The Scientific Journal of University of Benghazi
SJUOB
http://journals.uob.edu.ly/sjuob

Effect of Some Heavy Metal Ion on the Efficiency of Some Natural Dyes Solar Cells with Titanium Dioxide

Hamdy AB. Matter [1*], Tariq M. Ayad [2]

1-2 Chemistry Department, Benghazi University, Elwahate Jalow, Libya.
1 High Institute of Engineering and Technology, El-Arish, Eygpt.

Received 04 / 02 / 2022; Accepted 15 / 06 / 2022

الملخص

صُنِعَت الخلايا الشمسية من أصباغ طبيعية مثل صبغة الأنثوسيانين المستخرجة من عصير التوت وأوراق الحناء والكركديه وصبغة البيتالين المستخرجة من البنجر والملفوف الأحمر وصبغة الكركمين الصفراء المستخرجة من الكركم مع ثاني أكسيد التيتانيوم. واستخدمت أيونات بعض المعادن مع بعض الأصباغ في تكوين أقطاب الخلية بأكسيد التيتانيوم وأكسيد الزنك حيث يُسَخَّن الخليط إلى 450 درجة مئوية وصنع أقطاب كهربائية لها قدرة أعلى على امتصاص الأصباغ الطبيعية مما أدى إلى زيادة تيار الخلية ورفع النسبة المئوية. من كفاءة الخلية. الأصباغ الحمراء الطبيعية (صبغة الأنثوسيانين مع المعادن Cd وZn وPb وHg وCu، DSSCs المحسّسة للصبغة لها كفاءة خلوية تبلغ 1.340٪، 1.326٪، 1.147٪، 1.369٪، و1.325٪ على التوالي وصبغة بيتالين، مع المعادن Zn و Hg و Cu، تتمتع DSSCs الحساسة للصبغ بكفاءة خلوية تبلغ 1.369٪ و 1.385٪ و 1.261٪ على التوالي، والأصفر الطبيعي (صبغة الكركمين) مع المعادن Zn و Pb، وهي صبغية حساسة تتمتع DSSCs بكفاءة الخلية 1.301٪ و 1.384٪ على التوالي. عملت على زيادة التوصيل الكهربائي للأقطاب الكهربائية. ربما تعمل هذه المواد غير العضوية عوامل تجميع لهذه الأصباغ على أقطاب الخلية مما يزيد من كفاءة الخلية.

الكلمات المفتاحية: الخلية الشمسية، ثاني أكسيد التيتانيوم، الأصباغ الطبيعية، الأقطاب الكهربائية، الفبركة.

Abstract

Solar cells were made from natural pigments such as the anthocyanin pigment extracted from berry juice, henna leaves and roselle, betalain dye extracted from beets and red cabbage, and yellow curcumin dye extracted from turmeric with titanium dioxide. The ions of some metals are used with some dyes in the formation of cell electrodes with titanium oxide and zinc oxide. The mixture is heated to 450 ºC and makes electrodes that have a higher ability to absorb natural dyes, which increased the cell current and raised the percentage of cell efficiency. Natural red dyes (anthocyanins dye with the metals Cd, Zn, Pb, Hg, and Cu, dye-sensitized DSSCs have cell efficiency of 1.340%, 1.326%, 1,147%, 1,369%, and 1,325%, respectively. Betalain dyes, with the metals Zn, Hg, and Cu, dye-sensitized DSSCs have the cell efficiency of 1.369%, 1.385%, and 1.261%, respectively,) and natural yellow(curcumin dye) with the metals Zn, and Pb, dye-sensitized DSSCs have the cell efficiency of 1.301%, and 1.384%, respectively. This worked to increase the electrical conductivity of the electrodes. Possibly these inorganic substances act as aggregation factors for these pigments on the poles of the cell, which increases the efficiency of the cell.

Keywords: solar cell - titanium dioxide (tio2) - natural dyes- the photovoltaic - fabrication.

1. INTRODUCTION

Solar cells which used dye-senses photoanode, electrolyte system, and counter electrodes were developed in recent years, especially those which use natural dye as sensitizer dyes, biopolymer electrolytes, green photoanode semiconductors, and natural carbon electrodes to fabricate the dye-sensitized solar cells (DSSCs) [1]. The DSSCs used photosensitizers like the harda fruit-based natural dye with 3.52% efficiency [2]. TiO_2, ($Cu-TiO_2$), and ($N-TiO_2$) nanoparticles were fabricated in the eucalyptus solar cells (DSSCs) [3]. TiO_2 - chlorophyll and betalain dye were synthesized naturally (DSSC) with an efficiency of about 0.11% [4]. Natural betalain dye, with $Ni_{0.5}Zn_{0.5}Fe_2O_4$/carbon (NZF/C), prepared solar cell with an efficiency of 2.75% [5]. Amaranthus and Henna leaves- TiO_2, fabricated solar cell [6].

