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Influence of the Adsorption of Phycocyanin on the Performance in DSS Cells: and Electrochemical and QCM Evaluation

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The influence of some coadsorbents and different pH values on the efficiency of DSS cells assembled with phycocyanin was evaluated using quartz crystal microbalance (QCM) and electrochemical techniques as impedance spectroscopy (EIS) and cyclic voltammetry (CV). Chlorophyll, heptadecanoic acid and 7.5 or 8.5 pH values were applied when nanostructured TiO_2 electrode was dipped in the dye solution. Best efficiency conversion values were obtained when using fatty acids as coadsorbents, reaching a conversion efficiency of 0.04 % for open cells.

Keywords: DSSC, phycocyanin, coadsorbents, QCM, EIS

1. INTRODUCTION

Dye sensitized solar cells (DSSC) or Grätzel cells are interesting alternative photovoltaic cells to silicon based devices, with conversion efficiency quite close to those get with commercial ones, and without the disadvantages linked to the extraction of silicon [1-6].

In the beginning, they were based on natural dyes as those used by plants in photosynthetic paths. They resemble natural photosynthesis, using organic dyes to harvest the incident light and then leading to charge separation, followed by a flow of electrons [7-9].

Even when literature on the topic showed a great increase in the last years, the use of natural dyes still represents an attractive alternative to silicon ones. The low cost of fabrication of cells based on their use, besides the environmental benefits related to their employment, makes them especially interesting for emergent countries.

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It was reported that natural dyes based cells showed efficiencies values until 2 %, with good stability. Many natural dyes extracted from flowers, leaves, fruits and beverages are used as sensitizers for DSSC. Anthocyanins, chlorophyll, xanthophyll, flavones and carotene are examples of compounds responsible for the absorption peaks present at such natural species [10-15].

Previously, we reported the evaluation of the use of phycocyanin from Spirulina spp. as sensitizer for DSSC. Phycocyanin, an accessory pigment to chlorophyll, is a pigment-protein complex from the light-harvesting phycobiliprotein family, along with allophycocyanin and phycoerythrin. The blue phycocyanin has promising characteristics to be use in such devices [16]. High extinction coefficients ($2.3 \cdot 10^5$ L $mol^{-1}cm^{-1}$ at 615 nm), in addition to suitable redox potentials (Eox = 1.2 V vs. Ag/AgCl) and a value of 1.96 V for $E_{0,0}$ (i.e., the energy difference between the vibrationally relaxed levels of the first electronic excited state, S1, and the ground state, S0), predicts electron transfer with anatase-TiO_2 and I^-/I_3^- from the electrolyte.

Nevertheless, after dipping the working electrode in the phycocyanin containing solution, the amount of adsorbed protein is very low, affecting the efficiency of the assembled cell. Two main reasons could explain such behavior: the protein is soluble in water, a solvent that can also be very easily adsorbed to anatase, and it is a big size compound (36 kDa) made of two subunits.

For this reason, the aim of this work was to evaluate the addition of coadsorbents as chlorophyll or heptadecanoic acid, and two different working pH values, 7.5 or 8.5, when phycocyanin solutions are used to sensitize the nanostructured TiO_2 of the working electrode. Modification of electrode surface using other compounds that adsorbs easily than the protein, or modification of protein charge, could affect the adsorption of the phycocyanin onto TiO_2 containing electrodes. Moreover, pH increase could affect electron transfer towards the TiO_2, because Fermi energy levels depend on pH values.

2. EXPERIMENTAL PART

MilliQ water and reagent grade chemicals were used without further treatment.

Phycocyanin was extracted from commercial capsules of Spirulina spp. The content of three capsules (about 1 g) was mixed with 20 ml of water, and then the mixture centrifuged at 5000 g for 20 min. When desired, the solution was purified using exclusion chromatography with Sephadex G-25.The procedure is followed by UV-Visible measurements, and the fraction with the highest Abs621/Abs280 ratio was selected. Protein concentration after exclusion chromatography was ca. 4 μM.

