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# Natural Dye-Sensitized Solar Cell Based on Nanocrystalline $TiO_2$

(Sel Suria Terpeka Pewarna Semula Jadi Berasaskan Nanohablur $TiO_2$)

KHALIL EBRAHIM JASIM*

ABSTRACT

*During the last quarter of the twentieth century there have been intensive research activities looking for green sources of energy. The main aim of the green generators or converters of energy is to replace the conventional (fossil) energy sources, hence reducing further accumulation of the green house gasses GHGs. Conventional silicon and III-V semiconductor solar cell based on crystalline bulk, quantum well and quantum dots structure or amorphous and thin film structures provided a feasible solution. However, natural dye sensitized solar cells NDSSC are a promising class of photovoltaic cells with the capability of generating green energy at low production cost since no vacuum systems or expensive equipment are required in their fabrication. Also, natural dyes are abundant, easily extracted and safe materials. In NDSSC, once dye molecules exposed to light they become oxidized and transfer electrons to a nanostructured layer of wide bandgap semiconductors such as $TiO_2$. The generated electrons are drawn outside the cell through ohmic contact to a load. In this paper we review the structure and operation principles of the dye sensitized solar cell DSSC. We discuss preparation procedures, optical and electrical characterization of the NDSSC using local dyes extracted from Henna (*Lawsonia inermis *L.), pomegranate, cherries and Bahraini raspberries (*Rubus *spp.). These natural organic dyes are potential candidates to replace some of the man-made dyes used as sensitizer in many commercialized photoelectrochemical cells. Factors limiting the operation of the DSSC are discussed. NDSSCs are expected to be a favored choice in the building-integrated photovoltaics (BIPV) due to their robustness, therefore, requiring no special shielding from natural events such as tree strikes or hails.*

*Keywords: Building-integrated photovoltaics (BIPV); nanocrystalline layer; natural dye sensitize solar cell NDSSC; photoelectrochemical cell*

ABSTRAK

*Sejak suku abad yang lalu, aktiviti penyelidikan bagi mencari sumber tenaga hijau sangat giat dilakukan. Matlamat utama penjana atau penukar tenaga adalah untuk menukar sumber tenaga konvensional (fosil) dan mengurangkan pengumpulan gas rumah hijau (GHGs). Sel suria konvensional berasaskan bahan pukal hablur, telaga kuantum dan struktur bintik kuantum atau amorfus dan filem nipis daripada bahan silikon dan semikonduktor III-V menawarkan kemungkinan penyelesaian. Walau bagaimanapun, sel suria terpeka pewarna semula jadi (NDSSC) merupakan kumpulan sel fotovoltan dengan keupayaan penjanaan tenaga hijau pada kos yang lebih rendah disebabkan tiada sistem vakum atau kelengkapan mahal diperlukan untuk penghasilannya. Selain itu, sumber pewarna semula jadi sangat banyak dan ia adalah bahan yang selamat. Di dalam NDSSC, apabila molekul pewarna terdedah kepada cahaya, ia akan teroksida dan memindahkan elektron ke lapisan nanostruktur yang mempunyai jurang tenaga yang lebar seperti $TiO_2$, melalui sentuhan ohmik elektron yang terhasil dikeluarkan dari sel dan terus ke beban. Dalam kajian ini, kami mengkaji struktur dan prinsip operasi sebuah sel suria terpeka pewarna DSSC. Kami membincangkan prosidur penyediaan, pencirian optik dan elektrik sebuah NDSSC menggunakan pewarna tempatan yang diekstrak daripada inai (*Lawsonia inermis *L.), pomegranat, ceri and rasberi Bahrain (*Rubus *spp.). Pewarna semula jadi ini merupakan calon yang berpotensi untuk menggantikan sebahagian pewarna buatan manusia yang digunakan sebagai pemeka di dalam sel fotoelektrokimia komersial. Faktor pengehad operasi DSSC juga dibincangkan. NDDSC dijangka menjadi pilihan yang diminati untuk bangunan-terkamir fotovoltan (BIPV) disebabkan kelasakkannya, justeru ia tidak memerlukan perlindungan khusus daripada fenomena semula jadi seperti pukulan pokok dan hujan batu.*

*Kata kunci: Bangunan-terkamir fotovoltan; lapisan nanohablur; sel fotoelektrokimia; sel suria terpeka pewarna semulajadi*

## INTRODUCTION

Harnessing energy from sun rays is so far considered as one of the effective solutions in generating green energy. Solar cells are the basic block of solar array where the absorption of light quanta of specific energy results in generation of charge carries. The photogenerated charge carries deliver their energy to some external load where it converted to any other desirable energy form. In 1991, Graetzel and co-workers (Hara & Arakawa 2003; Kalyanasundaram & Gratzel 1998; Nazerruddin et al. 1993; O'Regan & Gratzel M. 1991) came up with the methodology to dye-sensitize colloidal $TiO_2$ film as a way to fabricate low-cost, high-efficiency solar cells. This was a remarkable development of a non-silicon based solar cell where the overall light-to-electric energy conversion efficiency close to 12% in diffuse daylight has been reported (O'Regan & Gratzel 1991). Extensive review of dye sensitized solar cell (DSSC) can be found in ref (Hara & Arakawa 2003; Kalyanasundaram & Gratzel 1998) and references cited therein. It might be possible in the near future to achieve commercial DSSC production for indoor applications such as calculators (Hara & Arakawa 2003).

