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Fruit extracts and ruthenium polypyridinic dyes for sensitization of TiO_2 in photoelectrochemical solar cells

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Abstract

Dye-sensitization of nanocrystalline n-type TiO_2 was achieved by using fruit extracts as a natural source of sensitizers. Fresh extracts of chaste tree fruit ("maria-preta", *Solanum americanum*, Mill.), mulberry ("amora", *Morus alba*, L.) and cabbage-palm fruit ("açaí", *Euterpe oleracea*, Mart) were employed as TiO_2 sensitizers in thin-layer sandwich-type photoelectrochemical solar cells. Conversion of visible light into electricity was accomplished with natural sensitizers resulting in I_{sc} and V_{oc} values similar to those obtained employing traditional synthesized dyes. Fill-factor values from 0.40 to 0.61 were obtained with the fruit extracts. The photoelectrochemical performance of such cells and the use of natural sensitizers, as an alternative to commonly used synthetic dyes based on *cis*-[$(dcbH_2)_2RuLL'$], $dcbH_2$ = 4,4′-$(CO_2H)_2$-2,2′-bipyridine and L/L′ = SCN^-, X^-, etc., are discussed.

Keywords: Natural dyes; Photoelectrochemical solar cell; TiO_2 sensitization; Energy conversion

1. Introduction

Dye-sensitized photoelectrochemical solar cells are devices for the conversion of visible light into electricity based on sensitization of wide bandgap semiconductors. The sensitization approach enables the generation of electricity with irradiation of energy lower than the bandgap of the semiconductor. The progress of such devices occurred with the development of nanostructured porous semiconductor films onto which light absorbing dye molecules are adsorbed [1–4]. Synthetic inorganic dyes, such as ruthenium(II) polypyridyl complexes with carboxylated ligands, are commonly employed as molecular sensitizers since these species present intense visible metal-to-ligand charge transfer bands. The carboxylic groups enable the necessary electronic coupling between the sensitizer and TiO_2 surface. As a result of visible light absorption, dye species are electronically excited resulting in efficient electron transfer from the carboxylic groups into the semiconductor [5–14].

Sensitization of wide bandgap semiconductors by natural extracts has been reported [15–18] and the subject is indicated for didactic demonstrations/experiments of dye-sensitized photoelectrochemical solar cells [16,17]. Photocurrents observed using several natural pigments are reported and ascribed to anthocyanines, that belong to a group of natural dyes responsible to several colors in the red–blue range found in fruits, flowers and leaves of plants [19,20].

The present work extends our investigations involving natural dyes as semiconductor sensitizers [21,22] and reports the successful use of extracts of chaste tree fruit (maria-preta, *Solanum americanum*, Mill.), mulberry (amora, *Morus alba*, L.) and cabbage palm fruit (açaí, *Euterpe oleracea*, Mart) as natural sensitizers in photoelectrochemical solar cells. Mulberry and chaste trees are widely spread over the Brazilian territory. Cabbage palm is well disseminated around the Amazon region.

2. Experimental

2.1. Materials

All chemicals employed were reagent grade or of the best available purity. 4,4′-Dicarboxylic acid-2,2′-bipyridine, $dcbH_2$, and $RuCl_3 \cdot XH_2O$ (Strem Chemicals) as well as NaSCN (Carlo Erba) were used as received.

2.2. Preparation of dye-sensitizer solutions

The standard synthetic sensitizer *cis*-$(dcbH_2)_2Ru(NCS)_2$, $dcbH_2$ = 4,4′-$(CO_2H)_2$-2,2′-bipyridine, was prepared following the procedures described in the literature [5]. The

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synthesis of $[(dcbH_2)_2Ru(isq)_2]^{2+}$ (isq = isoquinoline) [9], $[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ (CNpy = 4-cyanopyridine) [14], $[(dcbH_2)_2Ru(ppy)(H_2O)]^{2+}$ (ppy = 4-phenylpyridine) and $[(dcbH_2)_2Ru(ppy)_2]^{2+}$ [10] are described elsewhere.

The extracts of chaste tree fruit and mulberry were obtained from fresh fruits. The clean fruits were crushed and added to ethanol (Merck). The commercial cabbage palm pulp was directly suspended in ethanol. When necessary, the mixtures were centrifuged and diluted HCl was added to adjust the pH, inducing stronger dissolution of dyes. All solutions were protected from direct light exposure.