Chlorophyll a was extracted from the same commercial capsules as phycocyanin, and then added to to the solution containing the phycocyanin protein (molar ratio 27 to 1). If desired 1 mM heptadecanoic acid (SIGMA, ≥ 98 %) solution was added to the dipping solution.

UV-Vis measurements were carried out at a SPECORD 200 Plus from Analytic-Jena, in the 200-800 nm range.

For DSS cells, FTO/TiO_2 electrodes (DYESOL, screen printed with Dyesol's DSL 18NR-AO Active Opaque Titania paste) and FTO/Pt (screen printed with Dyesol's Pt1 Platinum Catalyst) were

used as working and counter electrodes. The selected electrolyte was 50 mM iodide/tri-iodide in acetonitrile (SOLARONIX Iodolyte AN-50).

After the solar cells were assembled, current voltage measurements were performed with a CHI 604E potentiostat a potential scan rate v = 0.05 Vs^{-1}, at room temperature (in the dark and under illumination using a solar simulator from ABET Technologies, 1 sun, 1.5 AM). Electrochemical impedance spectroscopy measurements were carried out in the frequency range 0.1 Hz to 3 MHz, with potentials between 0 and 0.7 V in the dark.

A CHI 440 potentiostat/galvanostat time - resolved quartz crystal microbalance was employed for QCM and EQCM measurements. The working electrode was a circularly shaped Ti/Au/TiO_2 layer with a calculated surface exposed to the electrolyte of 0.215 cm2 (provided by RenLux Crystal). The system was completed with a Pt wire counter electrode, and a saturated Ag/AgCl as reference electrode. Potential during the EQCM measurements are reported against the Ag/AgCl reference electrode. Measurements for QCM were made in time-resolved mode, thus the frequency difference of the working crystal and the reference crystal was measured. The reference crystal had an oscillation frequency of 8.000 MHz. Adsorption measurements were carried out at open circuit potential.

3. RESULTS AND DISCUSSION

Different solutions were utilized to sensitize the mesoporous FTO/TiO_2 electrodes. Table 1 shows a brief description of the different used solutions.

Assembled solar cells showed different behaviors depending on these dye solution composition, as observed in the measured conversion efficiency.

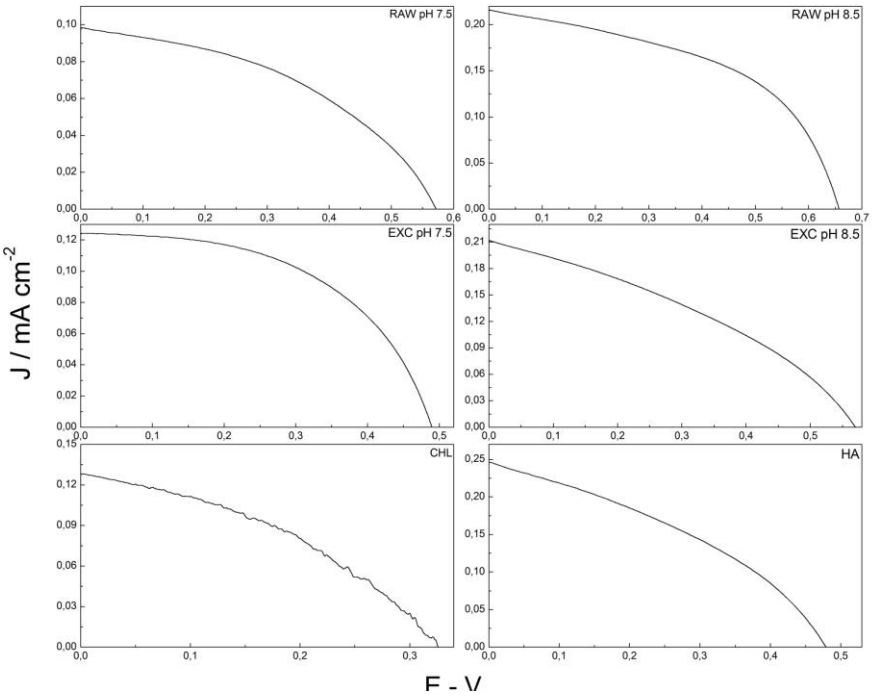

Figure 1. J vs. V profiles for cells sensitized with different dyes: RAW and EXC phycocyanin (at two pH values), and EXC purified protein with the addition of chlorophyll and heptanoic acid.