*Correspondence: Hamdy AB. Matter

hamdy.matter@gmail.com

Lemon- TiO_2, parsley- TiO_2, spinach- TiO_2, hibiscus-rosa sinensis- TiO_2, pomegranate fruit- TiO_2 and vegetable beetroot- TiO_2 used as sensitizers, and examine the efficiency in preparation of (DSSCs) [7]. Nasturtium (*Tropaeolum majus*) flower petals as sensitizers in (DSSCs) with an efficiency of 0.28% [8]. Chokeberry juice dyes with silicon formed (DSSCs) [9]. Malva verticillate- TiO_2 and Syzygium cumini- TiO_2 are co-sensitizers in DSSCs, with an efficiency η = 14.80 %, and, 16.35 %, respectively [10]. From Crocus sativus (Saffron), Allium cepa L (red onion), Malva sylvestris (Mallow), and Oregano (Origanum vulgare) extract natural dyes with TiO_2 used as the sensitizer to fabrication (DSSCs), and efficiency of less than 2% [11]. the 2,2′-bipyridine (bipy) increased the voltage and circuit current of (DSSCs) fabricated using natural dyes bixin and norbixin [12]. Graphene is also used in natural DSSCs [13]. Beetroot-ZnO, Eosin y- ZnO, and yombotumtum- ZnO, used for fabrication (DSSCs), with efficiencies 0.75%, 1.17%, and 2.65%, respectively [14]. Anthocyanins- TiO_2 used for fabrication (DSSCs), with an efficiency of 2.82 % [15]. Anthoxanthin dyes are rich in Moringa flowers which are used for fabrication (DSSCs) [16]. (beetroot-MnO_2), (Dragon fruit-MnO_2) and (prickly pear fruit-MnO_2) using PVdF/PTHF/EC/KI/I_2/n-MnO_2 polymer nanocomposite

 ISSN:Online 2790-1637, Print 2790-1629; National Library of Libya, Legal number : 154/2018

electrolyte for fabrication (DSSCs) [17]. Beetroot (red dye), and spinach (green dye) were used as a sensitizer for natural (DSSC), red dye efficiency, η = 0.56% but green dye, η = 0.49% [18]. a mixture of natural dyes using nano-crystalline TiO_2 as a sensitizer, and cell efficiency η of 0.03 % [19]. Celosia Cristata, as photosensitizers, for natural (DSSC), and the efficiency was 1.38% [20]. Natural dye from the leaves of *Peltophorum pterocarpum*- TiO_2 is used for fabrication (DSSC) [21]. Malabar spinach (green dye) and red spinach (red dye), and were used as a sensitizer for TiO_2 photoanode-based (DSSC) and the efficiency was 0.847% [22]. Red dye (extracted from red spinach) and yellow dye (extracted from turmeric), DSSCs fabricated with $TiCl_4$, have a photoconversion efficiency of 0.416% and 0.921%, respectively [23]. Natural dye extraction from *Areca catechu*- TiO_2 was used for fabrication (DSSC), and the efficiency was 0.38% [24]. Graphene oxide (GO)- TiO_2 with Hibiscus rosa-sinensis dye was the highest efficiency, η = 0.55% for fabrication (DSSC) [25]. *Cassia fistula* flower extract, a natural dye, was used as a photosensitizer-(TiO_2) to fabricate (DSSC), with efficiency, η = 0.21% [26]. *Musa acuminata bracts* as a photosensitizer, using a spin coating method for fabrication (DSSC), with the largest conversion efficiency being 4% [27]. Purple cabbage extract, a natural dye, was used as a photosensitizer - TiO_2 to fabricate (DSSC), with a conversion efficiency of 0.162% [28]. *Indigofera tinctoria* was used as a photosensitizer - to fabricate (DSSC), with a conversion efficiency of 0.114% [29]. *Ardisia elliptica* dye- ZnO as a sensitizer for fabricated DSSC, with photo conversion efficiency (PCE) of 0.04% [30]. *Porphyridium cruentum* - (TiO_2) as a photosensitizer to fabricate (DSSC), with an efficiency of 0.569% [31].

