined to environmental concerns and the fears concerning the inevitable oil reserves depletion, have empowered the search for new energetic sources. Organic photovoltaic cells or Grätzel cells are a solution for collecting solar energy. Searching for new materials for this type of solar cells is normally a trial-and-error procedure. Assembling components to make a solar cell in the laboratory, is a difficult and expensive task. In this work it is studied the electrochemical behaviour of substances that can be used as sensitizers in solar photovoltaic cells when in contact with a given semiconductor. This procedure can simplify the process of joining a new dye/semiconductor pair with optimum performance when designing new photovoltaic cells.

Keywords: ZnO, nanostructures, semiconductor/dye interface, flavonoid

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1. Introduction

The nowadays “mature” technologies for solar energy harvesting include two basic types. The first type, and more developed one, is based on solar cells made from silicon or divalent metal chalcogenides (CdTe, $Cd_xZn_{1-x}Se$, CdS), as well as combination of elements of groups III and V of the Periodic Table (GaAs,$Ga_xIn_{1-x}P$, InP, etc.) (1; 2). Alternative, efficiency can be improved by stacking individual layers of several of these materials. The second type is the development of Grätzel cells (3; 4). In this type of cells, an organic molecule able to pass to an excited electronic state in the presence of electromagnetic radiation, losses this excessive energy by donating electrons to a semiconductor.

First released in 1991 with an efficiency of 7.1 %, this initial Grätzel cell efficiency was improved continuously and several years later its efficiency is above 11 % (4). Nowadays it is commonly accepted that these cells can have a similar efficiency to the conventional silicon cells, and may reach, theoretically, an approximate yield of 27% (4; 5; 6; 7).

After the initial success of the organic solar cells, several improvements were tried. Amongst these improvements are noticeable the use of different semiconductors, such as ZnO (8; 9) or InP (10), in order to replace the widely used TiO_2. On the other hand, several authors have substituted the initially used organometallic complexes by natural or nature-inspired materials as quercetin (10), carotenoids (11) or phtalocyanins (8; 12).

It has been claimed that natural dyes work poorly in this type of cell, when compared with synthetic, structure-tailored ones. But it seems an inexact idea, as a pair semiconductor/dye will display a maximum performance if their orbital levels matching is adequate (13; 14). In this line of reasoning Kumara's group have published several papers dealing with the role of doping, or at least surface modifications in the efficiency of solar cells (6; 15; 16). In part inspired in these facts, several studies have been appeared having the purpose of characterising the solid-liquid interface involving semiconductors (10; 17; 18; 19; 20).

There is not an *a priori* method to test the harvesting suitability of semiconductor/dye pairs, Cook and co-workers (14; 21) have tried to correlate results of x-ray absorption spectroscopy with DFT studies in order to understand the shift of the transition energies observed by NEXAFS in a series of metal complexes with porphyrins. Moreover, they intended to calculate the position of the LUMOs of these molecules. However, here is tried another approach based on the redox characteristics of flavonoids. Then, the main objective in this work is to study electrochemically several ZnO/dye pairs, in order to verify if the electron transfer in these systems are observable in cyclic voltammetric experiments. This approach have been used before (see (22)), but still lacks of systematisation. Another objective of this work is to generate data that can be useful for the purpose of knowledge systematisation of the use of electrochemical techniques for performance prediction of organic photovoltaic cells. The validity of the electrochemical approach from the orbitalic point of view will be tested by comparing the experimental data here collected with the result of semiempirical calculations.

2. Experimental

7-hydroxyflavone, 7-methoxyflavone and 3,7-dihydroxyflavone were all from Sigma-Aldrich, KI was from BDH and I_2 was from Aldrich. The supporting electrolyte was KI_3 prepared with the molar ratios $0.05M\,I_2\,and\,0.5M\,KI$ in deionised water. All the solutions were prepared by dissolving $0.01\,mol$ of the desired flavonoid in $10\,ml$ of deionised water, then adding $5\,ml$ of the supporting electrolyte and completing $25\,ml$ with deionised water. No pH buffer was used.

The preparation of ZnO films has been described elsewhere (23). In brief, $Zn(NO_3)_2$ precursor solutions were spin-coated on commercial aluminium substrate. These substrates were dried at 150 °C, after each deposition cycle. Finally the overall dried films were heated at 300 °C to promote phase formation. Then ZnO nanostructures were grown on the top of this initial film. The usual way to attach nanostructures to a surface generally implies several depositions and transformation steps, normally by expensive techniques as chemical vapour deposition or electrooxidation (reduction), followed by etching ofthe so obtained surfaces (see (28; 29; 30; 31)), among others. However, the procedure already developed in our group (23) allows the formation of ZnO "mugs" by a cheap and fast spin-coating deposition of a sol-gel precursor solution (see Figure 2). With this method the surface covering by a very thin film was nearly 100% as found by SEM analysis. At the same time an important area of that surface is covered by these peculiar mug-shaped nanostructures.

