International Journal of Control, Energy and Electrical Engineering (CEEE)
Vol.3-Issue.1- 2016
pp. 41-45

Fabrication and Characterization of Dye-Sensitized Solar Cells Using TiO_2 Photo-Anode

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***Abstract*— Dye-sensitized solar cells (DSSCs) were fabricated by sensitizing dioxide titanium TiO_2 photo-anode using a series of natural dye extracted from plant sources of Mallaw, anthocyanin and saffron. Optical properties of sensitized dyes were investigated by UV–vis spectroscopy. We have noticed that the absorption of the Mallow and anthocyanine are more significant compared to the other dyes.**

The anatase phase of the dyed TiO_2 nano particles were synthesized by the modified sol–gel method and analyzed by XRD measurements. The natural dye was mixed during the synthesis of TiO_2 nano particles to obtain dyed titanium dioxide nano particles which were used as photo- anode for DSSC.

The typical current-Voltage curves of our solar cells were measured under AM 1.5 using a power density of 100 mW/cm^2. The mallow cell shows a good fill factor of 0.75 and a noticeable photoelectric conversion efficiency of 0.50%. This sensitizer owns the best photovoltaic performance among the two other natural dyes.

***Keywords*—Dye sensitized solar cells, natural dye, semiconductor, current-voltage, dioxide titanium, efficiency.**

I. Introduction

Among all the renewable power sources, solar energy is the most easily usable, inexhaustible, peaceful, and adjustable to enormous applications [1]. Solar energy is the most available energy source on the earth because of an almost infinite reserve that can cover all the energy demand associated with human activity. In this context, photovoltaic conversion of solar energy is a major challenge. At present, the most efficient photovoltaic cells are those which use inorganic materials such as silicon (90% of the market), and achieving high conversion efficiencies of around 25% in the laboratory [2]. However, Because of their high cost associated with technological constraints in their manufacture, the research in alternative and less expensive materials is necessary [2]

Dye-sensitized solar cells (DSSCs) based on the photosensitization of nanocrystalline TiO_2 electrodes are considered as a promising solution alternative to silicon-based solar cells applications [3].

The performance of DSSC is mainly related to the dye sensitizer adsorbed on the surface of TiO_2 [4]. The dye absorption spectrum and the anchorage to the surface area of the semiconductor TiO_2 are significant parameters for determining DSSC efficiency [5, 6]. Transition metal compound such as ruthenium polyridyl complexes were used widely as effective dye-sensitizer, they have higher life time and light to electron conversion efficiency. However, their high synthesis cost leads to give much attention to the natural dyes [7]. We use some usual natural dyes. Some of them have already been used, but the others are local dyes and we try to check the opportunity to realize good solar cells using those pigments.

The work reported here aims on demonstrating the fabrication and characterization of dye-sensitized solar cell as a low-cost cell in Tunisia.

II. Principle of operation

Contrary to a conventional solar cell which the same material has the function to absorb light and separate the charge carriers (PN junction), these two spots are separated in a dye sensitized solar cell. The light absorption process is

ISSN: 2356-5608

performed by dye molecule and the separation of the electrical charges is done by the nanocrystal semiconductor that has a wide gap [2].

A typical DSSC is composed of nanocrystal semiconductor film, sensitizing dye, electrolyte and counter electrode [8]. Among them, the dye molecules (sensitizers) collect photons and produce the excited electrons from the highest occupied molecular orbital in the ground state to the lowest unoccupied molecular orbital (LUMO) in the excited state as shown in fig.1. The injected electrons are transported into the conduction band of the TiO_2 and finally diffuse across the interconnecting network of TiO_2 nanoparticles to the electrode and are collected to supply the external loads as described in fig 1. The oxidized dye accepts electrons from the electrolyte (redox mediator) regenerating the ground state and new cycle is started

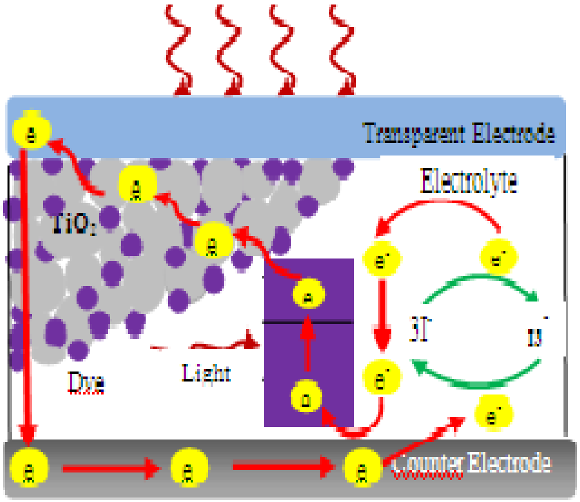

Fig. 1: Schematic structure and principle operation of DSSC.

