CLEAN AND RENEWABLE ENERGY FROM DYE-SENSITIZED SOLAR CELLS USING FRUIT EXTRACTS

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Abstract

Successful conversion of visible light into electrical output was achieved by using natural dyes as wide-bandgap semiconductor sensitizers in Dye-Sensitized Solar Cells. Blue-violet anthocyanins from Jaboticaba (Jaboticaba, Myrtus cauliflora, Mart) and Java Plum (Jambolão, Eugenia jambolana, Lam) were employed as light absorbing dyes attached to nanostructured mesoporous TiO_2 film of the photoanode. Photocurrent and photovoltage as high as 2.75 mA cm^{-2} and 590 mV were obtained for solar cells sensitized by Jaboticaba extracts with P_{max} = 778 μW cm^{-2} and ff = 0.48. Under the same conditions, the performance of a Java Plum sensitized solar cell was I_{sc} = 2.5 mA cm^{-2}, V_{oc} = 439 mV, P_{max} = 465 μW cm^{-2} and ff = 0.42.

Keywords: Dye-sensitized solar cell, Natural dyes, Clean and renewable energy, Energy conversion

1. Introduction

An energy system infrastructure is fundamental for worldwide technological and economic achievements. Fossil fuel based energy has to be converted into new energy systems in the 21st century by incorporating novel technologies derived from advancements in science (Murakami Iha et al., 2003).

One of such systems is the Dye-Sensitized Solar Cell, which is the result of exploiting several new concepts and materials, such as nanotechnology and molecular devices, and is one of the new approaches for photovoltaic technology. This device is based on chemical concepts, in which the separation of charge carriers is kinetically controlled by the chemical reactions involved. An efficient and low cost solar cell can be produced due to the simple materials employed in the production of these cells. Moreover, the processes generate a very small quantity of residues, which does not pollute, resulting in environmentally friendly devices with low energy demanding production technologies.

Sensitization of wide band-gap semiconductors by natural pigments has been reported to obtain a photoeletrochemical solar cell with reduced cost and/or an ecological alternative for educational purposes. In most of cases, the observed photocurrents are ascribed to anthocyanins, which are commonly found in berries and are responsible for the intense purplish violet color observed in these fruits (Smestad, 1998, Smestad and Grätzel, 1998, Olea et al., 1999).

In this work we extend our investigations involving natural dyes as semiconductor sensitizers (Garcia et al. 2003a) and report photoeletrochemical parameters of Java Plum (Jambolão, Eugenia Jambolana, Lam) to complete our previous communication with

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preliminary measurements (Garcia et al., 2003b.), as well as successful results obtained with a new dye, extracted from thich skin of Jaboticaba fruits (Jaboticaba, Myrtus cauliflora, Mart). Java Plum and Jaboticaba are tropical fruits, widely spread over the Brazilian territory. Solar cells with these new dyes have good light harvesting properties and perform efficient electron injection into semiconductor.

2. Experimental Section

2.1 Materials

All solvents and chemicals employed for preparations were reagent or HPLC grade.

2.2 Preparation of dye sensitizer solutions

The synthetic dye *cis*-$[Ru(dcbH_2)_2(NCS)_2]$, named N3, was prepared following the reported procedure (Nazeeruddin et al., 1993) and used as a standard.

The extracts of Java Plum and Jaboticaba were obtained by following the reported procedure (Garcia et al., 2003a). Solutions for electronic spectra were centrifuged in order to remove the pulps and some residual fragments.

2.3 Measurements

Absorption spectra were recorded on a Hewlett Packard 8453 UV-Vis spectrophotometer. Short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) measurements were obtained as previously described (Garcia et al., 1998a,b).

Photoelectrochemical experiments were carried out by using the dye-sensitized TiO_2 films in a thin-layer solar cell arrangement depicted in Figure 1, as described previously (Garcia et. al., 2003a).