Cyclic Voltammetry measurements were carried out in a home-made potentiostat apparatus (see scheme in Figure 1). The control software for this cyclic voltammeter was made in GNU C++ 4.0. The behaviour of this home-made apparatus was compared with the behaviour of a GAMRY Reference 600 potentiostat (24). A scheme of this equipment is shown in Figure 1.

Semiempirical PM3 optimization of the molecules were carried out. For this purpose, chemical structures were generated by the Gabdit GUI package (25). The GAMESS package (26), which follows the original MOPAC coding (27) was used for these calculations. Even when the PM3 method is somewhat inaccurate and inferior in predictive quality when compared to the nowadays affordable DFT methods. However, PM3 parametrization was used because is a very fast method, that give quick results aiming to direct future studies.

3. Results and Discussion

The "mug" shape of the obtained nanostructured films, allows large surface area. This large surface area ensures an appreciable electron transfer from the solution to the electrode. However, it is known that several properties such as electron confinement or band structure, are different when passing from bulk materials to nanostructures. This fact affects the orbital matching between the semiconductor and the dye, and there is not an easy way to predict the final band structure of a nanostructured material (32; 33).

The cyclic voltammetry of 7-hydroxyflavone at a glassy carbon electrode (Figure 3) under illumination, apparently shows two reduction peaks at around 0.05 and $0.3V$, respectively, versus an Ag/AgCl reference electrode. This can be explained taking into account resonant equilibrium, which allows two ring positions that can be oxidized/reduced, as shown in Figure 4 (top). A similar experiment but without illumination shows a single peak at $0.05\,V$. In the experiment performed under illumination, the electronic transfer processes are favoured, as evidenced (Figure 3) by the higher amounts of electric current passing for the system at these two voltages (0.05 and $0.3V$,), and by the faster increase of the passing current at electric potentials higher than $0.7\,V$. Some experimental work is being carried to clarify the nature of the observed peaks. However it is our opinion that the peak at $0.3V$ corresponds to the carbonyl group at position 4, which is the most oxidized group. Moreover, the peak the 0.05 must be due to the reduction of one of the bonds of the oxygen situated at position 1, but we have not obtained clear experimental information to confirm these assumptions . The process seems to be highly irreversible because the peaks disappeared after 7-15 cycles, indicating a progressive consumption of the original flavonoid. Probably, this can be a consequence of some transformation on the flavonoid rings. Some of these transformations for the A-ring were observed by Krishnamachari and coworkers (34) and are depicted in Figure 5 for the case of kaempferol oxidation. Finally, in Figure 3 it is also observed the behaviour of the glassy carbon electrode with the support electrolyte (marked as “Water”). As can be seen there is no appreciable electrochemical processes occurring in the support electrolyte when compared with the magnitude of the results obtained when 7-hydroxyflavone was used.

When the glassy carbon electrode is substituted by a ZnO/Al electrode (Figure 6) two principal changes are observed: first, at electrode potentials lower than $-0.55V$, it is observed a rectifying effect, characteristic of a semiconductor material and second, higher amounts of charges are allowed to pass across the electrode. In the same Figure 3, it is also observed the cyclic voltammetry of the support electrolyte at the same ZnO/Al electrode (marked as "Water") and as expected, no net electrochemical redox phenomena is observed.

This behaviour was described by Hoyer and Weller (35), who observed that when the dye is added to the supporting electrolyte several processes related to anodic-type current appeared. These processes are evidenced as a photocurrent related activity. Appearing in the interval +500 and -200 mV, these photo-currents are absent in the experiments carried out with the supporting electrolyte alone (marked as "Water" in Figure 6).

In Figure 7 is shown the results of the cyclic voltametry of 7-methoxyflavone at a glassy carbon electrode. The differences between the process in dark and under illumination, in 7 methoxyflavone is less pronunciated when compared with the case of 7-hydroxyflavone. It can be rationalized that 7-methoxyflavone is a poorer sensitizer compound than 7-hydroxyflavone is.

However, in this case it is observed only one reduction peak at approximately at $0.3V$ versus the Ag/AgCl reference electrode. As in 7-methoxyflavone there is a methyl group attached to the oxygen atom at position *7*, stable resonant structures like those described for 7-hydroxyflavone does not exist (See Figure 4, bottom), then the type of equilibrium described for 7-hydroxyflavone cannot be afforded. The same irreversibility of the described peaks, already described in the case of 7-hydroxyflavone, is observed here.

