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Photoelectrochemical and spectrophotometric studies on dye-sensitized solar cells (DSCs) and stable modules (DSCMs) based on natural apocarotenoids pigments

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ABSTRACT

We present a study on dye-sensitized solar cells (DSCs) and we fabricate dye-sensitized solar modules (DSCMs) based on natural apocarotenoids extracted from the achiote's seeds (annatto). Use of less polar solvent such as diethyl ether improves the bixin concentration in the annatto extract which, was employed as sensitizer in the devices. We measure IPCE max (~33%) and estimate $\phi_{inj} \geq 0.438$ for annatto. By accurate and progressive optimization of both TiO_2 multilayer photoanode and of electrolyte composition an efficiency (η) around 1.6%, is achieved, with an improvement of about ~742% compare to the best performance for annatto extract, so far reported. DSCM shows stability which overcomes 1000 h (shelf-life test), under 1 sun, and produces a battery capacity of ~46.8 Ah, the equivalent to ~15 type AAA standard battery, in a similar time period. Although annatto based DSCMs are still below the efficiency requirements for practical applications for large scale industry, our encouraging results, testify the potentiality of this pigment in the production of non-toxic, cheap, long term stable and environmentally friendly vegetable based solar devices, as alternatives to batteries for small electronic goods market.

1. Introduction

One of the main target of contemporary scientific research is finding a solution to the urgent need for a clean and cheap energy source. In recent years, the photovoltaic (PV) technologies experimented many advances in efficiency, cost and robustness. Currently, three main types of PV systems can be categorized: ***i***) *p-n* semiconductor junction cells, ***ii***) dye-sensitized solar cells (DSCs) and ***iii***) organic photovoltaic cells (OPVCs) [1].

Since their appearance in the 1991 [2], DSCs have drawn a lot of attention in the scientific community due to their ease of fabrication, low cost and competitiveness with other PV based on *p-n* junctions. A typical DSC is assembled placing in succession a transparent photoanode (or working electrode, WE), a counter-electrode (CE) and in between, an electrolyte solution to promote the charges transfer by means of redox mediator (usually iodide/iodine redox couple, I^-/I_3^-, although other redox mediators have been successfully tested [3]). Generally, the photoanode consists of a dye-sensitized mesoporous wide band semiconductor layer (TiO_2, ZnO, SnO_2, etc.) deposited on a transparent conductive glass substrate (TCO). The working principle of a DSC is based on two main processes: ***i***) energy light absorption and, ***ii***) electron transfer [4]. Under light irradiation, the dye molecules capture the incident photons generating electron/holes pairs. The resulting electrons, at excited states, are then injected into the conduction band (CB) of the TiO_2 and transported to the electron-collecting CE who transfer them to the electrolyte. The electrolyte reduces the oxidized dye, which is reported to the ground state, becoming ready to absorb another incident photon, and the cycle begins again turning many times. In this framework, the dye appears as an essential component of the DSC and, in this regard, many natural and artificial sensitizers have been investgated [4].

Despite of their low efficiency, natural dyes have collected a lot of attention by scientific community [5,6,7] because their large available, easily and safety extraction form fruit/plants and non-toxicity. Among the large family of natural pigments, carotenoids have been explored due to their light absorption ($\varepsilon \sim 10^5$ $Lmol^{-1}{\cdot}cm^{-1}$) in the

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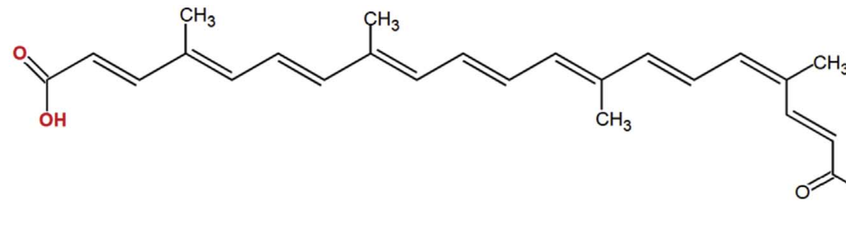

Fig. 1. Chemical structure of bixin (R = CH_3) and norbixin (R = H). The schematized 6,6′-diapocarotenoids, are the main components in the mixture of the present study and are presented as 9′-cis isomers. However, many other isomers may theoretically occur as each double bond may be either cis or trans.

380 ÷ 550 nm range of the visible solar spectrum as well as their capability to produce charge carriers by light excitation [4]. In photosynthetic membranes, carotenoid polyenes and chlorophylls participate in singlet and triplet energy transfer processes, enhancing the rate of light absorption and the suppression of singlet oxygen sensitization, respectively. [8,9] Further, it is also thought that they can mediate the dissipation of excitation energy during periods of excess light absorption [10].

When in solution carotenoids are generally photochemically not reactive, however, they can undergo unimolecular isomerization and act as quenchers of the triplet states of other molecules through energy transfer. This lack of reactivity is presumably due to the very short lifetime of their singlet excited state (50 ps < τ < 10 ps), preventing diffusion-controlled bimolecular processes, as well as to the vanishing low yield of intersystem crossing to the longer-living triplet species. [9,11,12] A reasonable and practicable pathway to overcome the kinetic limitation imposed by the short singlet excited state lifetime can be the choice of an appropriate carotenoid molecular arrangement which, covalently bonded to the electron acceptor, ensures a rapid photoinduced electron transfer (*ps*- or *sub-ps* time scale) towards the electron acceptor, efficiently competing with the carotenoids excited state decay [13].

