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Solar cells based on the use of photosensitizers obtained from Antarctic red algae

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ABSTRACT

Dye sensitized solar cells assembled using red dyes extracted from Antarctic algae were evaluated. Among all collected algae, the best performances were showed with samples coming from *Plocamium hookeri*, *Delesseria lancifolia* and *Iridaea obovata*. Cells were evaluated using conventional electrochemical techniques and electrochemical impedance spectroscopy. The measured conversion efficiency was lower than 0.04%, using solar simulator with a power of 1 sun, 1.5 AM.

1. Introduction

Dye sensitized solar cells (DSSC) or Grätzel cells are an interesting alternative to conventional photovoltaic-silicon based cells, with conversion efficiency quite close to the commercial ones, and without the disadvantages related to the silicon extraction process (Bahadori and Vuthaluru, 2010; Bella et al., 2015; Grätzel, 2000).

DSSC have had an explosive growth since they were developed by Grätzel nearly thirty years ago. In the beginning, they were based on natural dyes, as those used by plants in photosynthesis. They use organic dyes to harvest the incident light, leading a flow of electrons (O'Regan and Grätzel, 1991; Tributsch, 2004).

DSSC are based on the use of colored dyes as photosensitizers, which are able to trap the energy coming from the solar radiation in the visible range (Govindaraj et al., 2015). They contain a nanoporous oxide layer at the heart of the system, normally composed with titanium dioxide (TiO_2) under the form of anatase (Grätzel, 2003). The dye, laid on a monolayer film, is adsorbed to the surface of the titanium dioxide. Photo excitation of the pigment results in the injection of an electron into the conduction band of the oxide. The dye is then restored by the electron donation from the electrolyte, where a redox system such as iodide/triiodide couple is contained. Next, the iodide is regenerated by the reduction of triiodide at the counter electrode, and the circuit is completed through an electron migration at the external load.

Over the past few years, research on the topic has significantly increase driven by the motivation of finding new forms of energy. Nevertheless the reported efficiencies remain low (ca. 12%) (Grätzel and Zakeeruddin, 2013; Grätzel, 2015; Nazeeruddin et al., 2011). In this regard, the use of natural dyes might represent an attractive and cheap alternative, especially for developing countries, to synthetic commercial reactants.

It has been reported that natural dyes-based-cells showed efficiencies values up to 2% and 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 some examples of the compounds responsible for the absorption of light (Calogero et al., 2015; Calogero et al., 2014; Calogero et al., 2012; Shalini et al., 2015; Ananth et al., 2015). In previous works, we evaluated the use of phycocyanin from *Spirulina platensis* in DSSC. This protein, with a similar chemical structure to the phycoerythrin, showed promising results, with a conversion efficiency of 0.03% (Enciso et al., 2013).

The aim of this work was the extraction of the dyes responsible for the red color in Antarctic algae. In such organisms, the phycoerythrin is abundant. The red pigment has characteristics that made this protein an interesting candidate for its use as cells sensitizers: the maximum absorption band at 550 nm has a high molar decadic absorption coefficient value (ca. 10^5 M^{-1} cm^{-1})(Sampath-Wiley and Neefus, 2007; Oi et al., 1982) and the free carboxylic acid groups present at the chromophore are able to anchor the nanostructured titanium dioxide semiconductor (Fig. 1). The adsorption of the dye is a crucial step in the construction of the device to assure the electron flow in the cell. Once electron are transferred to the TiO_2, provided that iodide recombination is negligible, current flow will follow a path towards the counter electrode, where regeneration of the dye with the redox couple iodide/tri iodide of the electrolyte takes place (Sepulveda-Ugarte, 2011; Glazer et al., 1982; Van Der Weij-De Wit et al., 2006).