III. Materials and Experimental

The Transparent Conductive Oxide (TCO) coated glass (TCO22-7: 2 mm thick glass substrate with a 7 Ω/sq fluorine doped tin oxide coating on one side 5.00×5.00 cm^2) was employed. We have used nanocrystalline TiO_2 synthesized after a simple modification of the sol gel process, pipets, mortar and pestle, water bath, tweezers, scotch Magic, hot plate (Stuart) and dye extracted from the natural product.

A. Preparation of Sensitizers Natural Dyes.

In this paper, we have used natural dye extracted from a plant called Karkade (Hibiscus), Mallaw and saffron. Given two beakers, for one, Mallaw powder (5.25 g) and the other for saffron powder (3.25 g) and put into each beaker 40 ml of ethanol, mixed each with a Pasteur pipette and allowed to stand for 10 minutes and take the upper solution with a syringe.

Dry dark red Karkade flowers were crushed in a juice mixer. The resulting finely ground powder (10.00 g) was soaked in a 250 ml Erlenmeyer flask with 100.00 ml ethanol. The mixture was magnetically stirred gently at 60 °C for 20 min. The mixture was then cooled, for 20 min, and filtered to obtain finally the antocyanin pigment.

B. Preparation of Photoanodes and the DSSC.

The sol–gel process with a simple modification was used for the synthesis of the dyed TiO_2 powder. The mixing of the natural dye during the synthesis of TiO_2 results a colored precipitation according to the dye used and this suspension was also dried at 150°C for 10h to obtain fine particles of dye mixed TiO_2.

The obtained dyed TiO_2 powder nanoparticles were grinded and made into a homogeneous paste. A film of TiO_2 was coated and repeated twice using doctor-blade technique to form a thick layer. Then, it was sintered at a temperature of 200°C for 3h to remove the organic benders and solidify the TiO_2 on the conductive glass substrates. After, the photo electrode dyed TiO_2 was immersed again for 10 h in the natural dye.

The counter electrode was coated with a catalytic material for electron transfer platisol T / SP and the photo-anodes were joined together. The liquid electrolyte (I^+/I_3^- , Iodolyte AN-50) was poured through the fine holes in the two electrodes carefully and sealed to prepare TiO_2 based conventional DSSC.

C.Characterization

The photoanodes were characterized by using an X-ray diffractometer (XRD), and has been performed using an X'pert Pro X-ray diffractometer (Δ2θ = 5–60°, 0.033° as increment, integration time 50 s and Cu Kα1 radiation, λ = 1.5406 Å). To evaluate the absorbance of films we used the UVvis spectrophotometer (UV-Cecil CE 3041) in the region 400-800 nm.

The current-voltage characteristic of realized DSSC was measured under AM1.5 using a density of power 100 mW/cm2 and Keithly electrometer 6517A at room temperature. Reading parameters were carried out by developed software using LabVIEW through the RS232 serial intelligent and operator procedures Keithly device.

IV. R Results and Discussions

A. *Structural and Optical Properties of the Synthetized Films*

Figure 2 gives the structural phase and crystalline size information of the powder X-ray diffraction pattern of the TiO_2 nanoparticles powder and the dyed thin film annealed at 200°C for 3 h obtained by modified sol–gel method and deposited by doctor blade. A crystalline phase corresponding to the titanium oxide anatase phase with a preferential orientation (101) characterized by the high intensity was noticed. The average particle size of the dyed TiO_2 nanoparticles in anatase phase varied from 10 nm to 26.58 nm.

