Current Applied Physics 16 (2016) 651–657

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Transparent quasi-solid state dye-sensitized solar cells sensitized with naturally derived pigment extracted from red seaweed

Andreas Rapsomanikis [a], Dimitra Sygkridou [a, b, **], Evangelos Voutsinas [c], Elias Stathatos [a, *]

[a] Nanotechnology and Advanced Materials Laboratory, Department of Electrical Engineering, Technological-Educational Institute of Western Greece, GR-26334 Patras, Greece
[b] Physics Department, University of Patras, 26500 Patras, Greece
[c] Department of Civil Engineering, Technological-Educational Institute of Western Greece, GR-26334 Patras, Greece

ARTICLE INFO

Article history:
Received 21 November 2015
Received in revised form
13 March 2016
Accepted 23 March 2016
Available online 25 March 2016

Keywords:
Red seaweed
Natural pigment
Phycobilins
Dye-sensitized solar cell
Quasi-solid state electrolyte

ABSTRACT

Red seaweeds collected at Kefallinia Greek Island are examined for the first time as possible sensitizers in third generation photovoltaic cells. In particular, red seaweeds were collected and different solvents were used to extract their pigment through a simple procedure, in order to be used as a natural sensitizer for dye-sensitized solar cells. The dye solution with enhanced absorption in the visible spectrum was submitted to further absorption tests, where different pH and dye solution's temperature were tested to determine whether it affects the amount of the adsorbed dye on nanocrystalline TiO_2 films. Solutions made with natural dye extracted from red algae in different solvents were used for the sensitization of TiO_2 photoanodes and fabrication of quasi-solid state dye-sensitized solar cells some of which exhibited very satisfactory results compared with the published values so far of other seaweed dyes. The solar cells were examined in terms of *J*–V characteristic curves under simulated solar illumination and the best performing ones were also tested under dark conditions, while electrochemical impedance spectroscopy was used to evaluate electrodes and electrolyte interfaces. The optimal results were obtained for an acidic dye solution (pH = 3) and for pigment's solution temperature of 35 °C where cells showed a short circuit current density of 1.26 mA/cm^2 and an open-circuit voltage of 0.66 V.

1. Introduction

In the past decades, dye-sensitized solar cells (DSSCs) have come to the forefront of the research focused on producing low cost electrical energy through solar energy conversion devices by utilizing the incoming solar radiation [1]. The overall concept of the dye-sensitized solar cells arises from the photosynthetic process occurring in plants. As chlorophyll absorbs light from the sun and converts it into chemical energy in plants, accordingly the dye molecules in dye-sensitized solar cells capture light and produce electrical energy. The sensitizer's cost constitutes the lion's share of the total cost for the fabrication of the dye-sensitized solar cells. Therefore, it wasn't unexpected when in an attempt to lower this cost, many groups directed their field of research on testing natural dyes and pigments extracted from flora organisms in order to replace the commercially available ones [2–7].

Natural pigments have certain advantages as there are no resource limitations, they don't cause any harm to the environment and are easily prepared [8]. Also, they have high absorption coefficients and light harvesting efficiency [6]. The natural pigments can be classified into three categories (a) chlorophylls, (b) carotenoids and (c) phycobilins [9]. The type of solvent used for the extraction, determines which natural pigment will be isolated. Chlorophylls (a, b, c and d) and carotenoids (carotenes and xanthophylls) are both insoluble in water and so organic solvents must be used to isolate them, whereas phycobilins are water soluble as they are attached to water-soluble proteins [9].

Up until now many natural dyes have been extracted and tested for sensitizing dye-sensitized solar cells. Calogero et al. extracted

* Corresponding author. Department of Electrical Engineering, Technological-Educational Institute of Western Greece, GR-26334 Patras, Greece.
** Corresponding author. Department of Electrical Engineering, Technological-Educational Institute of Western Greece, GR-26334 Patras, Greece.
E-mail addresses: dsigridou@upatras.gr, dim.sigridou@gmail.com (D. Sygkridou), estathatos@teiwest.gr (E. Stathatos).

http://dx.doi.org/10.1016/j.cap.2016.03.018
1567-1739/

chlorophylls from frozen brown alga of the genus *Undaria pinnatifida* and reported an efficiency of 0.178% [10]. Sengupta, Mondal and Mukherjee extracted chlorophyll and betalain dyes from fresh spinach leaves and beetroots and afterwards each dye separately or a mixture of them was used to sensitize zinc oxide dye-sensitized solar cells. The best result, with an overall efficiency of 0.294%, was achieved for cells sensitized with the mixed dyes due to the wider absorption spectrum [11]. Shanmugam et al. tested three natural dyes extracted from three types of grasses *Hierochloe Odorata, Torulinium Odaratum* and *Dactyloctenium Aegyptium*. The dye-sensitized solar cells fabricated with the dye extracted from *Hierochloe Odorata* exhibited a maximum efficiency of 0.46% [12]. Suyitno et al. examined the stability of dye-sensitized solar cells based on natural dye extracted from papaya-leaf, with the acidity of the dye adjusted by the addition of benzoic acid. The highest performance of 0.28% was recorded for cells sensitized with natural dye from papaya leaves at pH 3.5 [13]. Ananth et al. showed that using *Caesalpinia sappan* heartwood extract as sensitizer the solar light to electron conversion efficiency for titanium dioxide DSSCs was found to be 1.1% [14].