When 7-methoxyflavone is in contact with a ZnO/Al electrode (Figure 8) a similar situation arises, i.e., a noticeable separation between the direct and the inverse processes is observed. In this case, the charge migrating into or out of the solution is lower than in the case of 7-hydroxyflavone. Besides, as in the previous case, no well defined peaks are observed.

The cyclic voltammetry of 3,7-dihydroxyflavone at a glassy carbon electrode (Figure 9) shows a complex pattern in the region $0.05 - 0.4V$. This pattern accounts for the presence of three groups which are able to be oxidized and/or reduced. Those groups are the hydroxyl moieties at positions 3 and 7 and the carbonyl group at position 4. This pattern agrees with the observed ones in the previous experiments for 7-hydroxy- and 7-methoxyflavone.

Figure 10 shows the cyclic voltamogram of 3,7-dihydroxyflavone at a ZnO electrode in dark and under illumination. As in the case of 7-hydroxyflavone and 7-methoxyflavone, there is a difference in charge transfer between the direct and the inverse processes. Besides, like in the 7-hydroxyflavone and

7-methoxyflavone cases, the intensity of the current is higher when illumination was used.

Figure 11 shows the relationship between the HOMO and LUMO of the here studied flavonoids and those of the ZnO (as an estimate for the energetics of its conduction and valence bands). As can be seen the LUMO orbitals are situated at higher energetic level of the ZnO LUMO. Then, when ZnO electrodes are used, a closed relationship exists between the flavonoid orbitals and the semiconductor orbitals (13). This fact makes possible the promotion of an electron from the excited orbitals of the dyes into the ZnO conduction band. As expected by the experimental trends, 7-hydroxyflavone is the flavonoid in which the LUMO energy is closest to the conduction band of ZnO while 3,7-dihydroxyflavone is the flavonoid with more differences between these two energy levels. The HOMOs of ZnO and the 7-hydroxyflavonoid are very similar energetically. This similarity promotes maximum interaction between these chemical entities. Moreover, minimum energy offset of these orbitals controls the losses of the charge separation and increases the open circuit voltage (14). When under illumination, electrons jumps more easily to excited states. In these cases, if a good match between donor and acceptor orbitals exists, higher electrical current intensity are expected.

4. Conclusions

Flavonoids as redox substances have irreversible reduction peaks observed cyclic voltammetry at glassy carbon electrodes experiments. However, the same experiment at ZnO electrodes shows a very different behaviour. As expected, the rectifying effect of the semiconductor is observed in the experiments performed. This behaviour can be described, as a suppression of the electronic conduction at electric fields lower than $0.0\,V$. This account for some electrical processes do not involving a true oxidation or reduction of the participating species. Even when no oxidation or reduction peaks are observed, this separation between the curves accounts for electrical polarization differences of the molecules at the semiconductor surface.

Ssemi-empirical calculations are considerate as moderately accurate tools for predicting the behaviour of complex chemical systems. However the results of our calculations shows a good correlation with the experimental results..

5. Acknowledgments

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[1] J.D. Beach, R.T. Collins, and J. A. Turner. Band-Edge potentials of n-Type and p-Type GaN. *Journal of The Electrochemical Society*, 150(7):A899–A904, July 2003.

[2] B.A. Gregg and M.C. Hanna. Comparing organic to inorganic photovoltaic cells: Theory, experiment, and simulation. *Journal of Applied Physics*, 93(6):3605–3614, March 2003.

[3] B. O'Regan and M. Grätzel. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. *Nature*, 353(6346):737–740, October 1991.

[4] M. Grätzel. Solar energy conversion by Dye-Sensitized photovoltaic cells. *Inorganic Chemistry*, 44(20):6841–6851, October 2005.

[5] A. Hagfeldt, G. Boschloo, H. Lindström, E. Figgemeier, A. Holmberg, V. Aranyos, E. Magnusson, and L. Malmqvist. A system approach to molecular solar cells. *Coordination Chemistry Reviews*, 248(13-14):1501–1509, July 2004.

[6] G.R.R.A. Kumara, K. Tennakone, I.R.M. Kottegoda, P.K.M. Bandaranayake, A. Konno, M. Okuya, S. Kaneko, and K. Murakami. Efficient dye-sensitized photoelectrochemical cells made from nanocrystalline tin(IV) oxidezinc oxide composite films. *Semiconductor Science and Technology*, 18(4):312–318, 2003.

[7] M.D.K. Nazeeruddin and M. Grätzel. Conversion and storage of solar energy using dye-sensitized nanocrystalline TiO2 cells., 2004.