Figure 1 shows the measured J vs. V curves under light irradiation for cells stained by the six different solutions explained at Table 1. It is important to take into account that efficiency values exposed here are an average from at least 3 repetitions of each sensitized condition. But in some cases, as RAW and EXC at pH 8.5, J vs. V curves showed a great variation of Jsc and Voc values from cell to cell and also from cycle to cycle.

Table 1. Two types of phycocyanin solutions were used to prepare the electrodes: one coming from the Spirulina capsules (and therefore, mixed with other compounds, mainly chlorophyll) called RAW and other obtained after purification using Sephadex (EXC). The pH of these solutions was adjusted to 7.5 or 8.5. Moreover, some experiments were also performed with the addition of chlorophyll (CHL) or heptadecanoic acid (HA) to the EXC phycocyanin solution, at pH = 7.5.

name	**solution composition**	**procedure**
RAW	Mainly phycocyanin	MilliQ water added to capsules and then centrifuged.
EXC	Phycocyanin	after Sephadex exclusion
CHL	Chlorophyll and phycocyanin (molar ratio 27 to 1, EXC to CHL)	after Sephadex exclusion, includes addition to EXC solution
HA	heptadecanoic acid and phycocyanin (molar ratio 240 to 1, HA to EXC)	includes addition to EXC solution

Table 2. Photovoltaic properties for cells assembled using different sensitizers. All measurements were performed under AM 1.5G one sun light intensity of 100mWcm^{-2} and the active areas were 0.7 cm^2 for all the cells.

	RAW pH 7.5	RAW pH 8.5	EXC pH 7.5	EXC pH 8.5	CHL	HA
Jsc	0.10 mA/cm^2	0.21 mA/cm^2	0.13 mA/cm^2	0.21 mA/cm^2	0.13 mA/cm^2	0.24 mA/cm^2
Voc	0.57 V	0.65 V	0.49 V	0.57 V	0.33 V	0.48 V
Jmp	0.066 mA/cm^2	0.14 mA/cm^2	0.09 mA/cm^2	0.12 mA/cm^2	0.084 mA/cm^2	0.14 mA/cm^2
Vmp	0.39 V	0.49 V	0.38 V	0.35 V	0.2 V	0.3 V
FF	0.45	0.50	0.53	0.36	0.39	0.37
n	0.025%	0.07%	0.033%	0.044%	0.017%	0.043%