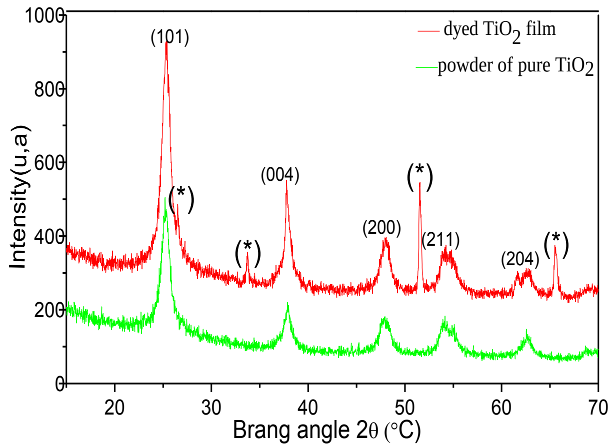

Fig .2: XRD spectra of pure powder, dyed TiO_2 film sintered at 200°C. (*): Substrate F.SnO_2.

The absorption spectrum of the extracted dye diluted in ethanol was measured using UV–Vis spectrophotometer as shown in figure 3.

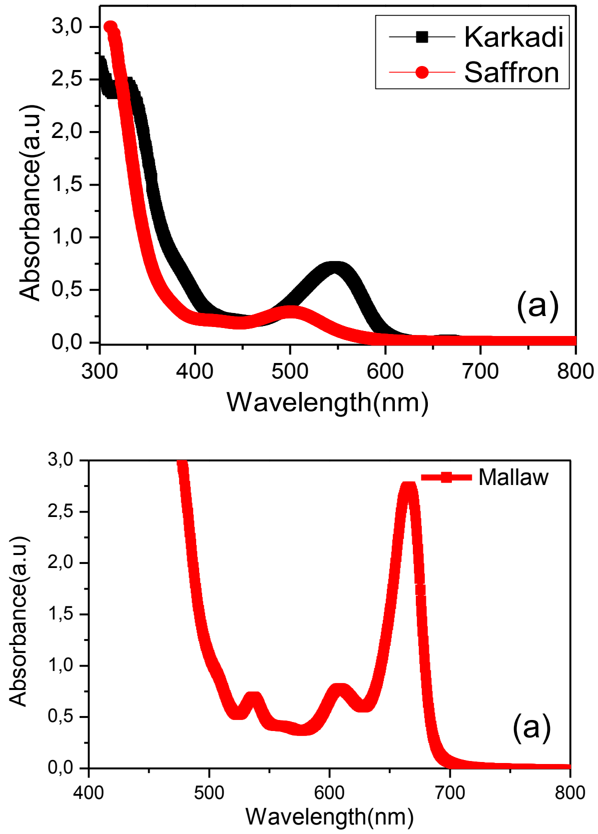

Fig. 3: UV – Vis Absorption spectra of natural dyes.

The anthocyanin dye exhibits a small hump at 350 nm and another peak around 540 nm (fig3.a). The arise of these two peaks is attributed to the combined effect of the anthocyanins and the purple red betanin pigments as reported earlier by. Giusti et al. and Zyoud et al. [9, 10]. The saffron exhibits a broad absorption band in the green close to 500nm attributable to the mixture of betanin.

For the Mallaw, the absorption peaks arise at wavelength 480 nm (blue light) and 665 nm (red light) (fig3.b). The absorption peaks match well with the characteristic absorption data of chlorophyll dye [11].

The absorption spectrum of the extracted dye adsorbed on TiO_2 films in fig.4 revealed the improvement of the light photon absorption and the extension of the absorption edge which is shifted to the higher energy compared to the pure TiO_2 [10]. It is clear especially for the Mallaw dye which his absorption spectra was more shifted to the high energy than the anthocyanin dye and it has a dominant absorption in this region of the spectra. This late indicates that the chemical reaction between the Mallaw molecules and the TiO_2 surface is more important compared the two other dyes.

The intensity of same peaks of the two dye adsorbed on TiO_2 films become very weak and there is some others are suppressed when mixed with TiO_2.This late can be interpreted by that these types of natural dye molecules are strongly adsorbed to the oxide surface which leads to enhancement of the absorption.

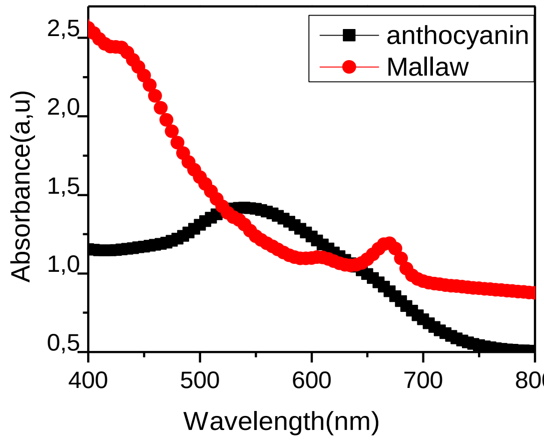

Fig. 4: Absorption spectra of dyes absorbed on TiO_2.

