Natural Photosensitizers for Dye Sensitized Solar Cells

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Received: 25.11.2012 Accepted: 19.12.2012

Abstract- Dye-sensitized solar cells (DSSCs) were constructed by using the Lawsonia inermis leaves, Sumac/Rhus fruits, and Curcuma longa roots as natural sensitizers of anatase-based nanostructure TiO$_2$ thin film Paint-coated on ITO conducting glass. The orange-red Lawtone, red purple anthocyanin and yellow Curcumin are the main components in the natural dyes obtained from these natural products. A blend of 50 wt% chitosan and 50 wt% polyethylene oxide (PEO) was used as a solid state thin film electrolyte. The polymer blend was complexed with ammonium iodide (NH$_4$I) and some iodine crystals were added to the polymer–NH$_4$I solution to provide I$^-$/I$_3^-$ redox couple. The ionic conductivity of the polymer electrolyte is 1.18x10$^{-5}$ S cm$^{-1}$ at room temperature. Structural and optical properties of the semiconductor thin films were characterized by X-ray diffractometer and UV-VIS spectrophotometer respectively. The XRD shows nanocrystalline structures for TiO$_2$ thin films (D=13nm). The photovoltaic properties of the cell have been studied and the best overall solar energy conversion efficiency of 1.5% was obtained, under AM 1.5 irradiation, with the red purple Sumac/Rhus extract, that showed a reasonable current density (Jsc = 0.93 mA/cm$^2$).

Keywords- natural photosensitizers, DSSCS, solid state electrolyte, photovoltaic;solar energy

1. Introduction

The energy and fuel crisis is the prime concern worldwide. Fossils fuels are facing rapid resource depletion, but the demand for energy is growing day by day and many countries around the world have no alternative but to increase domestic oil process. So there is an urgent need of sustainable energy resources, such as the solar energy, which is considered as an environmentally friendly, novel alternative and promising candidate to address this problem.

However, solar energy has a limited application that directly related to its high cost of the per watt electricity generated. In present time, technology of solar cells based on crystalline silicon is facing a problem of silicon-based raw materials. So, low cost alternatives and hence new types of low cost solar cells is an urgent issue. Dye-sensitized solar cells (DSSCs), a new type of solar cells, have attracted considerable attention due to their environmental friendliness and low cost of production. A DSSC is composed of a nanocrystalline porous semiconductor electrode-absorbed dye, a counter electrode, and an electrolyte containing iodide and triiodide ions. In DSCs, the dye as a sensitizer plays a key role in absorbing sunlight and transforming solar energy into electric energy. Numerous metal complexes and organic dyes have been synthesized and utilized as sensitizers. The DSSCs sensitized by Ru-containing compounds are reaching, 11-12%, the highest efficiency as reported by Chiba and Islam [1, 2]. However, noble metals limited in amount, and costly in production. On the other hand, natural dyes are cheap, abundant and reaching a lower efficiency of 9.8% [3]. However natural dyes have often presented wfv problems as well, such as complicated synthetic routes and low yields. Nonetheless, the natural dyes found in flowers, leaves, and fruits can be extracted by simple procedures. Due to their cost efficiency, non-toxicity, and complete biodegradation, natural dyes have been a popular subject of research. Thus-far, several natural dyes have been utilized as sensitizers in DSSCs. Calogero and Marco reported that a conversion efficiency of 0.66% was obtained using red Sicilian orange juice dye as sensitizer [4]. Rosella is
employed as sensitizer for DSSC with efficiency reported by Wongcharae et al. as 0.70% [5].

Roy et al. indicated that when using Rose Bengal dye as sensitizer, the Jsc and Voc of their DSSC reached 3.22mAcm−2 and 0.89 V, respectively, resulting in a 2.09% conversion efficiency [6]. Furthermore, Wang et al. carried out structural modification of coumarin and used the coumarin derivaive dye as sensitizer in their DSSC, which provided an efficiency of 7.6% [7-10]. For ideal performance and excellent efficiency, electrolyte should have high ionic conductivity so that it can transfer oxidized/reduced species to respective electrodes efficiently and should prevents back electrode reactions completely. Polyethylene oxide (PEO) has some exceptional properties of good mechanical strength, film forming properties and excellent ability to form complex with the ionic salts. Polymeric electrolyte is an ideal choice used in lithium ion batteries, supercapacitors, photoelectrochromic display devices and solar cells [11-13].

Organic liquid electrolytes dye-sensitized solar cell (DSSC) have attractive features of high energy conversion efficiency and low production cost as reported by Regan et al and Nazeeruddin et al [14, 15].