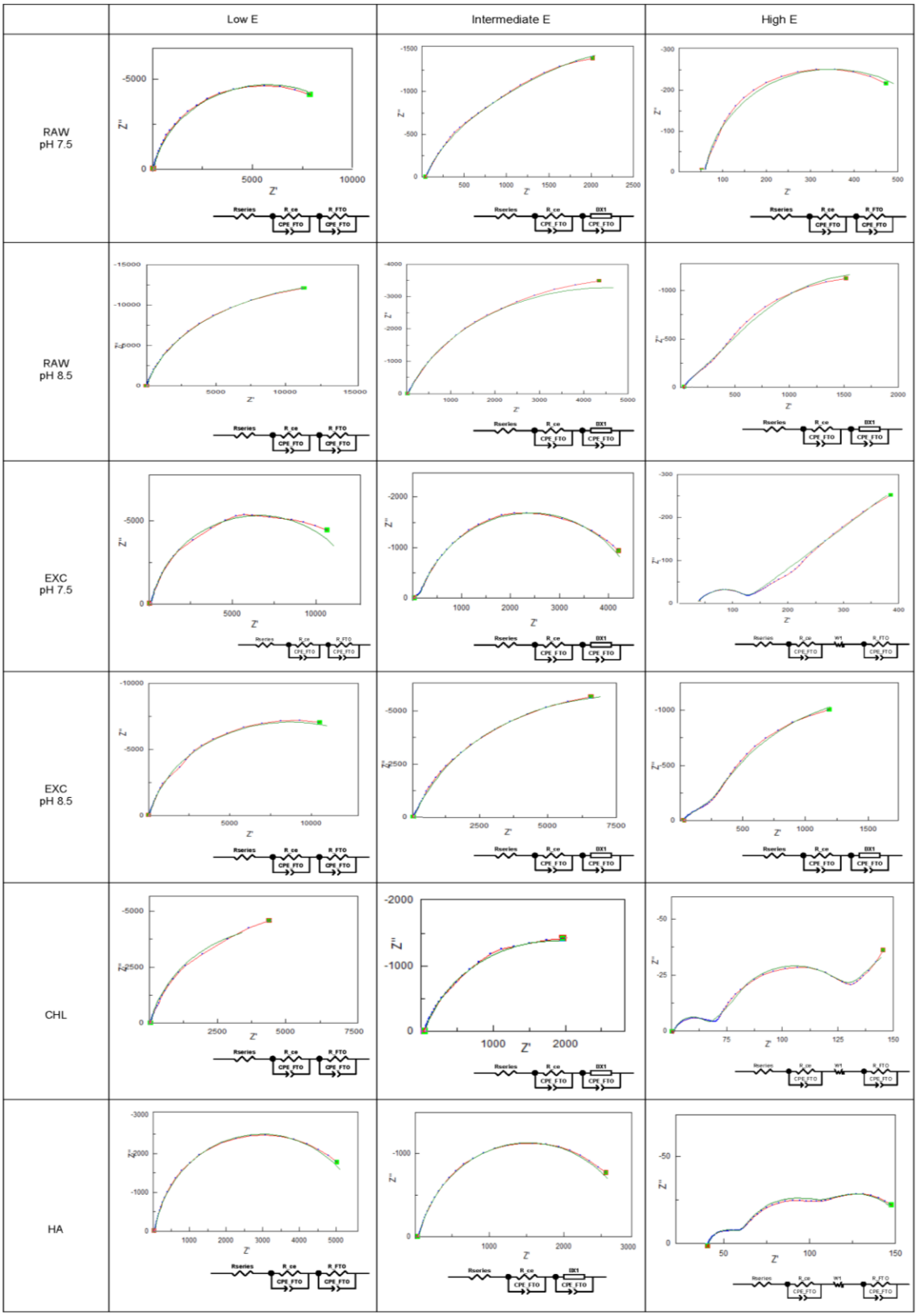

Figure 2. Measured data values superimposed to fitted results for evaluated assembled cells under different conditions, in darkness. For low E showed results were measured at 0.3 V. For intermediate E showed results were measured at 0.4 V or 0.5 V (for RAW at both pH values). And for high E showed results were measured at 0.7 V or 0.6 V (RAW and EXCL pH 8.5).

Thus, with these remarks in mind, some highlights can be deduced. Firs the devices assembled with RAW phycocyanin showed the best performance, but the failure percent (i.e. cells that did not work) was higher. On the contrary, results in case of HA cells were reproducible and therefore, with 0.04 % power conversion efficiency (PCE), showed the best sensitizing conditions.

To understand these behaviors, measurements using quartz crystal microbalance and impedance spectroscopy were carried out.

Figure 2 shows main EIS results, whereas table 3 shows the main circuit elements values obtained at 0.4 or 0.5 V after fitting the measured data.

At this table, Rce represents electron transfer at the counter electrode, Rtrans represents the electron diffusion processes in the nanostructured TiO_2 film and also the transport resistance at the dye/TiO_2 interface, and where Rrecomb refers to electron recombination between TiO_2 and the redox iodine containing couple the recombination process with the redox couple members.

In line with results observed when measuring efficiency, resistances values showed similar tendencies. At pH 7.5, lower R values were obtained for cells containing HA and phycocyanin, showing also a good difference between Rrecomb and Rtrans (Rrecomb near 20 times higher).