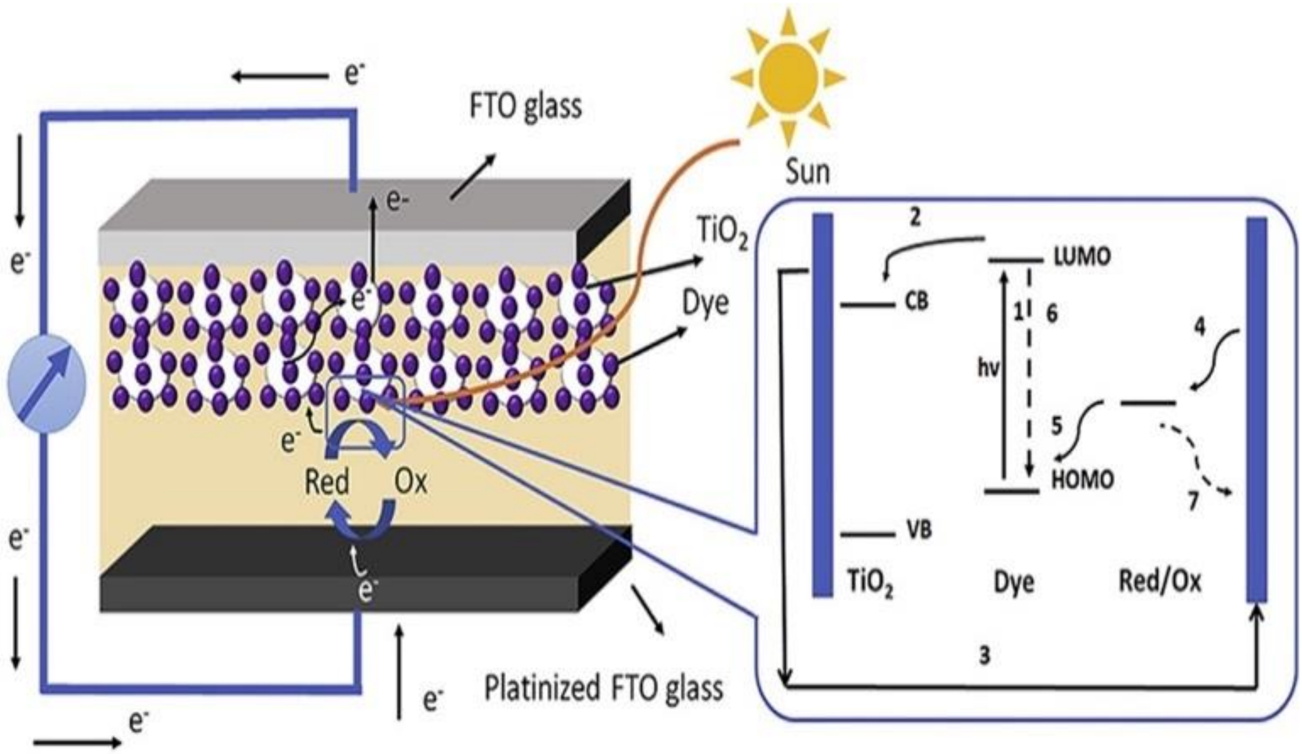

Figure. 1. A model of (DSSC); structure and function[1].

Fig. 1 shows the structure and function of a DSSC model. The cell consists of 2 electrodes. One is an oxide-semiconductor mesoporous layer precipitated onto fluorine-doped tin oxide (FTO) glass and fabricated by a natural dye, which works as a photoanode. The second is platinized FTO glass as a counter electrode, also called a cathode. An electrolyte was placed between the two electrodes. The most natural DSSC liquid electrolyte was I^- /I_3^- redox couple dissolved in an organic solvent like 3- acetonitrile. The electricity of the cell is produced by the transfer process of the electron displayed in the inset section in **Fig. 1**. When the dye acts as a sensitizer in the cell, the electron receives solar radiation, from the highest occupied molecular orbital (HOMO) and exits to the lowest unoccupied molecular orbital (LUMO). Electrons are then injected into the oxide metal semiconductor conduction band. Then the electrons transfer to the external circuit through the anode electrode and cathode electrode. The electrons are received to the external circuit; they change the redox couple material's state from oxidized to reduced. The electrons obtained from the reflection of the redox couple utilize dye regeneration. This cycle is appointed until electricity is gathered.

2. EXPERIMENTAL

2.1. Materials

All chemicals originated from the U.K. and are used as is without any more purification. TiO_2, mulberry fruits, henna levees, and roselle, contain (anthocyanins dye), beta vulgaris (beet), and red cabbage, contain betalain dye and yellow dye was extracted from turmeric containing (curcumin dye), 10^{-3} M of $Pb(NO_3)_2$, Ag NO_3, $Cu(NO_3)_2$. $6H_2O$, $Zn(NO_3)_2$. $6H_2O$, Cd

$(NO_3)_2$. $6H_2O$ and $Hg(NO_3)_2$. $2H_2O$. Citric acid ($C_6H_8O_7$), polyethylene glycol ($HO[C_2H_4O]_nH$), titanium IV isopropoxide ($C_{12}H_{28}O_4Ti$), iodine (I_2), potassium iodide (KI), ethylene glycol ($C_2H_6O_2$), and 3-methoxypropionate (MPN) as the electrolyte

2.2. Preparation of the anode

TiO_2 paste was prepared by adding a homogeneous mixture of 1.0 g of (TiO_2), to 0.005 ml of Triton X-100 ($C_8H_{17}C_6H_4[OCH_2CH_2]$), 3 ml of 0.1 M citric acid ($C_6H_8O_7$), 0.01 ml of polyethylene glycol ($HO[C_2H_4O]_nH$), and 0.01 ml of titanium IV isopropoxide ($C_{12}H_{28}O_4Ti$). An (FTO) fluorine-doped tin oxide glass substrate (surface resistivity = 8 Ω / sq. and transmittance > 80 %) was cleaned on its surface. Prepared TiO_2 paste was distributed on the conducting side of the FTO glass substrate. The active area cell was 2 ×5 cm^2. A single-layered TiO_2 nanoporous film was air-dried and heated at 450 ºC in a furnace for 1h and left for 6h to cool. The single-layer thickness of TiO_2 film was about 10-15 mm. We prepared two different anodes: (1) FTO/TiO_2 and (2) M-treated FTO/TiO_2. For the M-treated FTO/TiO_2, the FTO/TiO_2 was treated in 0.001 M Metal ion solution by keeping the FTO/TiO_2 in Metal ion solution for 1h at 80 ºC. Then, the Metal ion-treated FTO/TiO_2 device was cleaned with distilled water, air-dried, heated to about 450 ºC in a furnace for 1h and left for 12 h to cool.

Green synthesis metal oxide photoanodes: A green anode synthesis by using an "aqueous" solution to prepare TiO_2–ZnO composite photoanodes for DSSCs. $Zn(NO_3)_2$ was added to a suspension of TiO_2 powder and an isopropanol-water mixture. Then the suspension was sonicated for 90 min. before electrophoretic deposition (EPD). Next, the layer obtained was dried at room temperature and used for DSSCs.