[8] G.D. Sharma, R. Kumar, S.K. Sharma, and M.S. Roy. Charge generation and photovoltaic properties of hybrid solar cells based on ZnO and copper phthalocyanines (CuPc). *Solar Energy Materials and Solar Cells*, 90(7-8):933–943, May 2006.

[9] C.-Y. Chou, J.-S. Huang, C.-Y. Lee, and Chi.-F. Lin. ZnO nanorod-based polymer solar cells with optimized electrodes. In *Optical MEMs and Nanophotonics, 2008 IEEE/LEOS Internationall Conference on*, pages 100–101, 2008.

[10] Ö. Güllü and A. Türüt. Photovoltaic and electronic properties of quercetin/p-InP solar cells. *Solar Energy Materials and Solar Cells*, 92(10):1205–1210, October 2008.

[11] E. Yamazaki, M. Murayama, N. Nishikawa, N. Hashimoto, M. Shoyama, and O. Kurita. Utilization of natural carotenoids as photosensitizers for dye-sensitized solar cells. *Solar Energy*, 81(4):512–516, April 2007.

[12] V.P. Singh, B. Parsarathy, R.S. Singh, A. Aguilera, J. Anthony, and M. Payne. Characterization of high-photovoltage CuPc-based solar cell structures. *Solar Energy Materials and Solar Cells*, 90(6):798–812, April 2006.

[13] F. De Angelis, A. Tilocca, and A. Selloni. Time-Dependent DFT study of [Fe(CN)6]4- sensitization of TiO2 nanoparticles. *Journal of the American Chemical Society*, 126(46):15024–15025, November 2004.

[14] Peter L Cook, Xiaosong Liu, Wanli Yang, and F. J Himpsel. X-ray absorption spectroscopy of biomimetic dye molecules for solar cells. *The Journal of Chemical Physics*, 131(19):194701–194701–10, 2009.

[15] G.R.R.A. Kumara, K. Tennakone, V.P.S. Perera, A. Konno, S. Kaneko, and M. Okuya. Suppression of recombinations in a dye-sensitized photoelectrochemical cell made from a film of tin IV oxide crystallites coated

with a thin layer of aluminium oxide. *Journal of Physics D: Applied Physics*, 34(6):868–873, 2001.

[16] G.R.A. Kumara, M. Okuya, K. Murakami, S. Kaneko, V.V. Jayaweera, and K. Tennakone. Dye-sensitized solid-state solar cells made from magnesiumoxide-coated nanocrystalline titanium dioxide films: enhancement of the efficiency. *Journal of Photochemistry and Photobiology A: Chemistry*, 164(1-3):183–185, June 2004.

[17] J.F. Gibbons, G.W. Cogan, C.M. Gronet, and N.S. Lewis. A 14% efficient nonaqueous semiconductor/liquid junction solar cell. *Applied Physics Letters*, 45(10):1095–1097, November 1984.

[18] K.B. Yoon. Electron- and charge-transfer reactions within zeolites. *Chemical Reviews*, 93(1):321–339, January 1993.

[19] M.V. Lebedev. Passivation at semiconductor/electrolyte interface: Role of adsorbate solvation and reactivity in surface atomic and electronic structure modification of III-V semiconductor. *Applied Surface Science*, 254(24):8016–8022, October 2008.

[20] N.S. Lewis. Chemical control of charge transfer and recombination at semiconductor photoelectrode surfaces. *Inorganic Chemistry*, 44(20):6900–6911, October 2005.

[21] Peter L Cook, Wanli Yang, Xiaosong Liu, Juan Mara Garca-Lastra, Angel Rubio, and F. J Himpsel. Unoccupied states in cu and zn octaethyl-porphyrin and phthalocyanine. *The Journal of Chemical Physics*, 134(20):204707–204707–7, 2011.

[22] O. Dvorak, A.H. De Armond, and M.K. De Armond. Photoprocesses at the liquid-liquid interface. 3. charge transfer details for photoactive metal complexes. *Langmuir*, 8(2):508–513, February 1992.

[23] P.A.R. Tafulo, M. Ferro, A. Guerreiro, and G. González-Aguilar. Engineering the crystal growth behavior: "On substrate" MOD formation of ZnO hollow spheres. *Applied Surface Science*, 256(10):3281–3285, March 2010.

[24] F.M.F. Mota. *Plataforma de medio para sensores electroqumicos.* PhD thesis, University of Porto, 2008.

[25] A.-R. Allouche. Gabedit: A graphical user interface for computational chemistry softwares. *Journal of Computational Chemistry*, 32(1):174–182, 2011.