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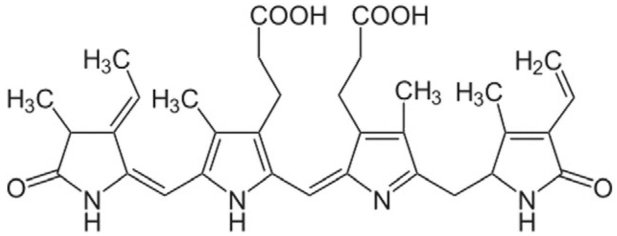

Fig. 1. Structure of the chromophore of the Phycoerythrin.

The use of dyes that could be easily obtained in such a singular place as the Antarctica, could offer a partial solution for the energetic problem there. In particular, dyes coming from algae would be a good alternative because red algae can be found in great abundance in southern seawater, and they are able to harvest sun light even in a place as poor in solar radiation as the Antarctica.

2. Experimental and methods

Algae were collected at the coasts of the King George Island and processed at the Uruguayan Artigas Antarctic Scientific Base (BCAA). Samples were cut in pieces and dipped in ethanol (95%).

UV–vis measurements were carried out at a SPECORD 200 Plus de Analytic-Jena, in the 350–800 nm range. Cyclic voltammetric measurements were performed at the BCAA using a DROPSENS uStat 400 potentiostat, at 0.1 Vs^{-1} potential scan rate at room temperature, using gold screen printed electrodes with silver pseudo reference electrode ($E = 0.269$ V vs. SHE).

To assembly the cell, FTO (*fluorine tin oxide*) electrodes were used as working electrodes covered with nanostructured TiO_2 (DYESOL™, screen printed with Dyesol's DSL 18NR-AO Active Opaque Titania paste, 0.7 cm^2), and Pt as the counter electrode. After dipping the TiO_2 electrode in the dye-containing solution, it was rinsed with ethanol and the cell was completed using acetonitrile with the iodide/tri iodide couple as electrolyte. The cell was evaluated using a CHI-604e potentiostat, under darkness and light conditions. Current vs. potential curves were performed at $v = 0.05\ Vs^{-1}$. EIS measurements were carried out in the range 0.1 Hz to 3 MHz, and BIAS potentials between 0 and 0.6 V at room temperature.

For measurements carried out under light, a solar simulator (ABET technologies) with 1 sun power, 1.5 AM was used.

3. Results and discussion

All collected samples were processed *in situ* at the BCAA. After extraction with ethanol, the mixture of dyes was analyzed using UV–visible spectroscopy. As showed in Fig. 2, the absorbance spectra showed the presence of phycoerythrin, among other compounds.

The phycoerythrin main absorption band is observed at 540 nm, while for chlorophyll *a* bands are detected at 430 and 662 nm, and for β carotenes at around 450 and 500 nm. The presence of phycocyanin is also confirmed at 620 nm. The absorption spectra suggest that by using a very simple extraction method is possible to get most of the relevant dyes contained in the evaluated algae (Jeffrey, 1976; Eriksen, 2008).

From the absorbance values, it is possible to calculate concentrations of phycoerythrin ($\varepsilon_{540} = 24.1 \times 10^5\ M^{-1}\ cm^{-1}$), phycocyanin ($\varepsilon_{620} = 2.8 \times 10^5\ M^{-1}\ cm^{-1}$) and chlorophyll *a* ($0.06\ A_{632} + 13.3\ A_{665}$–$4.52\ A_{649}$–$1.75\ A_{696}$, to get concentration in g m^3) at the appropriate wavelengths (Oi et al., 1982; Ritchie, 2008).

Calculated concentrations were ca. 6×10^{-7} M for phycoerythrin in *Iridaea obovata* and *Plocamium hookeri* and 12×10^{-7} M for *Delesseria lancifolia*. Moreover, chlorophyll *a* concentrations were 2×10^{-5} M for Iridaea and Delesseria and 0.76×10^{-5} for Plocamiun. Finally, phycocyanin concentration was 5 times lower than phycoerythrin in all evaluated samples.