However, presence of traditional organic liquid electrolytes in such cell has some problems such as a less long-term stability and a need for airtight sealing. One of the major problems of such DSSC is the electrolyte loss caused by the leakage and volatility of the electrolyte solution that lowers the durability of the cell.

Solid-state dye-sensitized solar cell did not need hermetic sealing, but energy conversion efficiency of them decreased in comparison to those of dye-sensitized solar cell with traditional organic liquid electrolytes. Various approaches to these problems have been tried so far. These approaches include employing a gel-type electrolyte to minimize the loss [16-20].

Natural dyes can replace synthetic dyes since they can be easily extracted from fruits, vegetable and flowers with simple and direct chemical procedures, whereas the earlier normally requires many steps procedures, organic solvents and, purification procedures [21-23].

The pigments are present in the different part of the plant including flowers petals, fruits, leaves, stems and roots. We report here the results of a series of experiments carried out on raw extracts of the following species: three types of natural dyes were extracted from leaves, flowers and roots, these are; Lawsonia inermis (Henna leaves), Sumac /sumach, (flowering plants) and Curcuma longa (turmeric) respectively. To the best of our best knowledge, natural dyes from Sumac are reported as sensizers of DSSCs for the first time. Figure 1 shows a schematic chemical structure of lawsone pigment in henna leaves.

Henna (Lawsonia inermis, also called henna tree) [24] is a flowering plant used since antiquity to dye skin, hair, fingernails, leather and wool. The name is also used for dye preparations derived from the plant. Henna's coloring properties are due to lawsone, (2-hydroxy-1,4-naphthoquinone) [25], also known as hennotannic acid, C_{10}H_{10}O_{2}, a burgundy organic compound that has an affinity for bonding with protein.

![Fig. 1. Schematic Chemical Structure of Lawsone pigment in Henna leaves](image)

Lawsone is primarily concentrated in the leaves. Fresh henna leaves will not stain color until the lawsone molecules are made available (released) from the leaves and they are smashed with a mildly acidic liquid. The lawsone will gradually migrate from the henna paste/solution into the outer layer of the skin and bind to the proteins in it known as keratin, creating a fast stain. Lawsone is a skin protective since it strongly absorbs UV light. Sumac is any one of approximately 250 species of flowering plants in the genus Rhus in the family Anacardiaceae. Sumacs grow in subtropical and temperate regions throughout the world, especially in Africa and North America [26].

Sumacs are shrubs and small trees that can reach a height of 1-10 meters (3.3-33 ft). The leaves are spirally arranged; they are usually pinnate compound, though some species have trifoliate or simple leaves. The flowers are in dense panicles or spikes 5-30 centimeters (2.0-12 in) long, each flower very small, greenish, creamy white or red, with five petals. The fruits form dense clusters of reddish drupes called sumac bobs. The dried drupes of some species are ground to produce a tangy purple spice [27]. Grounded dried fruits of sumac are usually purple-reddish in color, Tart and sour [28]. The pericarp owes its dark red color to anthocyanin pigments.

![Fig. 2. Anthocyanin chemical structure (R1 and R2 = -H) (R3, R4, R5, R6 and R8 = -OH) [29].](image)

Turmeric (Curcuma longa) is a rhizomatous herbaceous perennial plant of the ginger family, Zingiberaceae [30]. It is native to tropical South Asia and needs temperatures between 20 °C and 30 °C (68 °F and 86 °F) and a considerable amount of annual rainfall to thrive. When not used fresh, the rhizomes are boiled for several hours and then dried in hot ovens, after which they are ground into a deep orange-yellow powder commonly used as a spice in curries and other South Asian and Middle Eastern cuisine, for dyeing, and to impart color to mustard condiments. Its active ingredient is curcumin and it has a distinctly earthy, slightly bitter, slightly hot peppery flavor and a mustardy smell. Curcumin can be used to test the alkalinity or acidity of foods. It turns yellow in an acidic food, and it turns red in an alkaline food [31].