[26] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, Sh. Su, T.L. Windus, M. Dupuis, and J.A. Montgomery. General atomic and molecular electronic structure system. *Journal of Computational Chemistry*, 14(11):1347–1363, 1993.

[27] J.J. P Stewart. MOPAC: a semiempirical molecular orbital program. *Journal of Computer-Aided Molecular Design*, 4:1–103, 1990. 10.1007/BF00128336.

[28] C.H.Bae, S.M. Park, S.-E. Ahn, D.-J. Oh, G.T. Kim, and J.S. Ha. Sol-gel synthesis of sub-50 nm ZnO nanowires on pulse laser deposited ZnO thin films. *Applied Surface Science*, 253(4):1758–1761, December 2006.

[29] J.B. Cui and U.J. Gibson. Electrodeposition and room temperature ferromagnetic anisotropy of co and ni-doped ZnO nanowire arrays. *Applied Physics Letters*, 87(13):133108–3, 2005.

[30] X.-J. Huang and Y.-K. Choi. Chemical sensors based on nanostructured materials. *Sensors and Actuators B: Chemical*, 122(2):659–671, March 2007.

[31] Kwon, Park, and Park. Selective growth of ZnO nanorods by patterning of sol-gel-derived thin film. *Journal of Electroceramics*, 17(2):455–459, December 2006.

[32] T. Ghoshal, S. Kar, and S. Chaudhuri. ZnO doughnuts: controlled synthesis, growth mechanism, and optical properties. *Crystal Growth & Design*, 7(1):136–141, January 2007.

[33] A. Kara and T. S. Rahman. Vibrational dynamics and thermodynamics of surfaces and nanostructures. *Surface Science Reports*, 56(5):159–187, January 2005.

[34] V. Krishnamachari and and P. W. Pare L.H. Levine. Flavonoid oxidation by the radical generator AIBN: a unified mechanism for quercetin radical scavenging. *Journal of Agricultural and Food Chemistry*, 50(15):4357–4363, 2002.

[35] P. Hoyer and H. Weller. Potential-Dependent electron injection in nanoporous colloidal ZnO films. *The Journal of Physical Chemistry*, 99(38):14096–14100, 1995.

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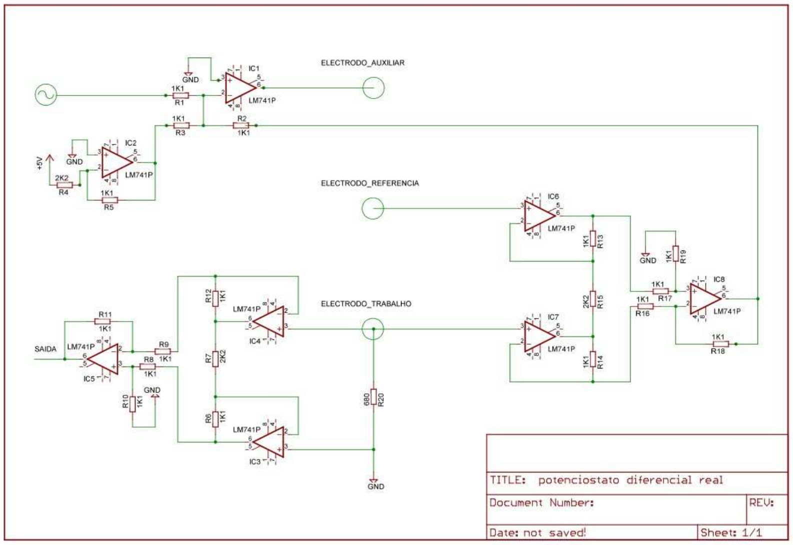

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Figure 1: Diagram of the cyclic voltammeter here used