The first main study on carotenoids as sensitizer for TiO_2 nanocrystalline mesoporous electrode was pioneered by Gao et al. [14] In their study, ITO (indium tin oxide) electrodes coated with TiO_2 nanoparticle layer and a synthetic carotenoid 8′-apo-β-caroten-8'oic acid (ACOA) deposited as sensitizer were investigated in a photo-electrochemical cell using a monochromatic light (λ = 426 nm). Despite the very low values of open-circuit voltage (V_{oc}) and short-circuit current density (J_{sc}) achieved, the importance of their investigation was the overcoming of the kinetic limitations for efficient electron photo-injection and carrier transport imposed by the short-life of single excited state of carotenoids through covalent bonds with the TiO_2 surface, via terminal carboxylate groups. In 2010 Gomez-Ortiz and co-worker [15], obtained purified carotenoids bixin and norbixin, from the extract of achiote seeds (annatto) by separation processes. Although their pioneering results demonstrated that it is relatively straightforward to obtain pure dyes from the achiote seeds, the best η of their cells using pure bixin was rather low (η = 0.37%) and significantly lower was that achieved by employing the annatto pigment (η = 0.19%).

In this framework, it is of interest to explore conditions under which *annatto* pigments from achiote seeds can elicit new interest as proper sensitizers in TiO_2 nanostructured photoanode to generate photocurrents in DSCs and in dye-sensitized solar modules (DSCMs).

Achiote is an American continent shrub that bears an inedible fruit containing red seeds [16] from which, a dark-red extract (annatto), widely employed in cosmetic and pharmaceutical manufactures, can be obtained. The seeds pericarp contains mainly *cis-bixin* (methyl hydrogen (9′Z)-6,6′-apocarotene-6,6′-dioate, molecular formula $C_{25}H_{30}O_4$, up to 80%), and *trans*- and *cis-norbixin* (6,6′-diapocarotene-6,6′-dioic acid and 9′-cis-6,6′-diapocarotene-6,6′-dioic acid molecular formula $C_{24}H_{28}O_4$, up to 20%). *Cis-bixin* is a water insoluble pigment constitutes by a long chain of alternating double conjugated bonds, with carboxylic acid and methyl-ester groups each at each end of the chain while *trans*- and *cis-norbixin* with a carboxylic acid moiety instead of methyl ester moiety are water soluble. In the following, because we investigate not purified apocarotenoids, we will design with *bixin* and *norbixin* both the *cis* and *trans* isomers and we will name *annatto* their mixture. Both *bixin* and *norbixin* are common in living organisms where their intense absorption bands in the visible spectral region are responsible for coloration and the beginning of specific photobiological responses. It is worth to emphasize the role of the chemical structure (see Fig. 1) in DSC/DSCM ambient. In bixin, the carboxylic group at C7 carbon atom in the conjugated long chain, being not methyl carboxy-ester, easily binds with the surface hydroxyl groups of the TiO_2 in an effective mono-dentate linkage. A feature also reported by Gomez-Ortiz et al. [15] which, found best results in *bixin* sensitized TiO_2 solar cell compared to those using *nor-bixin*. Moreover, the same authors determining ε of $1.9{\cdot}10^5$ $Lmol^{-1}{\cdot}cm^{-1}$ and $1.4{\cdot}10^4$ $Lmol^{-1}{\cdot}cm^{-1}$ for bixin and nor-bixin, respectively, proved the higher light-harvesting ability of bixin dye. In this work, we present a spectrophotometric and photoelectrochemical study on TiO_2 photoanode sensitized by annatto pigments extract from achiote seeds for DSCs and dye-sensitized solar modules (DSCMs) applications. We also demonstrate that the choice of a suitable solvent can overcomes long and tedious chromatographic purification processes. In addition, high- and long-time stability (more than 1000 h) of our annatto carotenoid extracted and improvements in the cell power conversion efficiency (~1.6%), with respect to the previously literature results, proved the potentiality of this sensitizer kind for both DSCs and DSCMs applications.

2. Experimental

2.1. Materials, dyes and pigment solution

All chemicals employed, such as DMPII (1,2-dimethyl-3-propylimidazolium iodide), MPII (1-methyl-3-propyl imidazolium iodide), TBP (4-ter-butyl-pyridine), MPN (methoxyproprionitrile), AN (acetonitrile), VN (valeronitrile), EA (ethyl acetate), AC (acetone), DEE (diethyl-ether) were reagent grade and used as received without any further purification. The conductive glass plate (FTO glass, Fluorine-doped SnO_2, surface resistivity 7 ohm/sq) and the Surlyn foils 25 μm thick employed for DSCs were purchased from Solaronix SA. Two extraction pathways of the achiote seeds pigments in acetone and ethyl-ether ambient were performed: ***i)*** achiote seeds (2 g) were immersed in 80 ml of acetone and sonicated for 1 h at room temperature and then filtrated, ***ii)*** the seeds (2 g) were sonicated for 1 h in 80 ml of ethyl-ether and then filtrated. Both solutions stored at 5 °C were stable for long time.

2.2. Preparation of TiO_2 anodes, platinum counter-electrodes and DSC assembly

FTO-glass substrates were cleaned in a detergent solution and washed with water/ethanol mixture. Then, the cleaned FTO-glass was pretreated by immersion in 100 ml $TiCl_4$/water solution (40 mM) at 70 °C for 30 min, washed again with water and ethanol and finally dried in