2.3. Preparation of the dye sensitizer

Natural red dyes were extracted from mulberry fruits, henna levees, and roselle, containing (anthocyanins dye), beta vulgaris (beet), and red cabbage, containing (betalain dye), and yellow dye was extracted from turmeric containing (curcumin dye), respectively. These plants were obtained from Jalow – Elwahat - Lybia. The red dyes were obtained from the following:

1. From mulberry fruits, fresh juice with solvent extraction (methanol: H_2O: acetic acid, 25:21:4) then, filtered the (red) colored solution was collected far from the light (to protect the dye from photodegradation). Anthocyanin was extracted in the solution with other dyes such as chlorophyll, less polar, or non-polar flavonoids or some pigments. Then anthocyanin dye was separated, by a liquid-liquid separation funnel; 50 ml of chloroform and 50 ml of anthocyanin dye solution were mixed properly for about 5 min and two different layers were formed in the separation funnel. In the bottom layer part chlorophyll, flavonoids, and some compounds were filtered out, and in the top part of the solution, anthocyanin, which is used as a sensitizer for NDSSCs. The concentration of anthocyanin dye was nearly 0.25 g/ 10 ml in the solution.
2. Henna leaves were cut into small parts in distilled water at a ratio of 10 g: 1ml. then they were taken in a beaker and heated at 60 ºC for about 60 min. Then, the leaves and stems were filtered out. The anthocyanins dye solution was collected and cooled far from light (to avoid photodegradation of the red dye). Anthocyanin was present in the solution with other pigments such as chlorophyll, less polar or non-polar flavonoids, and some compounds. The anthocyanins dye was extracted with ethanol and separated in the separation funnel as it was separated from mulberry.
3. Roselle (hibiscus flower) fresh red hibiscus flowers were cut into small pieces and added to distilled water in a ratio of 10 g: 1ml and then taken in a beaker and heated at 60 ºC for about an hour. Then, the leaves and stems were filtered out. The (red) colored solution was collected and cooled in the absence of light (to avoid photodegradation of red dye). Anthocyanin was present in the solution with other pigments such as chlorophyll, less polar or non-polar flavonoids, and other compounds. To separate anthocyanin, a liquid-liquid separation technique was followed. In a separatory funnel, 50 ml of citric acid and 50 ml of dye solution were taken and mixed properly. The aqueous solution of anthocyanin was used as a sensitizer for DSSCs. The concentration of red dye was approximately 0.30 g/ 10 ml in an aqueous solution.
4. Red beetroot (beta vulgaris), containing (betalain dye). The red beetroots were cut and soaked in water for two hours, filterated, and betalain was extracted by hydrochloric acid or citric acid. The aqueous solution of betalain dye was used as a sensitizer for DSSCs. The concentration of red dye was approximately 0.25 g/ 10 ml in an aqueous solution
5. Extraction from red cabbage, containing (betalain dye) was the same as red beetroot.
6. From turmeric containing (curcumin dye), used powdered turmeric of 2 g/10 ml was added to ethanol and kept far from direct sunlight for one day. Finally, solid residues were filtrated out and used as the sensitizer for DSSCs. The concentration of yellow dye was 160 mg/10 ml in the ethanol solution, and used for the yellow dye as dye-sensitized DSSCs.

2.4. Electrolyte preparation

A homogenous mixture of 0.127 g of iodine (I_2), 0.83 g of potassium iodide (KI), and 10 ml of ethylene glycol ($C_2H_6O_2$) was used as I^-/I^-_3 redox electrolyte solution and 3-methoxypropionate (MPN) as the electrolyte solvent. All chemicals were of laboratory grade and purchased from the U.K. This homogenous iodine electrolyte solution was kept in a dark container in the absence of any light [1].

2.5. Cathode preparation and cell assembly

The glass FTO was covered with carbon made by graphite for the cathode. The FTO/TiO_2 and M-dye treated FTO/TiO_2 were immersed in the dye sensitizer for 1h to fabricate a photoanode. The dye-absorbed anode (both FTO/TiO_2 and M-dye-treated FTO/TiO_2) or photoanode was cleaned with distilled water to remove any) uncombined natural dyes with photoanode. Then, it was dried at 40 °C for 1h and was inserted into the cell [1].