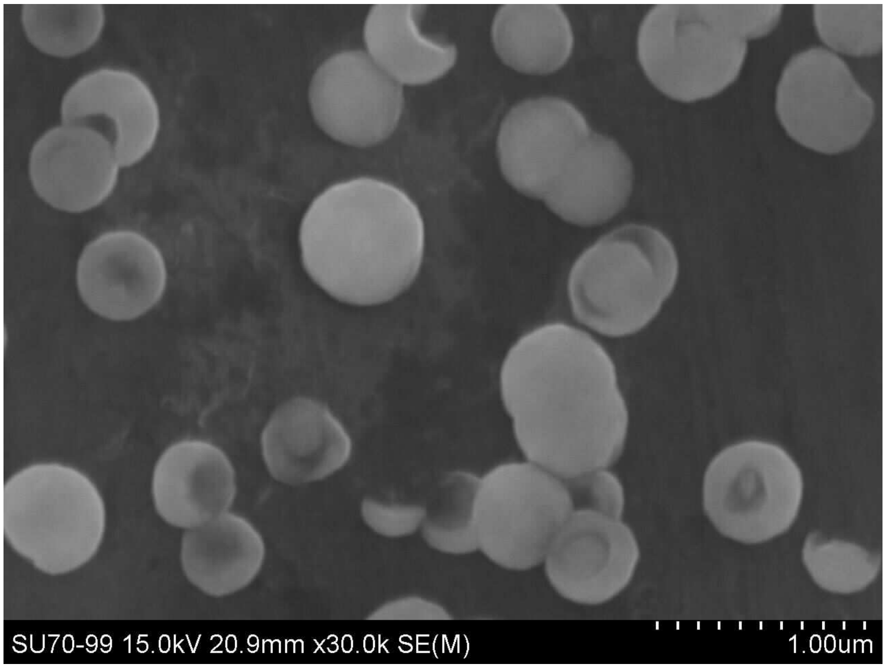

Figure 2: SEM micrograph of the obtained ZnO nanostructures

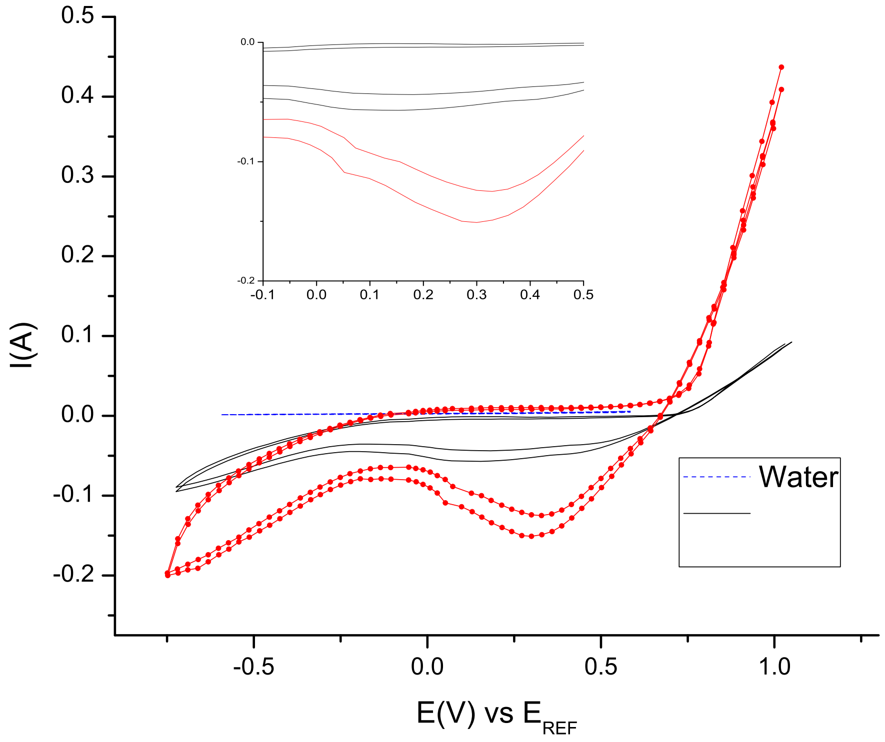

Figure 3: Cyclic Voltamogram of 7-hydroxyflavone at a glassy carbon electrode in dark and under illumination