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4. PEO is a widely used polymer for its good mechanical strength.
5. The ability to form complexes with ionic salts makes PEO a suitable choice for solar cells.
6. Natural dyes have a number of potential advantages over synthetic dyes.
7. The efficiency of DSSCs is significantly affected by the leakage and volatility of the electrolyte.
8. The use of gel-type electrolytes can help minimize these problems.
9. The practicality of solid-state DSSCs is still under development.
10. Henna has been used for centuries.
11. Sumac contains a variety of bioactive compounds.
12. Sumac berries are commonly used for dyeing.
13. Turmeric has been used in traditional medicine for centuries.
14. Curcumin, the main active compound in turmeric, has multiple health benefits.
Turmeric contains up to 5% essential oils and up to 5% Curcumin, a polyphenol. Curcumin is the active substance of turmeric and Curcumin is known as C.I. 75300, or Natural Yellow 3. The systematic chemical name is (1E, 6E)-1, 7-bis (4-hydroxy-3-methoxyphenyl)-1,6 heptadiene-3,5-dione. It can exist at least in two tautomeric forms, keto and enol. The keto form is preferred in solid phase and the enol form in solution. Curcumin is a pH indicator. In acidic solutions (pH < 7.4) it turns yellow, whereas in basic (pH > 8.6) solutions it turns bright red [32].

Fig. 3. Chemical Structures of Two Tautomeric Forms of Curcumin, keto and enol

As shown in Figure 1, 2, and 3, all dyes contain carboxylic functions which facilitate TiO$_2$ surface binding [33].

These extracted dyes were characterized by UV-VIS absorption spectra and the semiconductor thin films were characterized by X-ray diffractometer and UV-VIS spectrophotometer. The preparation and characterization of the polymer matrix as polymer electrolyte is investigated in our previous work [13]. The photovoltaic properties of the DSSCs using these extracts as sensitizers and PEO as polymeric solid state electrolyte were investigated. The energy conversion efficiency ($\eta$) of the solar cell devices were calculated by the values of open-circuit voltage ($V_{oc}$), short-circuits current density ($J_{sc}$), and fill factor (FF).

2. Experiment

We have prepared the solid state dye-sensitized solar cell devices, using natural dyes as photosensitizers, sandwiched with nanocrystalline semiconductor oxide of TiO$_2$ deposited and C-coated electrodes as working and counter electrodes respectively. The structure of the dye-sensitized solar cell device is shown in Figure 4. However the role of the polymer electrolyte is a channel for the redox couple.

Fig. 4. Schematic configuration of Natural dye photosensitizers / Solid state electrolyte junction

2.1. Preparation of TiO$_2$ Electrode (Photoanode)

The photoanode is prepared by adsorbing a dye (s) on a porous titanium dioxide, TiO$_2$ layer deposited on indium tin oxide, ITO conducting glass. By this approach, the dye extends the spectral sensitivity of the photoanode, enabling the collection of lower energy photons. The conductive glass plates (ITO glass, Indium-doped SnO$_2$, sheet resistance 15Ω/cm$^2$) and the titanium oxide (TiO$_2$) nanopowder (13 nm) were purchased respectively from Nikko Materials, Japan and Aldrich. Solvents and chemicals were used as received. The semiconductor paste was prepared by blending 20g of commercial TiO$_2$ nanopowder, 3ml of 0.1M acetic acid, and 20ml of ethanol. The resulting suspension was stirred for 2h and subsequently ultra-sonicated for additional 2h; the resulting mesoscopic oxide film was around 7-20 μm thick and opaque. Two edges of the ITO glass plate were covered with a layer of adhesive tape to control the thickness of the film and to mask electric contact strips. Successively the TiO$_2$ paste was spread uniformly on the substrate by sliding a glass rod along the tape spacer. After heating up the ITO glass spreaded TiO$_2$ nanoparticle to 100°C for about half an hour, the sintering process was completed and the TiO$_2$ deposited- electrode was cooled down from 100°C to 60°C at cooling rate of 3°C/min to avoid cracking of the glass.

2.2. Graphite Coated Counter Electrode

To prepare the counter (positive) electrodes, uncoated ITO plates were coated with carbon on the conducting side using a graphite rod or soft pencil to apply a light carbon film to the entire conductive side of the plate. Any loose graphite particles should be gently removed. This thin carbon layer serves as a catalyst for the triiodide-to-iodide regeneration reaction. For long-lasting the carbon-coated counter electrode was annealed at 450°C for a few minutes and washed with ethanol and gently blotted dry before the device is assembled.

2.3. Preparation of Solid State Polymer Electrolyte

The Polymer Electrolyte was prepared and characterized following the procedure reported in the literature of our previous work [13]. In these dye-sensitized solar cells, the polymer electrolyte, polyethylene oxide (PEO) was casted onto TiO$_2$ electrode impregnated natural dye as photosensitizers.