2.6. The method of cell preparation

A simple solar cell preparing parts of the cell brings two pieces. Clean the glass panels with alcohol, and be sure to hold them from the ends after cleaning. Test the connectivity of the glass by using a special device known as the milliameter, and determine the connected side of the glass, then place the two pieces side by side with care to place the connecting side from one of the two bottles to the outside, and the non-conducting side from the other side. Glue the glass together using a transparent adhesive, leaving a little on the edges to secure them well. Plating of sheets with tin oxide. Place two drops of titanium dioxide solution on the surface of the plate using the dropper, then distribute the solution evenly to the sides. Remove the adhesive tape from the plates, then place the plate containing the connected surface on top of a plate or an electric heating plate overnight to bake the titanium oxide above it. Clean the bottom plate of titanium oxide, and keep it in a closed place so that the dust does not collect above it. Prepare a bowl to place the dye in, which can be prepared from mulberry fruits, henna levees, and roselle, containing anthocyanins dye, beta vulgaris (beet), and red cabbage, containing (betalain dye), and yellow dye was extracted from turmeric contain (curcumin dye), respectively. Soak the dye-painted plate for ten minutes, making sure to place the side with the oxide painted down, and during this time, clean the second plate with alcohol. Check the clean sheet again with the multi-device, and mark the unconnected side with an x. Paint a thin layer of carbon paste on the side marked with x. Wash the soaked plate first in non-ionizing water, then with alcohol, then dry it with a clean tissue. Prepare the solar cell for installation. Install the plates using office clamps (alligators) on the exposed sides of the plates. Fix the black wire in the millimeter device on the visible side of the plate painted with oxide, and this plate is the negative electrode of the cell. Fix the red wire to the carbon-painted area marked with an X, which is the positive electrode in the cell. Place the solar cell under sunlight or another light source with the negative electrode directed upward, then measure the voltage or current of the current in the solar cell using the milliampere and voltage [3].

3. RESULTS AND DISCUSSION

In this study, mulberry fruits, henna leaves and roselle, which contain anthocyanins dye, beta vulgaris (beet) and red cabbage, which contain betalain dye, and turmeric containing curcumin dye, were used for preparing nano-solar cells; seven of these dyes can absorb sunlight and convert solar energy into electrochemical energy. According to this study, it is clear that mulberry fruits, beta vulgaris (beet), roselle, henna leaves, and turmeric have a positive impact on efficiency. Natural dyes were used as sensitizers for semiconductor TiO_2 as electron conductors. From the UV-vis study, the combination of dyes obtained a wide range of absorption spectra and absorbance of light than both individual dyes.

3.3. UV-vis spectroscopy

The absorption spectra of mulberry fruits, henna leaves, and roselle, which contain anthocyanins dye, beta vulgaris (beet), and red cabbage, which contain betalain dye, and turmeric containing (curcumin dye), were measured using a UV-vis spectrophotometer (JENWAY 6300) in the region of 350 nm - 800 nm. Curcumin is the main chemical ingredient in turmeric extract and appears in bright yellow. The absorption spectrum of ethanol extracted yellow dye was found in the range of 350 nm -520 nm which has a strong absorption peak at 420 nm. Red dyes are recognized to be rich in antho- cyanin dye and betalain dye. The absorption spectrum of distilled water-extracted red dye was found in the range of 400 nm- 600 nm, which has a peak of absorption at 520 nm.

Even without any inorganic metals, the resulting porous materials from natural dyes have remarkably excellent DSSC performance. A best DSSC performance can be achieved by incorporating inorganic compounds as inorganic materials can be well dispersed throughout porous carbon metals. The oxide increases the catalytic activities at the band uniformity of the inorganic metals and matches the I_3^- reduction potential. Combining the high surface area of the porous carbon or graphite material with the premium electronic properties of the inorganic metals is certain to decrease the R_{ct} values to below 5 Ω cm^2. Therefore, inorganic metals and natural dyes product-based materials have clear effects.

3.4. Photovoltaic cherctrisation of DSSCs

Both FTO/ TiO_2 and M-treated FTO/TiO_2 electrodes fabricated DSSCs, and sensitized with individual red dyes (anthocyanins dye and betalain dye) and yellow dye (curcumin dye) were measured using a calibrated solar simulator with a 500 W Xenon arc lamp and a light intensity of 100 mW/cm^2 at AM 1.5G. Open-circuit voltage (V_{oc}), and the short-circuit current (I_{sc}) were standardized experimentally. P_{max} (Eq. 1) and fill factor (FF) as (Eq. 2) were calculated from the all perporteis curve, and the cell efficiency was calculated by using (Eq. 3) :

$$P_{max} = V_{max} \times I_{max} \quad -------- \quad (1)$$

where V_{max} and I_{max} are the maximum voltage and current at P_{max}, respectively.

$$FF = \frac{P_{max}}{V_{oc} \times I_{sc}} ----------- \quad (2)$$

and,

$$\eta = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}} ---------. (3)$$

where P_{in} is the incident photon energy.

$$\%\eta = V_{oc(v)} \times I_{sc(mA)} \times FF ----- (4)$$

Table 1 the main cell parameters such as V_{oc}, I_{sc}, FF, and η % of DSSCs fabricated without metal ion treatment and natural dye extracted from mulberry fruits with six metal ions formed six different combinations with anthocyanins dye.

Metal add/anthocyanins dye	V_{oc} (V)	I_{sc} (mA)	FF	η %
Non-metal add	0.341	2.874	0.513	0.502
Pb^{2+}	0.355	3.654	0.521	0.675
Ag^{+}	0.420	4.324	0.533	0.967
Cu^{2+}	0.375	3.654	0.489	0.670
Zn^{2+}	0.490	4.984	0.543	1.326
Cd^{2+}	0.510	5.232	0.532	1.340
Hg^{2+}	0.364	3.537	0.496	0.638

From **Table 1**, DSSCs sensitized with 100% anthocyanins dye extracted from mulberry fruits show I_{sc} of 2.874 mA. By adding metal ions with dyes, the I_{sc} increased especially with Cd, Zn, and Ag ions, the maximum cell efficiency of η % 1.340, 1.326, and 0.967, respectively, due to, some additional components are usually incorporated. Then amorphous, mixed, and porous carbon metals are known for their weak cohsion to FTO; additional metal ions make strong adhesive materials must be combined. Additionally, amorphous carbon is low in conductivity; thus, conducting metal ions can also increase the conductivity of the counter electrode. The chemical structure of anthocyanins, which have hydroxyl groups, and some of them were a catechol group. They can act as chelating groups to attach the dye onto the metal ion surface. The hydroxyl groups showed better performance as chelating groups than the carboxylic group because the latter presents an electron-withdrawing perporteis [1]

Table 2, the main cell parameters such as V_{oc}, I_{sc}, FF, and η % of DSSCs fabricated without metal ion treatment and natural dye extracted from henna leaves with six metal ions formed six different combinations with anthocyanins dye.