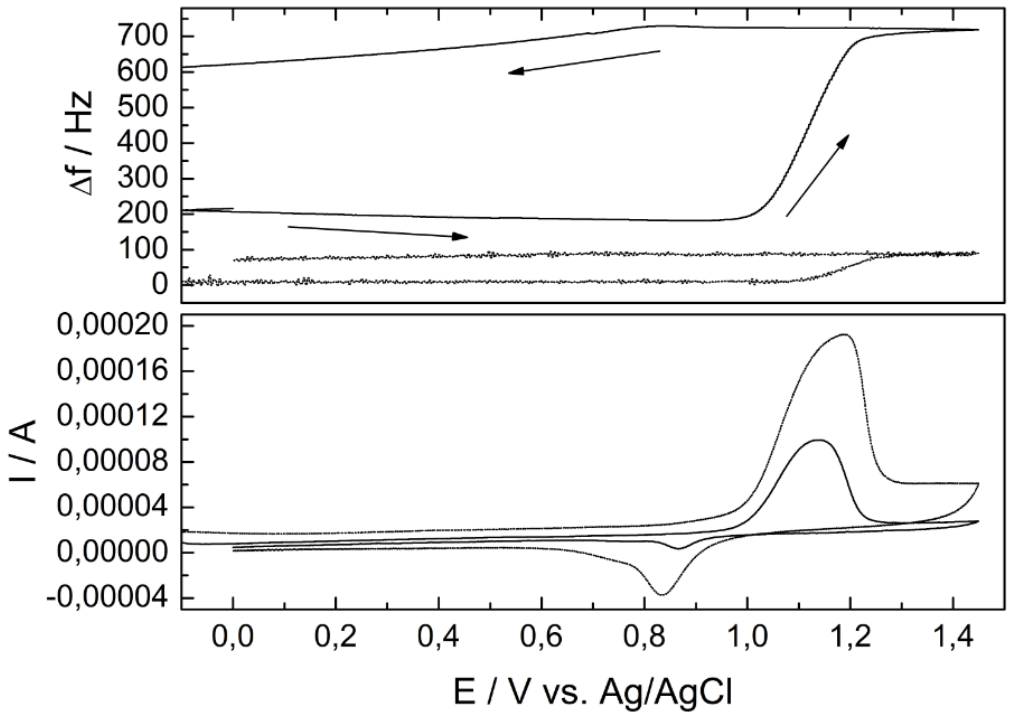

Figure 3. EQCM results for EXC phycocyanin (purified using Sephadex), pH 7.5 (full line) in the supporting electrolyte, compared with results obtained in the supporting electrolyte, 0.1 M NaNO3 (dotted line). Working electrode Ti/Au/TiO_2, 0.01 Vs^{-1}.

It is important to remark that cells sensitized with the protein at pH 8.5 (RAW or EXC) did not always work properly, fact that could be explained due to high resistance values presumably since the conduction band is shifted up by the fewer amount of protons at the surface in case of the lower pH. This leads to a higher Voc, as reported at the literature [17-19]. At pH 8.5 also Jsc vales were higher than values at pH 7.5 but there were still very low compared with reported values for other natural

dyes [10-14], even compared with those extracted in water. Low Jsc values could explain the low conductivity in the mesoporous metal oxide with lower Ef. The lack of reproducibility in cells assembled at pH 8.5 could be related with a phycocyanin more negatively charged at this pH value. Phycocyanin has an isoeletric point value of 5.8 [20] and therefore, at pH 8.5, is highly negatively charged, situation that could affect resistance at the TiO_2/dye interface. After electron injection from excited dye molecules, an electron accumulation in the mesoporous electrode is reported. Repulsion with the negative charged protein could be important enough to influence the cell function affecting the electron lifetime [21,22].

Table 3. The main circuit elements values obtained at 0.5 or 0.4 V after fitting the measured data.

Sensitizer	Potential	Rseries	Rce	Rrecomb	Rtrans
RAW pH 7.5	500 mV	48.9	6.8	2989	4877
EXC pH 7.5	400 mV	38.4	30.9	4512	269.3
CHL	400 mV	52.4	10.8	2042	5891
HA	400 mV	41.3	4.0	2909	143.5
RAW pH 8.5	500 mV	33.2	12.1	9010	13.55
EXC pH 8.5	400 mV	32.2	1.0	14861	2335

Once again, EIS results confirmed that the assembled devices with the addition of heptadecanoic acid to phycocyanin are able to convert more effective light into electricity current with a reproducible behavior.

