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Efficient and low cost devices for solar energy conversion: Efficiency and stability of some natural-dye-sensitized solar cells

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ABSTRACT

Dye-sensitized solar cells, named by us Dye-Cells, are one of the most promising devices for solar energy conversion due to their reduced production cost and low environmental impact, especially those sensitized by natural dyes. The efficiency and stability of devices based on natural sensitizers such as mulberry (*Morus alba* Lam), blueberry (*Vaccinium myrtillus* Lam), and jaboticaba's skin (*Mirtus cauliflora* Mart) were investigated. Dye-Cells prepared with aqueous mulberry extract presented the highest P_{max} value (1.6 mW cm^{-2}) with J_{sc} = 6.14 mA cm^{-2} and V_{oc} = 0.49 V. Photoelectrochemical parameters of 16 cm^2 active area devices sensitized by mulberry dye were constant for 14 weeks of continuous evaluation. Moreover, the cell remained stable even after 36 weeks with a fairly good efficiency. Therefore, mulberry dye opens up a perspective of commercial feasibility for inexpensive and environmentally friendly Dye-Cells.

1. Introduction

Conversion of solar energy into electricity is a key aspect for the sustainable development. Dye-sensitized solar cells, named by us Dye-Cells, are one of the most promising devices due to their reduced production cost, low environmental impact and a fair good efficiency [1–4].

Our laboratory has been working on several aspects related to the Dye-Cell technology, including characterization of semiconductor films and syntheses of dyes based on Ru(II) polypyridyl complexes [2,5–14]. Another interesting approach is the use of natural extracts as sensitizers, which are even more environmentally friendly and a low cost alternative to synthetic dyes. Anthocyanins from strongly colored fruits, leaves and flowers are capable to adsorb on the TiO_2 surface and inject electrons into its conduction band [2,15–19].

In this contribution, the efficiency and stability of Dye-Cells based on natural dyes from mulberry (*Morus alba* Lam), blueberry (*Vaccinium myrtillus* Lam), and jaboticaba's skin (*Mirtus cauliflora* Mart) are discussed.

2. Experimental

Crude aqueous extracts of mulberry, blueberry, and jaboticaba's skin were prepared as previously described [15], by crushing the fruits. The extracts were used without any further purification or pH adjustments. The complex *cis*-$[Ru(dcbH_2)_2(NCS)_2]$, N3, was prepared as reported in the literature [20], purified and used as a standard for the stability test. Colloidal TiO_2 was prepared by the sol–gel method and deposited on the FTO substrates (Pilkington TEC-15) as described elsewhere [14,20].

Dye-Cells with 0.5 cm^2 active area were built in a sandwich-type arrangement with a dye-sensitized TiO_2 photoanode and a counter-electrode (Pt-coated FTO), spaced and assembled using a thermoplastic film (Surlyn 1601-2, DuPont) under a heating treatment. The device was then hermetically sealed with an especial resin (DyeSol), after filling it with a liquid electrolyte (acetonitrile/propionitrile (1:1) solution, 0.3 mol L^{-1} of LiI, 0.03 moL L^{-1} of I_2 and 0.1 mol L^{-1} of pyridine).

The photoelectrochemical parameters were extracted from current–voltage curves obtained under a 91160 Newport/Oriel simulated solar radiation (AM 1.5; 100 mW cm^{-2}). IPCE spectra were measured with an Oriel system comprised by a 400 W Xe lamp coupled to a 0.5 m Czerny-Turner monochromator. Further experimental details are described elsewhere [6,14,19].

The stability tests were carried out in 16 cm^2 solar cells assembled in the same way as described for the 0.5 cm^2 ones. The electrolyte solution was filled by a vacuum technique and hermetically sealed as the 0.5 cm^2 solar cells. These solar cells, at room temperature, were exposed to AM 1.5 100 mW cm^{-2} simulated solar radiation and photoelectrochemical parameters were collected during 14 weeks by using a digital multimeter (Minipa).

3. Results

Absorption spectra of anthocyanidins (anthocyanins without the glycoside group) are mainly dependent on the substituent groups, R_1 and R_2 [21].

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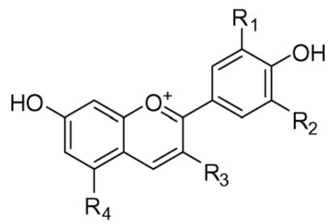

Their adsorption onto the oxide surface occurs through hydroxyl groups and absorption bands shift to lower energy, increasing the overlap with the solar spectrum.

The electronic spectrum of aqueous mulberry extract exhibits a maximum at 518 nm, which is red shifted when adsorbed on TiO_2 film (Fig. 1). The band is also broadened with a shoulder at 590 nm assigned to an adsorption of different species. IPCE spectrum of a Dye-Cell sensitized by mulberry extract shows that anthocyanins promote an efficient light harvesting and electron injection with maximum efficiency at 530 nm.

Besides mulberry, other two different natural extracts were evaluated as sensitizers and their photoelectrochemical parameters are listed in Table 1.

Dye-Cells sensitized by mulberry exhibit the best performance among the extracts investigated, which indicates that anthocyanins in this extract inject electrons more efficiently than the species in other fruits.

The differences found in the photocurrent of Dye-Cells investigated here can be justified by distinct electron injection efficiencies of anthocyanins [17,22,23] for each type of extract and can be influenced by the presence of other compounds [18].