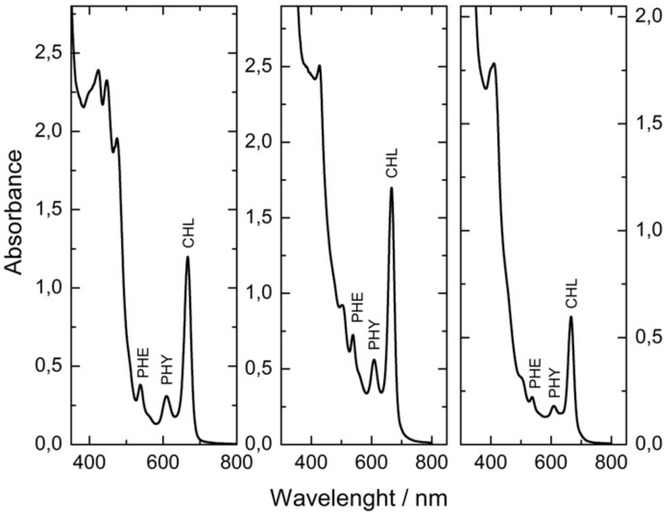

Fig. 2. Absorbance spectra for *Iridaea obovata* (left), *Delesseria lancifolia* (middle) and *Plocamium hookeri* (right). PHE represents phycoerythrin, PHY is phycocyanin and CHL chlorophyll *a*.

A second important step in the evaluation of a suitable dye to be used as sensitizer in DSS cells is the redox behavior. For this reason, cyclic voltammetric measurements using gold screen printed electrodes were performed at 0.1 Vs^{-1} potential scan rates.

Fig. 3 shows the characteristic voltammetric profiles observed in ethanol solutions containing the extracted mixture of dyes. The oxidation peak detected at ca. 1.1 V vs. pseudo reference electrode (0.269 V vs. NHE, normal hydrogen electrode) is attributed to the redox processes that come from the mixture of pigments in the algae, with the exception of chlorophyll *a*.

The reported redox potential value for chlorophyll *a* is 0.9 V (corrected with respect to the reference electrode used in this work) (Ishikita et al., 2005). That means, the contribution at ca. 1.1 V would arise from the redox behavior of the other dyes, mainly from phycocyanin and phycoerythrin (Enciso et al., 2013).

At this point the question about the suitability of the use of phycoerythrin as sensitizer arises. On one side the electron transfer from the dye to the TiO_2 must be possible. But also the regeneration of the oxidized dye (after electron transference to the semiconductor) must also take

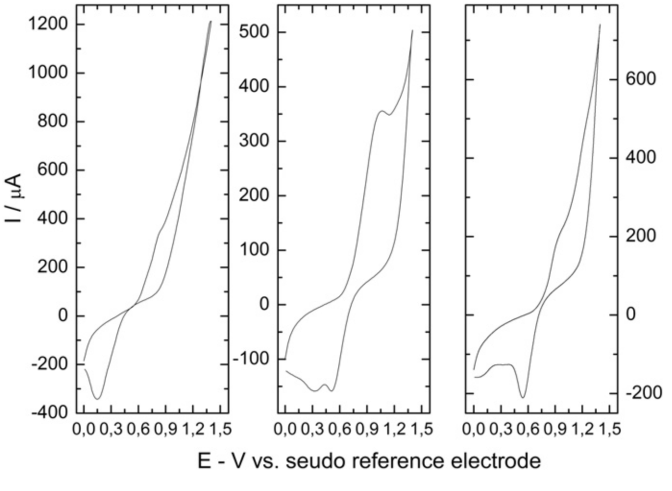

Fig. 3. Voltammetric profiles for ethanol extracted mixture of dyes at gold screen printed electrodes at 0.1 Vs^{-1}, room temperature. *Iridaea obovata* (left), *Delesseria lancifolia* (middle) and *Plocamium hookeri* (right).