Finally, and due to limitations to apply the Sauerbrey equation [23-24], for the evaluated systems exposed in this work microbalance measurements are considerer only in comparative terms. Mass deposition calculations were therefore not carried out.

Figure 3 shows measured results using EQCM for EXC pH 7.5 in the supporting electrolyte (0.1 M $NaNO_3$). Voltammetric profile is mainly determined by phycocyanin adsorption to Ti/Au/TiO_2 electrodes, as deduced by the great decrease in the redox peaks observed for the supporting electrolyte.

During the potential scan, adsorption of phycocyanin through the carboxylic group takes place, as reported for gold surfaces from ca. 0.4 V [25-28]. This adsorption is negligible for sufficiently cathodic electrode potentials and, along with the increase in the potential, an increase in the adsorption is observed. This increase reaches its maximum value in the region where the electro oxidation of the

metallic surfaces commences. The adsorption process of acid is reversible; whatever amount of adsorbate is formed at lower potentials it tends to desorbs from the surface at utmost positive potentials.

In some experiments (not shown), recorded in the supporting electrolyte after leaving the electrode overnight in the phycocyanin containing solution, the presence of two separated oxidation peaks was seen, one at 1.1 V (ascribed to oxidation of COOH groups from the protein) and the second at 1.3 V. Quartz microbalance results also confirmed the adsorption of the blue protein onto the electrode, because desorption of the molecule takes place at potentials higher than 1.0 V (as established by the great increase in the vibration frequency after reaching this value), while in the supporting electrolyte the increase is 7 times lower.

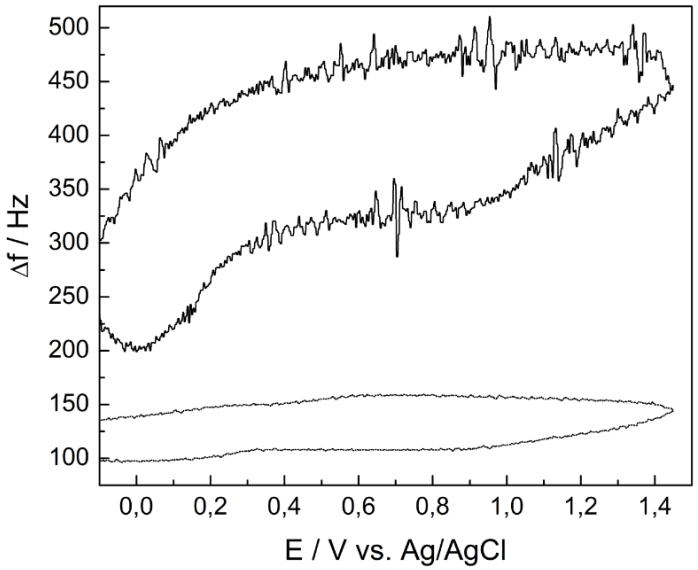

Figure 4. EQCM results for EXC purified phycocyanin with the addition of CHL (dot line) and the addition of HA (full line), recorded in the supporting electrolyte 0.1 M NaNO3. Working electrode Ti/Au/TiO_2, 0.05 Vs^{-1}.

It is interesting to interpret balance measurements carried out in the presence of CHL and HA. As figure 4 shows, both compounds are able to adsorb onto the electrode surface, as also reported at the literature [29-30]. The difference resides in what happen when phcyocyanin tries to reach the surface: in case of CHL, this small sized compound (906.3 g/mol) adsorbs onto TiO_2 and does not allows further adsorption of the protein to the surface, whereas HA adsorbs to TiO_2 at ca. 0 V, but desorbs at 0.4 V, leaving the surface available for the phycocyanin approach using the COOH anchoring groups. CHL acts then as sensitizer [31,32], but with lower efficiency values than phycocyanin; additionally, impedance measurements carried out in the presence of CHL were very noisy.