2.3. Thin-layer sandwich-type solar cell

Photoelectrochemical experiments were carried out by using the dye-sensitized TiO_2 films in a thin-layer solar cell depicted in Fig. 1. The sandwich-type cell consists of two electrodes composed by TCO substrates (Asahi Glass) and an intermediary redox layer. TiO_2 emulsion for photoelectrochemical measurements were obtained by hydrolysis of titanium isopropoxide following the procedure described in the literature [5,23]. The photoanode preparation requires the deposition of the nanocrystalline TiO_2 film over an FTO substrate, followed by the sintering of its particles at 450 °C. The dyes were rapidly attached to the TiO_2 surface by immersing the processed electrodes in ethanolic solutions of each dye. The counterelectrode presents a transparent thin film of platinum on its conductive surface (ITO). The mediator solution was prepared dissolving 0.20 g of I_2 (Merck) and 1.0 g of LiI (Aldrich) in 25 ml of a mixture (90:10) of acetonitrile (HPLC grade, Aldrich) and 3-methyl-2-oxazolidinone, NMO, (Aldrich) which was distilled under reduced pressure.

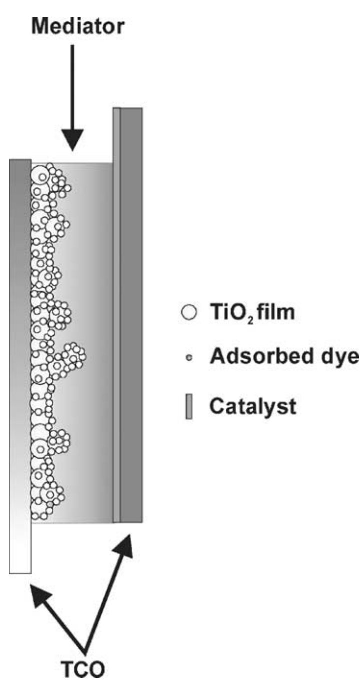


Fig. 1. Thin-layer sandwich-type photoelectrochemical solar cell and its components.

2.4. Physical 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 [9,10].

2.5. Photoelectrochemistry

Photocurrent and photovoltage measurements, as well as photoaction spectra, were obtained as previously described [9,10,13]. An Eco-Chemie PGSTAT–30 galvanostat/potentiostat system was employed for obtaining the current–voltage data. The potentiostat was programmed to execute a linear scan ($v = 10\,mV\,s^{-1}$) from 0 V to the observed open-circuit potential under cell irradiation, which was determined by an A.W. Sperry DM–8A multimeter. The *I–V* curves were obtained with a dye-sensitized solar cell under illumination provided by an overhead projector.

3. Results and discussion

The obtained fruit extracts were reasonably soluble in ethanol and resulted in deep colored solutions. Fig. 2 presents the absorption spectra of chaste tree fruit extract in ethanol and adsorbed onto TiO_2. The fruit extracts absorb visible light sensitizing the oxide semiconductor to low-energy irradiation. The broadening of the absorption band of the colored photoanode is related to the charge transfer interaction responsible for binding the dye to the oxide surface [24].

Wavelengths of maximum absorption obtained for extracts of chaste tree fruit, mulberry and cabbage palm fruit adsorbed onto TiO_2 electrodes (555, 553 and 552 nm, respectively) are slightly red-shifted, compared to the corresponding solution spectra (548, 543 and 545 nm, respectively). The binding between dye and the oxide semiconductor is reported to take place through the carbonyl and hydroxyl groups presented in cyanine-based dyes in natural pigments, which are capable of chelating to the Ti(IV) sites of the TiO_2 surface [16–18,20,25].

The performance of the natural sensitizers in the photoelectrochemical solar cells was monitored through electrical current and voltage outputs under overhead projector irradiation of 0.5 cm^2 dye-sensitized solar cells. Table 1 presents the values of I_{sc}, V_{oc}, maximum power (P_{max}) and fill-factor (FF) obtained for solar cells employing photoanodes with TiO_2 sensitized by chaste tree fruit, mulberry and cabbage palm fruit extracts. The table also presents the current and voltage values resulting in maximum power (I_{mp} and V_{mp}). Some variation on both photocurrent and photovoltage values occur due to slight inhomogeneity of the TiO_2 film on