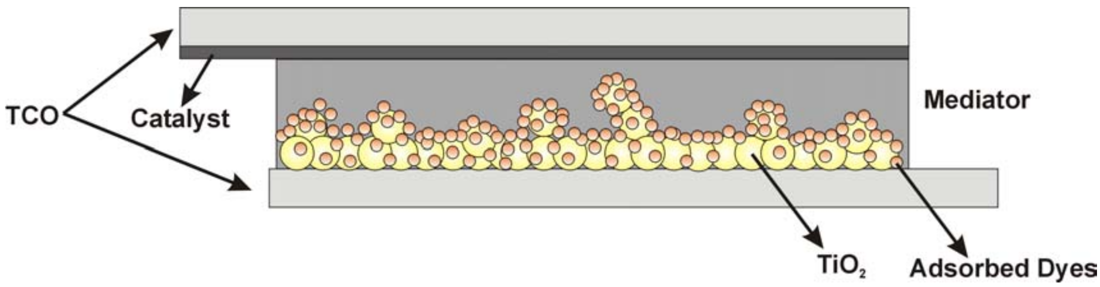


Figure 1. Thin-layer sandwich-type solar cell and its components

The sandwich-type solar cell consists of two electrodes having TCO (Transparent Conducting Oxide) substrates (Asahi Glass Co.) with a redox mediator in between. TiO_2 emulsion for photoelectrochemical measurements were obtained by hydrolysis of titanium isopropoxide using a sol-gel route as previously reported (Nazeeruddin et al, 1993, O'Regan and Grätzel, 1991). The photoanode was prepared by the deposition of the nanocrystalline TiO_2 film over an FTO substrate (Fluorine doped Tin Oxide – 7 Ω square^{-1}) by doctor blade technique followed by sintering its particles at 450 °C for 30 minutes. The dyes were attached to the mesoporous TiO_2 surface by immersing the processed electrodes in solutions of each dye. The counterelectrode had a transparent thin film of platinum, which acts as a catalyst, deposited onto ITO (Indium doped Tin Oxide – 10-20 Ω square^{-1}) conductive surface. The photoanode and the counterelectrode were set up in a sandwich arrangement shown in Figure 1, and a layer of mediator solution (0.20 g of I_2 and 1.0 g of LiI in 25 mL of a 90:10 mixture of acetonitrile and 3-methyl-2-oxazolidinone, NMO, previously distilled) was placed between them.

The performance of natural dyes as the semiconductor sensitizers was monitored through the current and potential output upon light irradiation of a photoelectrochemical solar cell with an effective area of 0.5 cm^2. Short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}), were obtained as previously described (Garcia et al., 2003a) using an Eco-Chemie PGSTAT-30 galvanostat/potentiostat system under irradiation provided by an overhead projector. The I-V curves were obtained by programming the potentiostat for a linear scan ($v = 10$ mV s^{-1}) from 0 V to the observed open-circuit photovoltage, determined previously by an A. W. Sperry DM-8A multimeter. The data were normalized to the according to reported values for N3 (Nazeeruddin et al., 1993) employed as a standard

3. Results and Discussion

3.1 Electronic Spectra

The absorption spectra of the fruit extracts are presented in Figure 2.