In this work, red algae of the genus *Laurencia Obtusa* were collected at the island of Kefallinia, Greece (38°15′N 20°30′E) and their pigment was extracted with a simple procedure. These specific seaweed species are well known in Kefallinia as their extract is used as a food colorant for local sweet products. Firstly, different solvents were used to extract the seaweed's natural pigment and the absorption spectra of the resulting solutions were tested. Secondly, the dye solution which had the wider absorption over the visible spectrum was further studied and different pH and dye solution's temperature were tested to determine whether it affects the amount of the adsorbed dye on TiO_2 films. Finally, dye-sensitized solar cells were fabricated, using the natural dye solutions as sensitizers and they were characterized electrically and through electrochemical impedance spectroscopy (EIS).

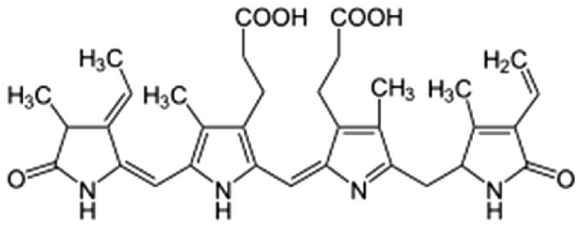
2. Experimental details

2.1. Materials

Commercially available O,O′-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeffamine® ED-600, Mr~600), 3-(Triethoxysilyl)propyl isocyanate, lithium iodide, iodine, 1-methyl-3-propylimidazolium iodide, *tert*-butyl pyridine, guanidine thiocyanate, chloroplatinic acid hexahydrate (H_2PtCl_6), and all solvents were purchased from Sigma-Aldrich and used as received. SnO_2:F transparent conductive electrodes (FTO, TEC8) 8 Ohm/square were purchased from Pilkington NSG Group. For transparent TiO_2 films, Titanium(IV) isopropoxide (Alfa Aesar, 97+%), Triton X-100 (polyoxyethylene-10-isooctylphenyl ether) surfactant (99.8%, Aldrich), glacial acetic acid (AcOH, Aldrich) and ethanol were used to make the TiO_2 solution.

2.2. Pigment extraction

Red seaweed species were collected in the island of Kefallinia and they were stored at a closed container at 9 °C until used. The red color of the seaweed is ascribed to the presence of the chromophore phycoerythrobilin in phycoerythrin (Scheme 1). Initially, four dye solutions were prepared each time altering the solvent used. The solvents that were tested were methanol, ethanol, a mixture of acetone with millipore (ultra pure) water (acetone/millipore water 80:20 v/v) and millipore water. To prepare the dye solutions, 5 g of the seaweed were soaked in 30 mL of solvent overnight and then it was filtered, to ensure that it didn't contain any residues from the algae strain.



Scheme 1. The chromophore phycoerythrobilin in phycoerythrin.

2.3. Preparation of TiO_2 photoanodes

The titania photoanodes were fabricated via the sol-gel method. In particular, 0.72 g of Triton X-100 was mixed with 4 mL of ethanol, followed by addition of 0.4 mL of glacial acetic acid and 0.32 mL of titanium(IV) isopropoxide under vigorous stirring [15–17]. After a few minutes stirring, the solution was deposited on the FTO glasses with a spin coating device (Spin150, APT Automation) at 1200 rpm for 10 s. The procedure was repeated several times until the optimum film thickness of 2 μm was obtained. After each film deposition layer, the glasses were calcined to 500 °C for 10 min using 20 °C/min heating ramp rate. The resulting films were highly transparent.

The sensitization of the TiO_2 films was carried out using the four dye solutions previously prepared, along with a fifth one where a few drops of acetic acid were added to the primary millipore water dye solution to adjust the pH to 3. The pH of the dye was verified by using a pH meter (Extech Instruments Palm Ph, model PH220). Since the millipore water dye solution had the wider absorption spectrum, acetic acid was added only to that dye solution to try to enhance the light harvesting efficiency by reducing the aggregation of the dye molecules [18]. The photoanodes were immersed into the five dye solutions and were left overnight to complete their sensitization. Various dye solutions' temperatures were tested (35 °C, 45 °C and 55 °C) to examine if and in what extent the temperature affects the cells' electrical parameters. The glasses were removed from the dye solutions and were rinsed with the proper solvent to remove the excessive amount of dye and dried in order to remove any solvent residues or humidity that could be present in the pores of the films.

2.4. Preparation of hybrid organic-inorganic material and quasi-solid state electrolyte

For the fabrication of the DSSCs a quasi-solid state electrolyte was used, based on a hybrid organic-inorganic material to contribute to the jellification process [19]. The quasi-solid state electrolyte was chosen as it combines the high ionic conductivity of liquids, while it reduces the risk of leaks and minimizes sealing problems during the cells' fabrication. The hybrid organic-inorganic material was prepared according to the following procedure. O,O′-Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeffamine® ED-600, Mr~600) and 3-isocyanatopropyltriethoxysilane (ICS; molar ratio ICS/diamine = 2) were put to react in a vessel (acylation reaction), producing urea connecting groups between the polymer units and the inorganic part.

The quasi-solid state electrolyte was synthesized by the following procedure: 0.07875 g of the functionalized alkoxide precursor was dissolved in a mixture of 1.6 g of sulfolane and 0.8 g of 3-methoxypropionitrile under vigorous stirring. Then, 0.368 g AcOH was added followed by 0.12 g LiI (0.27 M), 0.12 g 1-methyl-3-propylimidazolium iodide (0.14 M) and 0.06 g I_2 (0.071 M). To