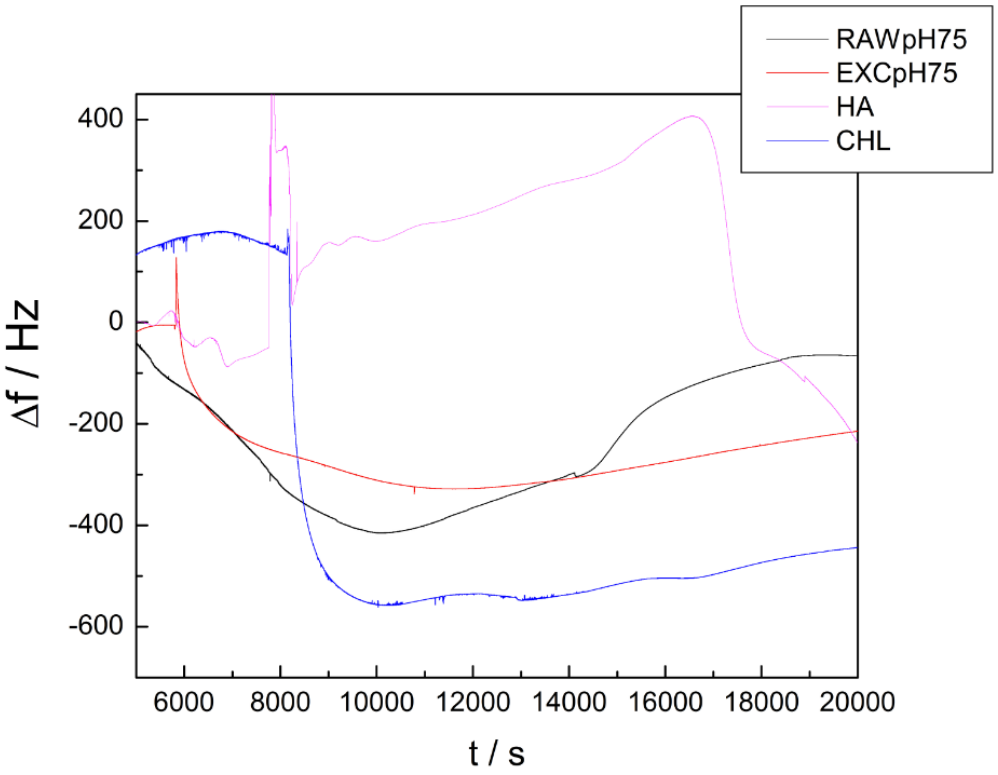

Figure 5. QCM profiles measured for RAW and EXC phycocyanin samples (pH 7.5), and EXC purified protein with the addition of chlorophyll and heptanoic acid, using Ti/Au/TiO_2 electrodes.

Also QCM experiments were performed, using samples or mixtures as described above. As can be observed in figure 5, and only considering frequency variations, phycocyanin is able to adsorb and desorbed from the electrode surface. This fact is detected in both cases, for RAW and for EXC phycocyanin, while for the first case the amount of deposited mass on the electrode is higher, as expected from a sample containing phycocyanin and other components (mostly chlorophyll). QCM also confirmed that CHL could adsorb on the electrode surface in a great extent and limiting protein access to the TiO_2 surface. And with respect to HA, deposition of the compounds on the electrode surface was not detected when a solution containing the phycocyanin and heptanoic acid is injected in the microbalance cell. So in this latter case, measured higher efficiency values in cells sensitized with the mixture could be explained not in terms of dye adsorption increase. HA could affect viscosity of the solutions or avoid hydrophobic interactions [33,34], preventing in this way the protein agglomeration, reasons that improve protein approach to the TiO_2 modified surface.

4. CONCLUSIONS

Different DSSC devices were assembled using phycocyanin as sensitizer to harvest the sun light. Adsorption of the protein to the nanostructured TiO_2 is very low, but can be improved changing the dipping conditions. Chlorophyll showed a strong competition for the electrode surface with the

blue protein, whereas heptanoic acid improved phycocyanin adsorption, as showed by QCM measurements.

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