Metal add/anthocyanins dye	V_{oc} (V)	I_{sc} (mA)	FF	η %
Non-metal add	0.384	2.634	0.525	0.531
Pb^{2+}	0.455	4.654	0.542	1.147
Ag^{+}	0.426	4.419	0.515	0.969
Cu^{2+}	0.381	3.638	0.473	0.655
Zn^{2+}	0.484	4.213	0.521	0.908
Cd^{2+}	0.502	5.232	0.544	1.428
Hg^{2+}	0.353	3.472	0.478	0.585

From **Table 2**, DSSCs sensitized with pure anthocyanins dye extracted from henna leaves show I_{sc} of 2.634 mA. By adding metal ions with anthocyanins dyes, the I_{sc} increased especially with Cd, Pb, and Ag ions, the maximum cell efficiency of η % 1.340, 1.147, 0.969, respectively. Due to some additional components that usually increased the porous, amorphous, and disorder of the surface and which have weak adhesion to FTO, additional adhesive materials, amorphous carbon is also known for its low conductivity, thus, conducting metals can also be increased into the counter electrode.

Table 3, the main cell parameters such as V_{oc}, I_{sc}, FF, and η % of DSSCs fabricated without metal ion treatment and natural dye extracted from roselle with six metal ions formed six different combinations with anthocyanins dye.

Metal add/anthocyanins dye	V_{oc} (V)	I_{sc} (mA)	FF	η %
Non-metal add	0.393	2.834	0.564	0.628
Pb^{2+}	0.423	3.456	0.523	0.764
Ag^{+}	0.412	3.463	0.512	0.730
Cu^{2+}	0.498	4.743	0.561	1.325
Zn^{2+}	0.423	3.431	0.533	0.773
Cd^{2+}	0.442	3.231	0.521	0.744
Hg^{2+}	0.512	5.126	0.522	1.369

From **Table 3**, DSSCs sensitized with pure anthocyanins dye extracted from mulberry roselle show I_{sc} of 2.834 mA. By adding metal ions with dyes, the I_{sc} increased especially with Hg, and Cu, ions, the maximum cell efficiency of η % 1.369, and 1.325, respectively, due to some additional components that are usually incorporated.

Table 4, the main cell parameters such as V_{oc}, I_{sc}, FF, and η % of DSSCs fabricated without metal ion treatment and natural dye extracted from (Beta vulgaris) red beetroot with six metal ions formed six different combinations with betalain dye.

Metal add/betalain dye	V_{oc} (V)	I_{sc} (mA)	FF	η %
Non-metal add	0.389	3.221	0.534	0.669
Pb^{2+}	0.421	3.345	0.562	0.791
Ag^{+}	0.399	3.124	0.497	0.698
Cu^{2+}	0.511	5.166	0.478	1.261
Zn^{2+}	0.523	4.921	0.532	1.369
Cd^{2+}	0.434	3.125	0.532	0.721
Hg^{2+}	0.456	3.126	0.524	0.746

From **Table 4**, DSSCs sensitized with pure betalain dye extracted from (Beta vulgaris) red beetroot show I_{sc} of 3.221 mA. By adding metal ions with dyes, the I_{sc} increased especially with Zn, and Cu, ions, with the maximum cell efficiency of η % 1.369, and 1.261, respectively, due to some additional components that are usually incorporated.

Table 5, the main cell parameters such as V_{oc}, I_{sc}, FF, and η % of DSSCs fabricated without metal ion treatment and natural dye extracted from red cabbage with six metal ions formed six different combinations with betalain dye.

Metal add/betalain dye	V_{oc} (V)	I_{sc} (mA)	FF	η %
Non-metal add	0.379	3.221	0.522	0.637
Pb^{2+}	0.388	3.345	0.521	0.676
Ag^{+}	0.411	3.351	0.512	0.705
Cu^{2+}	0.521	5.211	0.511	1.387
Zn^{2+}	0.423	3.822	0.489	0.790
Cd^{2+}	0.394	3.432	0.488	0.659
Hg^{2+}	0.525	5.126	0.515	1.385

From **Table 5**, DSSCs sensitized with pure betalain dye extracted from red cabbage show I_{sc} of 3.221 mA by adding metal ions with dyes, the I_{sc} increased especially with Zn, and Cu, ions with the maximum cell efficiency of η % 1.369, 1.261, respectively, due to, some additional components are usually incorporated.

Table 6 the main cell parameters such as V_{oc}, I_{sc}, FF, and η % of DSSCs fabricated without metal ion treatment and natural dye extracted from turmeric with six metal ions formed six different combinations with curcumin dye.