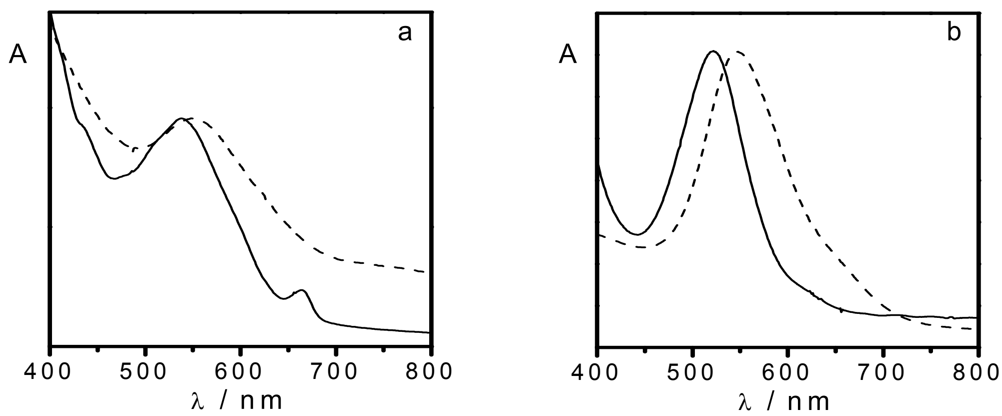


Figure 2. Electronic spectra of extract of Jaboticaba (a) and Java Plum (b) in ethanol (—) and adsorbed onto TiO_2 surface (- - -).

The broad band observed for both extracts, centered at 538 and 536 nm, respectively for Jaboticaba and Java Plum, is ascribed to charge transfer transitions of anthocyanins, responsible for the intense red-violet coloration of the fruits. In these figures are also observed the sensitization of the TiO_2 by these natural extracts, which is shown by the shifts of the absorption maxima to 548 nm for both compounds.

The chemical adsorption of anthocyanins is a result of condensation of its alcoholic protons with the OH present at the surface of the nanostructured TiO_2 film, as shown in Figure 3a. This attachment can also be enhanced by a chelating effect to the Ti(IV) ions, Figure 3b (Tennakone et al., 1997, Dai and Rabani, 2002a,b). This chemical adsorption to the semiconductor film broadens the absorption band and shifts it toward lower energies increasing the solar energy harvesting.

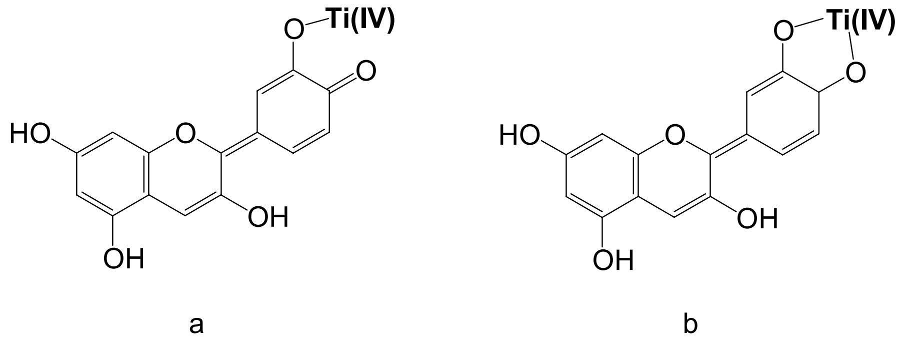


Figure 3. Schematic representation of anthocyanin attachment to TiO_2 surface.

3.2 Photoeletrochemistry

Photocurrent and photovoltage values as high as 2.74 mA cm^{-2} and 629 mV were obtained with overhead projector light irradiation over the solar cell sensitized by the Jaboticaba extract.

The current-voltage profiles obtained for cells employing photoanodes sensitized by Jaboticaba and Java Plum extracts are presented in Figure 4.

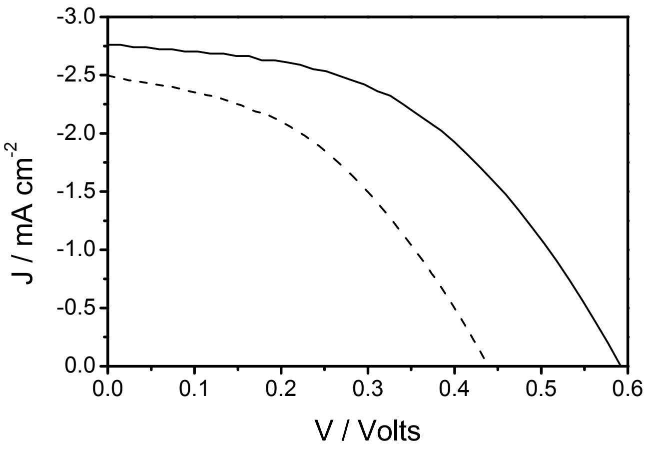
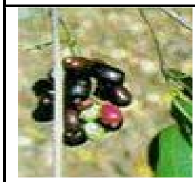


Figure 4. Current-potential curves for solar cells having the photoanode sensitized by extracts of Jaboticaba (——) and of Java Plum (– – –).