Most of works has emphasized that natural-dye-sensitized solar cells are not suitable for commercial purposes due to their low stability. However, recent experiments carried out in our laboratory using sealed cells have shown that Dye-Cells sensitized by natural dyes have kept their efficiencies constant. This high stability of the solar cells with natural extracts has been achieved by avoiding the contact of the sensitizer with air and water as well as by improving the sealing techniques. After filling the devices with the electrolyte solution by a vacuum technique there is no contact of the photoanode with air or water, which decreases anthocyanins decomposition processes. The devices have been hermetically sealed and this provided the observed stability under excitation.

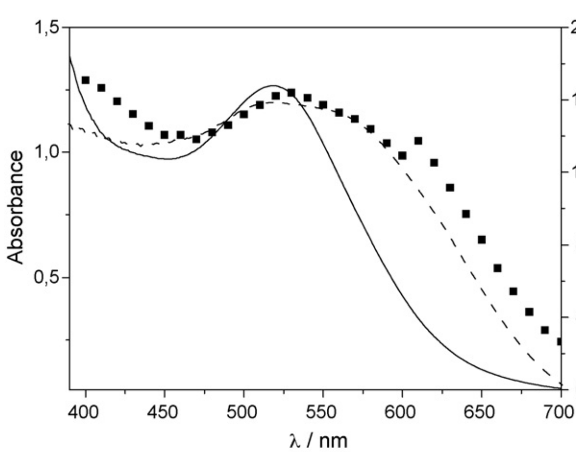

Fig. 1. Electronic spectra of aqueous mulberry dye (—) and TiO_2 film sensitized by mulberry dye (- - - -) and its IPCE (■).

Table 1
Photoelectrochemical parameters of Dye-Cells sensitized by different natural dyes.

	J_{sc} (mA cm^{-2})	V_{oc}/V	P_{max} (mW cm^{-2})	ff
Mulberry	6.1	0.49	1.6	0.52
Blueberry	1.0	0.59	0.4	0.61
Jaboticaba's skin	3.9	0.45	1.0	0.56

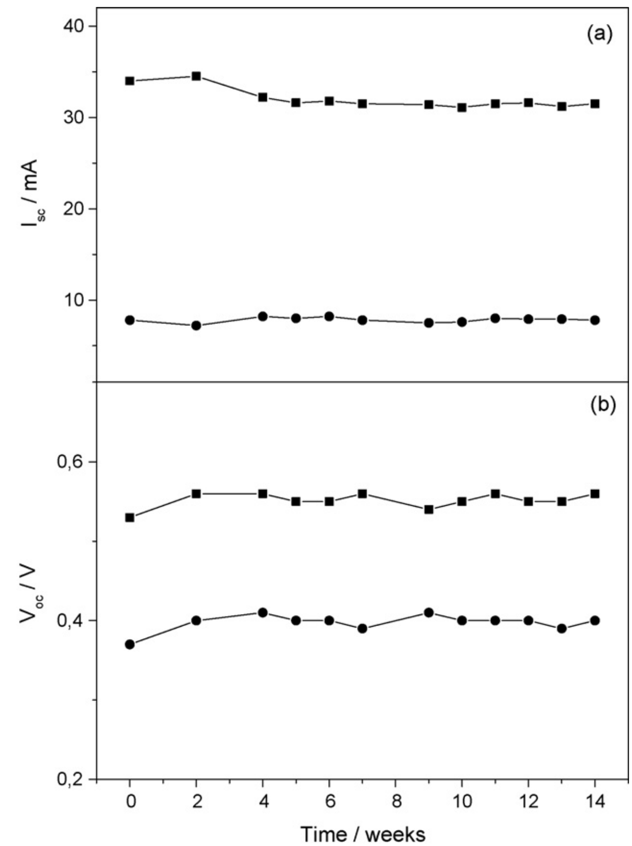

Fig. 2. Variation of I_{sc} and V_{oc} versus time for Dye-Cells sensitized by mulberry (●) and N3 (■) (AM 1.5; 100 mW cm^{-2}).

A 16 cm^2 active area Dye-Cell was built using extract of mulberry and its photoelectrochemical parameters were measured during 14 weeks. In Fig. 2, I_{sc} and V_{oc} values as a function of time for the mulberry sensitized Dye-Cell are compared with the N3 ones. The N3 dye was chosen as a standard to the comparison due to the well-known stability of solar cells with ruthenium polypyridyl complexes as sensitizers [24–27].

Despite the lower photocurrent of the mulberry sensitized Dye-Cell in comparison to that sensitized by N3, this cell exhibited a similar stability during the period investigated. In fact, devices sensitized by mulberry was operative for 36 weeks [28] and showed a commercial feasibility of natural extracts based Dye-Cells.

4. Conclusions

Natural dyes are environmentally friendly and inexpensive sources of sensitizers for Dye-Cells and have now proven to be commercially feasible. Mulberry, blueberry and jaboticaba's skin dyes were capable to sensitize TiO_2 electrodes and their respective cells exhibited comparable photoelectrochemical parameters. In particular, mulberry sensitized cells presented the best performance. I_{sc} and V_{oc} of sealed mulberry based solar cells were monitored during 36 weeks and remained constant within the experimental error.

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