2.4. Preparation of Natural Dye Sensitizers

The fresh Lawsonia inermis leaves and Curcuma longa roots were harvested in Kuala Lumpur Malaysia, while the red Sumac was taken from the Middle East. Lawsonia inermis leaves and Curcuma longa roots extracts were
prepared by crushing the fresh leaves and roots respectively. 30 ml of ethanol was added to the pastes and bring to boil for 30 minutes. The as prepared extract solutions were filtered to remove solid fragments and stabilized at pH = 2.5, 3.0, and 3.5 by addition of aqueous (0.1 M) HCl. Extracts further purification was avoided to check whether an efficient sensitization could be achieved with minimal chemical procedures. If properly stored, protected from direct sunlight and refrigerated at about +4°C, the acidic natural dye solutions (pH = 5.0) are usually stable, with a deactivation half-time of more than 12 months [34]. Ground dried fruits of sumac (Rhus) are usually purple-redish in color. Tart and sour, did not require HCl stabilization. The powder was soaked in ethanol and boiled for 30 minutes. TiO₂ coated electrodes were dipped in these solution extracts overnight (24 hours) for pigments stain.

2.5. Assembly of DSSC or Grätzel Solar Cell

The dye-sensitized solar cells were assembled by fixing a TiO₂ electrode casted with polymer electrolyte and a graphite counter electrode so that the dyed TiO₂ plates facing down onto the coated graphite anode. They should be placed so that they are slightly offset to allow connections (for the crocodile clips). The two electrodes were pressed against the electrolyte and clamped firmly in a sandwich configuration. By illuminating the cells with a light source/sun light, the voltage across each individual cell can be measured (Fig. 4).

3. Results and Discussion

3.1. XRD Patterns of TiO₂ Thin Films

The XRD patterns of TiO₂ thin films indicate that the films are crystalline. The diffraction peak at 2θ=25.50 conforms the TiO₂ anatase nano-structure to D=13 nm.

![Fig. 5. XRD pattern of TiO₂ films](image)

3.2. Absorption Spectra of pigment stained TiO₂

Figure 6 shows the UV-VIS absorption spectra of pure TiO₂ coated on ITO conducting glass and the adsorbed extracts on the TiO₂ electrodes of; TiO₂/Lawsone extract (orange-red), TiO₂/Sumac extract (purple) and TiO₂/Curcuma longa extract (yellow) for two sets of experiments carried out at (a) different layers (thickness) and constant pH=3.0 and (b) different pH and constant thickness (1 layer). These absorptions originate from π–π* transitions have pointed out their essential charge transfer character. Upon adsorption on the TiO₂ electrodes of all extracts the visible absorption band shifts to higher energy, showing a maximum absorption around 400-500 nm. The acidic environment was essential for obtaining sensitized photo-electrodes characterized by high optical densities, capable of wide absorption of visible photons in the 400-650 nm range. The reason is ostensibly related to protonation of carboxylic groups which are otherwise unable, in their anionic form to bind to the TiO₂ surface.

![Fig. 6. Absorption spectrum of pure TiO₂ film coated on ITO conducting glass and TiO₂ films adsorbed by three pigments; Lawsone, Sumac and Curcumin](image)

3.3. Photovoltaic Properties

Figure 7 shows the Variation of current-voltage curve of sumac, lawsonia, and curcuma based DSSCs. All experiments were carried out less than 1 sun illumination, (100 mW/cm², and air mass 1.5) with solid state electrolyte.
as long as the cell is illuminated and current flows through the electrical load. The reactions found in the solar cell are:

\[
\text{Dye} + \text{light} \rightarrow \text{dye}^* \\
\text{Dye}^* + \text{TiO}_2 \rightarrow \text{oxidized dye} \\
\text{Oxidized dye} + 3/2 \text{I}^- \rightarrow \text{dye}^* + 1/2\text{I}_3^- \\
1/2\text{I}_3^- + e^- (\text{counter electrode}) \rightarrow 3/2 \text{I}^- 
\]

4. Conclusion

In this work we have reported an investigation on three types of pigments as natural photosensitizers, describing and comparing their sensitization and Photoelectrochemical activities with respect to one another. The raw pigments simply extracted in acidic conditions from leaves, roots and fruits achieved solar energy conversion efficiency of 1.5%, which is the highest obtained among all sensitized cells. Natural dye based cells appear to be limited by low Voc and a large decrease in photocurrent, probably due to dye degradation. Finding different additives for improving Voc might result in larger conversion efficiencies. Although the efficiencies obtained with these natural dyes are still below the current requirements for large scale practical application, the results are encouraging and may boost additional studies oriented to the search of new natural sensitizers and to the optimization of solar cell components compatible with such dyes.

References