The performance of these solar cells were evaluated from the respective *I-V* profile in terms of short circuit current (I_{sc}), open circuit voltage (V_{oc}), maximum power output (P_{max}) and fill factor, obtained for each sensitizer. These parameters, listed in Table I, give evidence of an efficient conversion of light into electrical output promoted by both Jaboticaba and Java Plum extracts. On the other hand, extracts of some bark or fruits of other Brazilian plants, such as Barbatimao (Barbatimão, Stryphnodendron barbatimam, Mart), seeds of Lipstick tree (Urucum, Bixa americana, Poir), Brazilwood (Pau-Brasil, Caesalpinia echinata, Lam) among others, were also analyzed without significant photocurrent. This means that, when employed in regenerative photoelectrochemical solar cells, only selected extracts are capable of converting visible light into electricity.

Table I. Short circuit current (I_{sc}), open circuit voltage (V_{oc}), maximum power output (P_{max}) and fill factor obtained for solar cells sensitized by Jaboticaba or Java Plum extracts.

	Fruit extracts	I_{sc} / mA cm^{-2}	V_{oc} / mV	P_{max} / μW cm^{-2}	Fill factor
	Jaboticaba	2.75	590	778	0.48
	Java Plum	2.51	439	465	0.42

These results are similar to those reported for other extracts, such as chaste tree fruit and mulberry (Garcia et. al, 2003a, Polo et al. 2004), in which the sensitizers are also anthocyanins. The other dyes previously synthesized by the group (Garcia et al., 1998a,b, 2000, 2001a,b, 2002a,b), as well as standard compound N3, which is acknowledged as one of the best performing molecular sensitizers so far, when employed as the photoanode sensitizer under equivalent conditions present $V_{oc} \cong 720$ mV and $I_{sc} \cong 18$ mA cm^{-2} (Grätzel, 2001, Grätzel, 2000). These results show that the extract of Jaboticaba or Java Plum, adsorbed onto the semiconductor surface, acts as a good sensitizer and efficiently promotes electron transfer across the dye/semiconductor interface.

The use of natural dyes can achieve an almost cost free production of dyes for this novel device and can demonstrate several important scientific concepts (materials, semiconductors, molecular devices etc.), environmental chemistry besides renewable and clean energy.

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5. References

Dai, Q., Rabani, J., 2002a. Unusually efficient photosensitization of nanocristalline TiO_2 films by pomegranate pigments in aqueous medium. New J. Chem. 26, 421-426.

Dai, Q., Rabani, J., 2002b. Photosensitization of nanocrystalline TiO_2 films by anthocyanin dyes. J. Photochem. Photobiol. A: Chem. 148, 17-24.

Garcia, C. G., Lima, J. F., Murakami Iha, N. Y., 2000. Energy conversion: From the ligand field photochemistry to solar cells. Coord. Chem. Rev. 196, 219-247.

Garcia C. G., Murakami Iha N. Y., Argazzi R., Bignozzi C. A., 1998a. Sensitization of n-Type TiO_2 Electrode by a Novel Isoquinoline Ruthenium(II) Polypyridyl Complex. J Braz Chem Soc., 9, 13-15.

Garcia C. G., Murakami Iha N. Y., Argazzi R., Bignozzi C. A., 1998b. 4-Phenylpyridine as ancillary ligand in ruthenium(II) polypyridyl complexes for sensitization of n-type TiO2 electrodes. J. Photochem. Photobiol. A: Chem.,115, 239-242.

Garcia, C. G., Murakami Iha, N. Y., 2001a. An interdisciplinary experience on the development of Dye-Cell technology. Intern. J. Photoenergy, 3, 137-141.