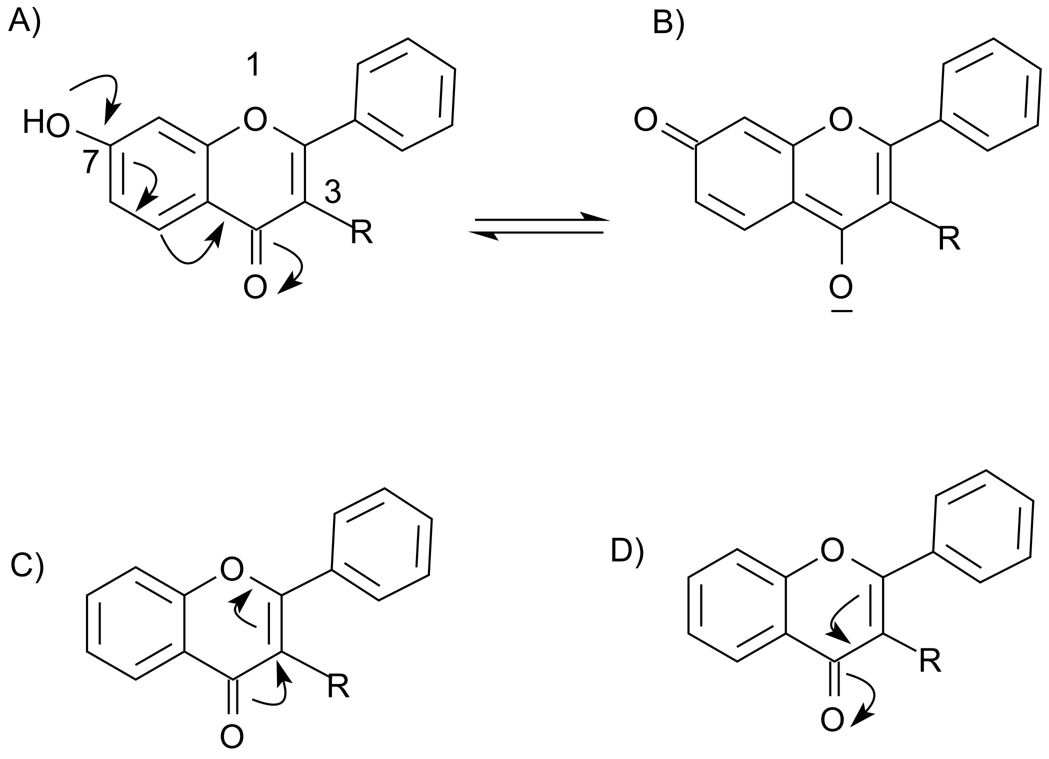

Figure 4: Estability of resonant structures in hydroxylated flavonoids. Flavonoids hydroxylated at position 7 (A) have stable resonant structures (B). In 3-hydroxyleted flavonoids, C) and D) no stable resonant structures are possible when the same logic is applied (position of interest marked with numbers in A)

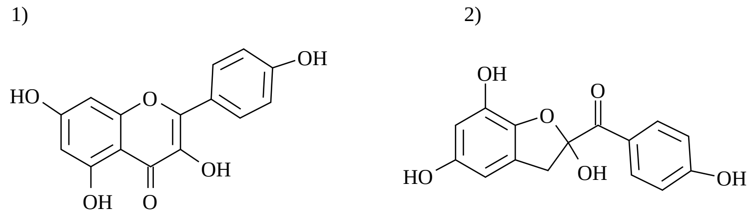

Figure 5: Kaempferol 1) and A-ring transformation in an oxidized kaempferol (see (34)).

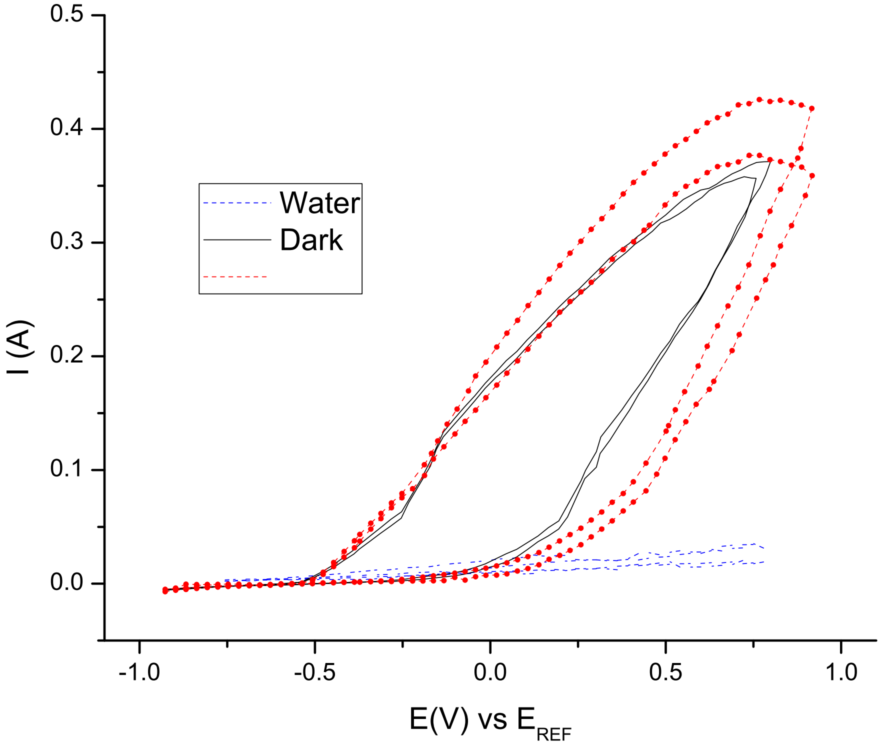

Figure 6: Cyclic Voltamogram of 7-hydroxyflavone at a *ZnO* electrode in dark and under illumination