Metal add/curcumin dye	V_{oc} (V)	I_{sc} (mA)	FF	η %
Non metal add	0.394	3.211	0.512	0.647
Pb^{2+}	0.531	4.996	0.522	1.384
Ag^{+}	0.352	3.421	0.513	0.617
Cu^{2+}	0.422	3.311	0.531	0.742
Zn^{2+}	0.512	4.878	0.521	1.301
Cd^{2+}	0.372	3.541	0.512	0.674
Hg^{2+}	0.326	4.412	0.487	0.700

From **Table 6**, DSSCs sensitized with pure curcumin dye extracted from turmeric show I_{sc} of 3.211 mA. By adding metal ions with dyes, the I_{sc} increased especially with Zn, and Cu, ions with the maximum cell efficiency of η % 1.369, 1.261, respectively, due to some additional components that are usually incorporated.

Finally, to sensitize natural-based DSSCs, factors like cost, chemical components, and environmental factors must be considered to correctly achieve DSSC performance.

4. CONCLUSIONS

DSSCs were fabricated with natural red dyes (anthocyanins dye and betalain dye), and yellow dye (curcumin dye), as well as with six different metal ions of these dyes. From the UV-vis absorption spectroscopy, the dyes have higher absorbance and accumulated absorption properties at all the visible regions, indicating that the dyes with metal ions absorb light better than the individual red dyes or yellow. Natural red dyes(anthocyanins dye with the metals Cd, Zn, Pb, Hg, and Cu, dye-sensitized DSSCs have the cell efficiency of 1.340%, 1.326%, 1,147%, 1,369%, and 1,325%, respectively and betalain dye, with the metals Zn, Hg, and Cu, dye-sensitized DSSCs have the cell efficiency of 1.369%, 1.385%, and 1.261%, respectively,) and natural yellow(curcumin dye) with the metals Zn, and Pb, dye-sensitized DSSCs have the cell efficiency of 1.301%, and 1.384%, respectively; dyes showed higher cell parameters than the DSSCs fabricated without metal ion additions. The cell efficiency with metal increased more significantly than when the DSSCs were fabricated without the addition of the metal ions which are a combination of dyes.

5. REFERENCES

1. Kusumawati, Y., Hutama, A. S., Wellia, D. V., & Subagyo, R. Natural Resources for Dye-Sensitized Solar Cells. Heliyon, 2021, e08436.
2. Yadav, V., Negi, C. M. S., Kumar, D. K., & Gupta, S. K. Fabrication of eco-friendly, low-cost dye-sensitized solar cells using harda fruit-based natural dye. Optical Materials, 2021, 111800.
3. Venumbaka, M. R., Akkala, N., Duraisamy, S., Sigamani, S., Poola, P. K., & Marepally, B. C. Performance of TiO2, Cu-TiO2, and N-TiO2 nanoparticles sensitization with natural dyes for dye-sensitized solar cells. Materials Today: Proceedings. 2021.
4. Kumar, B. A., Ramalingam, G., Karthigaimuthu, D., Elangovan, T., & Vetrivelan, V. Fabrication of natural dye-sensitized solar cell using tridax procumbens leaf and beetroot extract mixer as a sensitizer. Materials Today: Proceedings. 2021.
5. Oladipo, A. A., & Gazi, M. Ternary NiO. 5ZnO. 5Fe2O4/carbon nanocomposite as counter electrode for natural dye-sensitized solar cells: Electro-photovoltaic characterizations. Journal of Photochemistry and Photobiology A: Chemistry, 2021, 113665.
6. Sowmya, S., Prakash, P., Ruba, N., Prabu, A. N., Janarthanan, B., Reddy, V. R. M., & Hegazy, H. H. Fabrication of natural dye-sensitized solar cells with bulk TiO2 instead of nano-sized. Optik, 2021, 242, 166205.
7. Singh, P. K., & Shukla, V. K. Widening spectral range of absorption using natural dyes: Applications in dye-sensitized solar cell. Materials Today: Proceedings. 2021.
8. Singh, S., Maurya, I. C., Sharma, S., Kushwaha, S. P. S., Srivastava, P., & Bahadur, L. Application of new natural dyes extracted from Nasturtium flowers (Tropaeolum majus) as photosensitizer in dye-sensitized solar cells. Optik, 2021, 167331.
9. Błaszczyk, A., Joachimiak-Lechman, K., Sady, S., Tański, T., Szindler, M., & Drygała, A. Environmental performance of dye-sensitized solar cells based on natural dyes. Solar Energy, 2021, 215, 346-355.
10. Golshan, M., Osfouri, S., Azin, R., Jalali, T., & Moheimani, N. R. Co-sensitization of natural and low-cost dyes for efficient panchromatic light-harvesting using dye-sensitized solar cells. Journal of Photochemistry and Photobiology A: Chemistry, 2021, 417, 113345.
11. Jalali, T., Arkian, P., Golshan, M., Jalali, M., & Osfouri, S. Performance evaluation of natural native dyes as photosensitizer in dye-sensitized solar cells. Optical Materials, 2020, 110, 110441.
12. Carvalho, I. C., Barbosa, M. L., Costa, M. J. S., Longo, E., Cavalcante, L. S., Viana, V. G. F., & Santos, R. S. TiO2-based dye-sensitized solar cells prepared with bixin and norbixin natural dyes: Effect of 2, 2'-bipyridine additive on the current and voltage. Optik, 2020, 218, 165236.
13. Sharma, S. S., Sharma, K., Singh, R., Srivastava, S., Rana, K. B., & Singhal, R. Natural pigments: Origin and applications in dye-sensitized solar cells. Materials Today: Proceedings, 2021, 42, 1744-1748.
14. Ossai, A. N., Alabi, A. B., Ezike, S. C., & Aina, A. O. Zinc oxide-based dye-sensitized solar cells using natural and synthetic sensitizers. Current Research in Green and Sustainable Chemistry, 2020, 3, 100043.