Garcia, C. G., Murakami Iha, N. Y., 2001b. Photoelectrochemical solar cells using $[(dcbH_2)_2RuLL']$, L,L'= substituted pyridines, as nanocrystalline TiO_2 sensitizers. Intern. J. Photoenergy, 3, 131-135.

Garcia, C. G., Nakano, A. K., Kleverlaan, C. J., Murakami Iha, N. Y., 2002a. Electron injection vs. charge recombination in photoelectrochemical solar cells using cis-$[(dcbH_2)_2Ru(CNpy)(H_2O)]Cl_2$ as nanocrystalline TiO_2 sensitizer. J. Photochem. Photobiol. A: Chem., 151, 165-171.

Garcia C. G., Kleverlaan C. J., Bignozzi C. A., Murakami Iha N. Y., 2002b. Time-resolved experiments in dye-sensitized solar cells using $[(dcbH_2)_2Ru(ppy)_2](ClO_4)_2$ as a nanocrystalline TiO_2 sensitizer. J. Photochem. Photobiol. A: Chem., 147, 143-148.

Garcia, C. G., Polo, A. S., Murakami Iha, N. Y., 2003a. Fruit extracts and ruthenium polypyridinic dyes for sensitization of TiO_2 in photoeletrochemical solar cells. J. Photochem. Photobiol. A: Chem. 160, 87-91.

Garcia, C. G., Polo, A. S., Murakami Iha, N. Y., 2003b. Photoeletrochemical solar cell using extract of Eugenia jambolana, Lam as a natural sensitizer. An. Acad. Bras. Cienc. 75, 163-165.

Grätzel, M., 2000. Perspectives for dye-sensitized nanocrystalline solar cells. Prog. Photovolt. Res. Appl., 8, 171-185.

Grätzel, M., 2001. Photoeletrochemical Cells. Nature, 414, 338-344.

Murakami Iha, N. Y., Garcia, C. G., Bignozzi, C. A., 2003. Dye-sensitized photoeletrochemical solar cells. In: H. S. Nalwa, (Ed.), Handbook of Photochemistry and Photobiology, Vol. 1. American Scientific Publishers, Los Angeles, pp. 49-82.

Nazeeruddin, M. K., Kay, A., Rodicio, I., Humphry-Baker, R., Müller, E., Liska, P., Vlachopoulos, N., Grätzel, M., 1993. Conversion of light to electricity by *cis*-X_2bis(2,2'-bipyridyl-4,4'-dicarboxilate)ruthenium(II) charge-transfer sensitizers ($X=Cl^-$, Br^-, I^-, CN^-, and SCN^-) on nanocrystalline TiO_2 electrodes. J. Am. Chem. Soc. 115, 6382-6390.

Olea, A., Ponce, G., Sebastian, P. J., 1999. Electron transfer via organic dyes for solar conversion. Sol. En. Mat. Solar Cells. 59, 137-143.

O'Regan, B., Grätzel, M., 1991. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. Nature 353, 737-740.

Polo, A. S., Itokazu M. K., Murakami Iha, N. Y., 2004. Metal complex sensitizers in dye-sensitized solar cells, manuscript in preparation for Grätzel "Festschrift" issue of Coord. Chem. Rev.

Smestad, G. P., Grätzel., M., 1998. Demonstrating electron transfer and nanotechnology: A natural dye-sensitized nanocrystalline energy converter. J. Chem. Educ. 75, 752-756.

Smestad, G. P., 1998. Education and solar conversion: Demonstrating electron transfer. Sol. En. Mat. Solar Cells. 55, 157-178.

Tennakone, K., Kumarasinghe, A. R., Kumara, G. R. R. A., Wijayantha, K. G. U., Sirimanne, P. M., 1997. Nanoporous TiO_2 photoanode sensitized with flower pigment cyanidin. J. Photochem. Photobiol. A: Chem.108, 193-195.