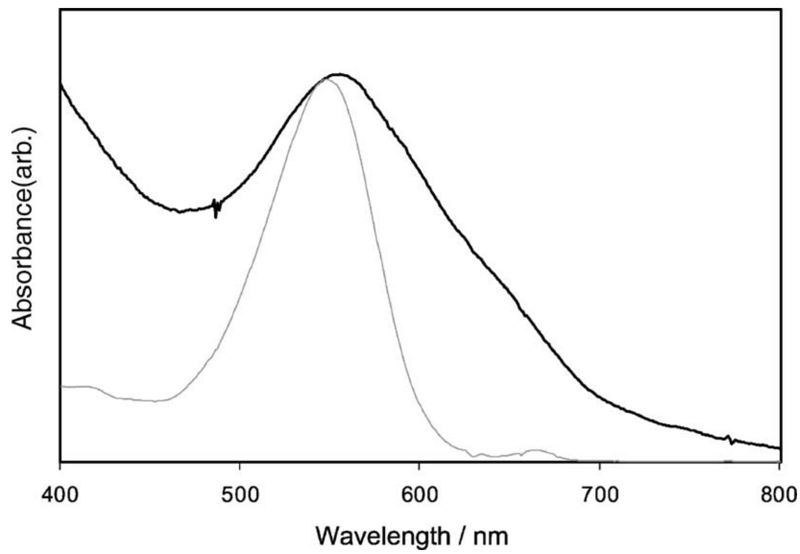
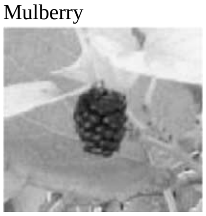


Fig. 2. Electronic absorption spectra of the extract of chaste tree fruit in ethanol (—) and adsorbed onto the TiO_2 photoanode (**—**).

the FTO surface and small differences in the irradiated area. The thickness of the semiconductor layers also presents some variations, therefore average values of several experiments are also presented. High I_{sc} and V_{oc} values are obtained with the fruit extracts. The synthesized standard compound *cis*-$(dcbH_2)_2Ru(NCS)_2$, which is acknowledged as one of the best performing molecular sensitizers so far [26], was employed as the photoanode sensitizer under equivalent conditions resulting in I_{sc} and V_{oc} values of 4.2 mA and 534 mV, respectively. The current and voltage

Table 1
Photoelectrochemical parameters obtained with solar cells employing photoanodes with TiO_2 sensitized by natural dyes

	I_{sc} (mA)	V_{oc} (mV)	I_{mp} (mA)	V_{mp} (mV)	P_{max} (μW)	FF
Chaste tree fruit						
	0.95	377	0.72	256	184	0.51
	1.05	403	0.79	266	209	0.50
	1.05	377	0.74	256	189	0.48
	1.18	403	0.82	256	210	0.44
Average	1.06	390	0.77	259	198	0.48
Mulberry						
	0.86	400	0.63	245	154	0.45
	0.86	400	0.63	245	154	0.45
	0.85	444	0.64	242	155	0.41
	0.85	444	0.63	242	151	0.40
Average	0.86	422	0.63	244	154	0.43
Cabbage-palm fruit						
	0.38	430	0.31	322	98.6	0.61
	0.36	454	0.29	342	98.8	0.61
	0.38	430	0.30	322	97.9	0.60
	0.37	454	0.31	332	102	0.60
Average	0.37	442	0.30	330	99.3	0.61

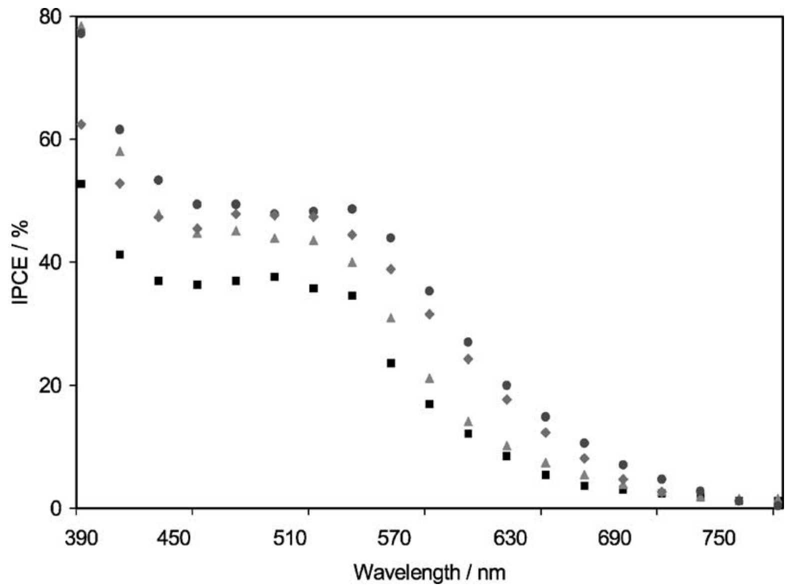


Fig. 3. Photocurrent action spectra of solar cells employing $[(dcbH_2)_2Ru(ppy)(H_2O)]^{2+}$ (●), $[(dcbH_2)_2Ru(isq)_2]^{2+}$ (■), $[(dcbH_2)_2Ru(ppy)_2]^{2+}$ (▲) and $[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ (◆) as TiO_2 sensitizers.