15. Prabavathy, N., Balasundaraprabhu, R., Kristoffersen, A. S., Balaji, G., Prasanna, S., Sivakumaran, K.,& Velauthapillai, D. Enhanced photostability of anthocyanin dye for increased efficiency in natural dye-sensitized solar cells. Optik, 2021, 227, 166053.

16. Megala, M., Mayandi, J., & Rajkumar, B. J. Optical absorption study of anthoxanthin-based natural dyes for dye-sensitized solar cells: Experimental and theoretical investigations. Materials Letters, 2020, 276, 128089.

17. Suganya, N., & Jaisankar, V. A Study on the effect of dye and polymer nanocomposite electrolyte on the performance of natural dye-sensitized solar cells. Materials Today: Proceedings, 2019, 14, 471-481.

18. Bashar, H., Bhuiyan, M. M. H., Hossain, M. R., Kabir, F., Rahaman, M. S., Manir, M. S., & Ikegami, T. Study on combination of natural red and green dyes to improve the power conversion efficiency of dye-sensitized solar cells. Optik, 2019, 185, 620-625.

19. Pathak, C., Surana, K., Shukla, V. K., & Singh, P. K.. Fabrication and characterization of dye-sensitized solar cells using natural dyes. Materials Today: Proceedings, 2019, 12, 665-670.

20. Hosseinnezhad, M., Rouhani, S., & Gharanjig, K. Extraction and application of natural pigments for fabrication of green dye-sensitized solar cells. Opto-electronics Review, 2018, m26(2), 165-171.

21. Sanjay, P., Deepa, K., Raj, M. V. A., Madhavan, J., & Senthil, S. Dye-Sensitized Solar Cells Using Natural Dye as Light-Harvesting Material Extracted From the Leaves of Peltophoroum Pterocarpum. Materials Today: Proceedings, 2019, 8, 123-129.

22. Kabir, F., Bhuiyan, M. M. H., Manir, M. S., Rahaman, M. S., Khan, M. A., & Ikegami, T. Development of dye-sensitized solar cell based on combination of natural dyes extracted from Malabar spinach and red spinach. Results in Physics, 2019, 14, 102474.

23. Kabir, F., Bhuiyan, M. M. H., Hossain, M. R., Bashar, H., Rahaman, M. S., Manir, M. S., and Ikegami, T. Effect of combination of natural dyes and post-TiCl4 treatment in improving the photovoltaic performance of dye-sensitized solar cells. Comptes Rendus Chimie, 2019, 22(9-10), 659-666.

24. Al-Alwani, M. A., Hasan, H. A., Al-Shorgani, N. K. N., & Al-Mashaan, A. B. S. Natural dye extracted from Areca catechu fruits as a new sensitiser for dye-sensitized solar cell fabrication: optimisation using D-Optimal design. Materials Chemistry and Physics, 2020, 240, 122204.

25. Mensah-Darkwa, K., Agyemang, F. O., Yeboah, D., & Akromah, S. Dye-sensitized solar cells based on graphene oxide and natural plant dye extract. Materials Today: Proceedings, 2021, 38, 514-521.

26. Maurya, I. C., Singh, S., Srivastava, P., Maiti, B., & Bahadur, L. (Natural dye extract from Cassia fistula and its application in dye-sensitized solar cell: Experimental and density functional theory studies. Optical Materials, 2019, 90, 273-280.

27. Madnasri, S., Wulandari, R. D. A., Hadi, S., Yulianti, I., Edi, S. S., & Prastiyanto, D. Natural Dye of Musa acuminata bracts as Light Absorbing Sensitizer for Dye-Sensitized Solar Cell. Materials Today: Proceedings, 2019, 13, 246-251.

28. Gu, P., Yang, D., Zhu, X., Sun, H., & Li, J. Fabrication and characterization of dye-sensitized solar cells based on natural plants. Chemical Physics Letters, 2018, 693, 16-22.

29. Rajan, A. K., & Cindrella, L. Studies on new natural dye sensitizers from Indigofera tinctoria in dye-sensitized solar cells. Optical Materials, 2019, 88, 39-47.

30. Dhafina, W. A., Salleh, H., Daud, M. Z., & Ghazali, M. S. M. Low-cost dye-sensitized solar cells based on zinc oxide and natural anthocyanin dye from Ardisia elliptica fruits. Optik, 2018, 172, 28-34.

31. Li, W., Pu, Y., Ge, B., Wang, Y., Yu, D., & Qin, S. Dye-sensitized solar cells based on natural and artificial phycobiliproteins to capture low light underwater. International Journal of Hydrogen Energy, 2019, 44(2), 1182-1191.