B. *Efficiency Studies*

The photovoltaic properties of the prepared DSSCs, i.e. short circuit current (Jsc mA/cm2), open circuit voltage (Voc, V), fill factor (FF), and efficiency (η, %), were determined from the I–V curve obtained under irradiation with white light (100 mW/cm^2). The fill factor and efficiency were calculated based on the following equations:

$$FF = \frac{J_{max} V_{max}}{J_{sc} V_{OC}} \tag{1}$$

$$\eta = \frac{P_{max}}{P_{in}} = \frac{V_{max} J_{max}}{P_{in}} = \frac{FF \times (V_{OC} \times J_{sc})}{P_{in}} \tag{2}$$

In figure 5, we give the measured current–voltage (*I-V*) characteristic of the different realized DSSCs.

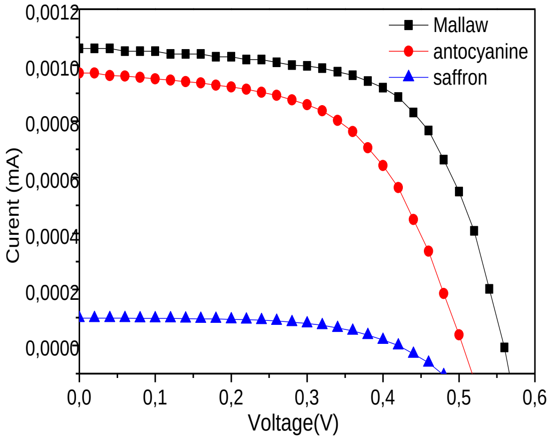

Fig. 5. Current-voltage curves for the DSSCs sensitized by natural dyes.

The typical *I-V* curves of the DSSCs fabricated show a typical behavior of a solar cell. As displayed in Table 1 and Fig. 5, the fill factors of these DSSCs ranges from 75% with the Mallaw sensitizer, 64 % for anthocynine dye to 38% with saffron. The Voc ranges from 559 mV with Mallaw as sensitizer to 500 mV with anthocyanine dye. The *Isc* varies from 1.06 mA with Mallaw as sensitizer to 0.1 mA for saffron. The efficiency of the DSSC realized reached 0.50% for the mallaw and 0.35 for saffron.

The solar cell sensitized by the Mallaw using chlorophyll derivatives as sensitizers have given relatively high conversion efficiency. This late is in agreement with the absorption spectrum which shows that the spectra of the Mallaw dye is more shifted to the high energy than the other dyes which results the reduce of the band gap, therefore more photon for theTiO_2 electrode to be converted into current and as a result a high efficient DSSC can be achieved.

The efficiency of this cell is improved compared to the result obtained by Torchani et al. [7]. This late can be due to the grain size of nanoparticle TiO_2 and the modified sol gel-process for the synthesis of the dyed TiO_2 nanoparticles which enhances the efficiency of electron conversion.

Table 1: Photo electrochemical parameters of the DSSCs sensitized by natural dyes extracted with ethanol

Natural dye	Jsc (mA cm^{-2})	V_{OC} (mV)	FF (%)	η (%)
Mallaw	1.06	559	75	0.50
Anotocyanine	1	500	64	0.40
saffron	0.1	450	52	0.35

V. Conclusion

An electricity conversion efficiency of 0.50% to 0.35% has been achieved for the DSSC sensitized with the different natural dyes extracted from Mallow, dry dark red Karkade flowers and saffron under the condition of irradiation of AM1.5 (100mW/cm^2).

The absorbance of the dye were determined and compared to the efficiency of the respective solar cells. We obtain an effective correlation between the absorption spectrum and the yield of the DSSCs. Optical absorption of antocyanine and especially the Mallaw is important compared to the saffron dye. Also, the *I-V* curves of l the DSSC using the Mallow and antocyanine as sensitizers have attractive values of the short current, open-circuit voltage and the fill factor.

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