values obtained with the natural extracts are comparable to those obtained with other inorganic compounds of the family *cis*-$[(dcbH_2)_2RuLL']$, L/L' = ancillary ligand, prepared in our lab. Incident monochromatic photon-to-current conversion efficiency (IPCE) ranging ~50% up to 550 nm are obtained with derivatives in which isoquinoline [9], 4-phenylpyridine [10] and 4-cyanopyridine [14] are employed as ancillary ligands. Fig. 3 presents the photocurrent action spectra obtained with solar cells employing $[(dcbH_2)_2Ru(ppy)(H_2O)]^{2+}$, $[(dcbH_2)_2Ru(isq)_2]^{2+}$, $[(dcbH_2)_2Ru(ppy)_2]^{2+}$ and $[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ as TiO_2 sensitizers.

The current–voltage curve obtained with solar cells employing the photoanode with TiO_2 sensitized by chaste tree fruit is presented in Fig. 4. Fill-factor values from 0.40 to 0.61 were obtained with the fruit extracts. The average P_{max} values obtained for the chaste tree fruit (198 μW) are superior to those obtained for the mulberry (154 μW) and the cabbage palm fruit (99.3 μW). Nevertheless, an analysis on the performance of each extract must consider the different absorbances of the dye-sensitized photoanodes.

Usually high photocurrent and photovoltage values are obtained with the TiO_2 photoanodes sensitized by the natural extracts. In our previous investigation, extracts of a Brazilian fruit known as java plum (Jambolão, *Eugenia jambolana*, Lam) were employed as a natural sensitizer in photoelectrochemical solar cells resulting in I_{sc} and V_{oc} values as high as 2.3 mA and 711 mV, respectively [21,22]. The results show that the fruit extracts, adsorbed onto the surface of a semiconductor, absorb visible light and promote electron transfer across the dye/semiconductor interface.

The straightforward preparation of efficient photoanodes with semiconductor oxides sensitized by natural dyes enables a cheaper and easier production of photoelectrochemical solar cells, inasmuch as both preparation and purification steps of synthetic dyes are unnecessary. Further investigation for the successful use of natural dyes should be performed. The acidity of dye solutions is found to affect the resulting photocurrent values [18]. Stability and long-term operation are fundamental issues for the development of such devices. Nevertheless, conversion of visible light into electricity by sensitization of TiO_2 with readily obtained natural extracts is an encouraging alternative to be further developed.

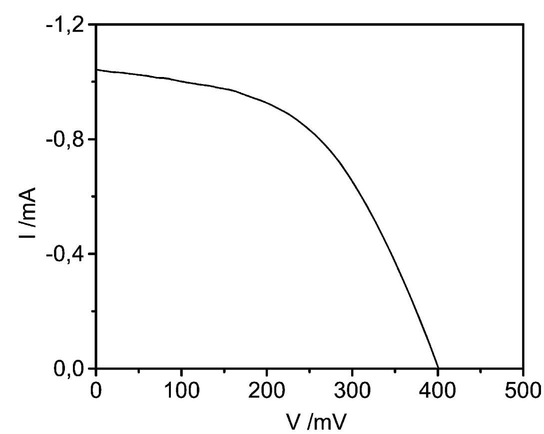


Fig. 4. Current–voltage curve obtained for photoelectrochemical solar cell employing photoanode with TiO_2 sensitized by chaste tree fruit.

4. Conclusion

Enhanced spectral response of TiO_2 to visible light has been successfully accomplished with the use of extracts of the fruits of chaste tree, cabbage palm and mulberry as natural sensitizers. The fruit extracts present good light harvesting properties and perform charge transfer sensitization of nanocrystalline n-type TiO_2. When employed in regenerative photoelectrochemical solar cells, the extracts convert visible light into electricity. The use of a natural source for the semiconductor sensitizer simplifies the steps involved in the preparation and purification of synthetic dyes enabling a faster, simpler and environmentally friendly production of solar cells and providing an interesting alternative to commonly used synthetic dyes. Long-term operation and stability are fundamental issues for the development of such devices and further investigation is currently in progress.

Acknowledgements

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