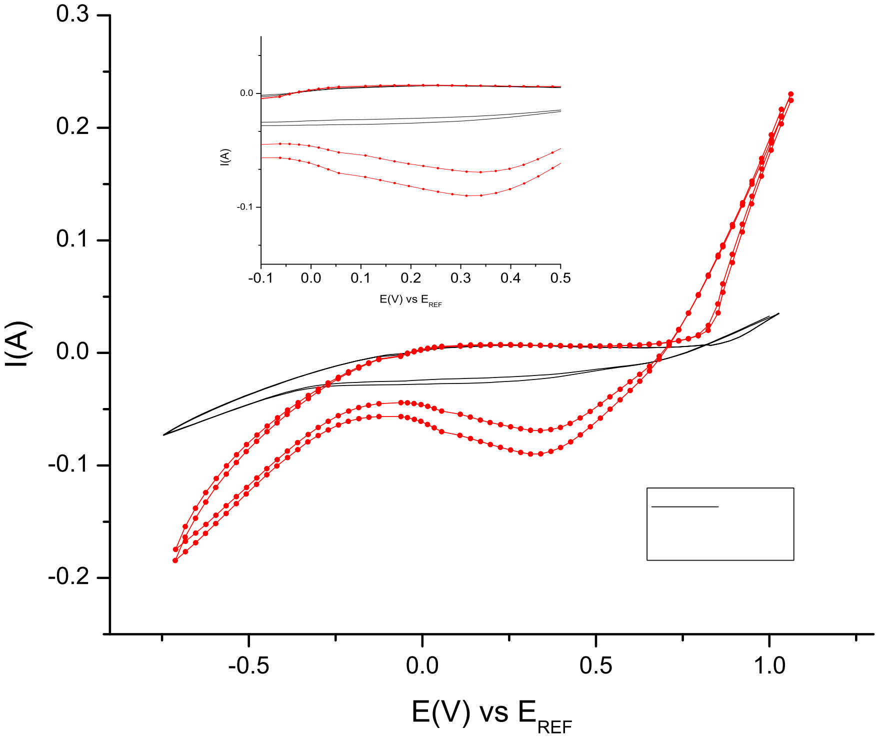

Figure 7: Cyclic Voltamogram of 7-methoxyflavone at a glassy carbon electrode in dark and under illumination

Figure 8: Cyclic Voltamogram of 7-methoxyflavone at a ZnO electrode in dark and under illumination

Figure 9: Cyclic Voltamogram of 3,7-dihydroxyflavone at a glassy carbon electrode in dark and under illumination

Figure 10: Cyclic Voltamogram of 3,7-dihydroxyflavone at a ZnO electrode in dark and under illumination

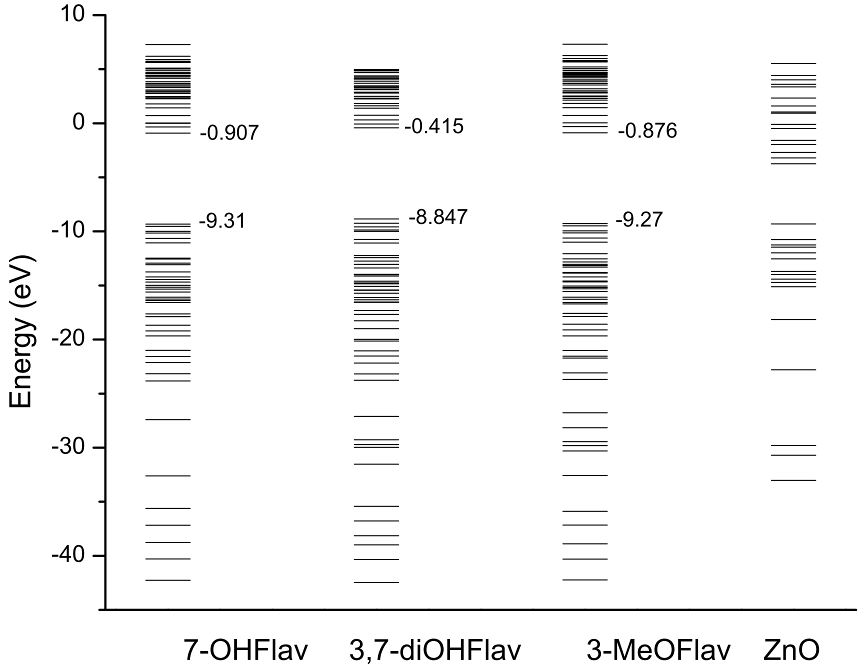

Figure 11: PM3 calculated electronic orbitals for ZnO and the flavonoids here studied. Top number are LUMOs energies and bottom ones are HOMOs