Figure 1 shows a schematic diagram illustrating the structure and operation principle of the dye-sensitized cell. The cell is composed of four elements: Conducting electrode and counter conducting electrode, nanostructured $TiO_2$ layer, dye molecules and electrolyte. The transparent conducting electrode and counter-electrode are coated with a thin conductive and transparent layer of tin dioxide ($SnO_2$). Nanocrystalline $TiO_2$ is deposited on the conducting electrode (photoelectrode) to provide the necessary large surface area where dye molecules get adsorbed onto. Upon absorption of sun light dye molecules get excited from the highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbitals (LUMO) state as presented in equation 1. Once an electron injected into the conduction band of the wide bandgap semiconductor nanostructured $TiO_2$ film the dye molecule (photosensitizer) become oxidized, equation 2. The injected electron is transported between the $TiO_2$ nanoparticles and then gets extracted to a load where the work done is delivered as an electric energy, equation 3. To mediate electron between the $TiO_2$ photoelectrode and the carbon coated counter electrode electrolyte containing $I^-/I_3^-$ redox ions is used to fill the cell. Therefore, the oxidized dye molecules (photosensitizer) are regenerated by receiving electrons from the $I^-$ ion redox mediator that will oxidized to $I_3^-$ (Tri-iodide ions), equation 4. The $I_3^-$ substitutes the donated electron internally with that from the external load and gets reduced back to $I^-$ ion, equation 5. Therefore, generation of electric power in DSSC causes no permanent chemical change or transformation.

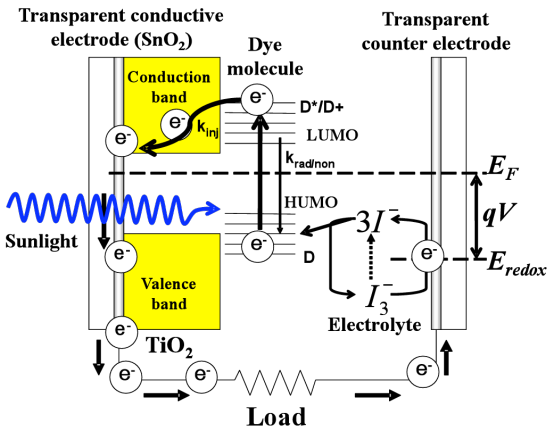


FIGURE 1. Schematic diagram illustrating the structure and operation principle of dye-sensitized cell

$$D + h\nu \rightarrow D^* \quad (1)$$

$$D^* + TiO_2 \rightarrow D^+ + e^-(TiO_2) \quad (2)$$

$$e^-(TiO_2) + \text{Electrode} \rightarrow TiO_2 + e^-(\text{Electrode}) + \text{Energy} \quad (3)$$

$$D^+ + e^- \rightarrow D + I^-_3 \quad (4)$$

$$2e^-(\text{Electrode}) + I^-_3 \rightarrow 3I^- + \text{Electrode} \quad (5)$$

The conducting electrodes are prepared such that they posses low sheet resistance and very high transparency in order to facilitate high solar cell performance. For the counter electrode of the cell to have high electro-catalytic activity it is coated with carbon (sooth) just before assembling the cell.

Also illustrated in Figure 1, the maximum potential produced by the cell is determined by the energy separation between the electrolyte chemical potential ($E_{redox}$) and the Fermi level of the $TiO_2$ ($E_F$). The smaller the energy separation between the HOMO and LUMO ensures absorption of low energy photons in the solar spectrum. Therefore, the photocurrent level is dependent on the HOMO-LUMO levels separation. This is analogous to inorganic semiconductors bandgap energy $E_g$. In fact, effective electron injection into conduction band of $TiO_2$ is highly enhanced with the increase of energy separation of LUMO and the bottom of the $TiO_2$ conduction band. Also, for the HOMO level to effectively accept the donated electrons from the redox mediator; the energy difference between the HOMO and redox potential must be more positive (Hara & Arakawa 2003).

Since the over all DSSC efficiency is proportional to electron injection efficiency in the wide bandgap nanostructured semiconductor, investigations has been escalated over the past decade where $ZnO_2$ nanowires, for example, have been developed to replace both porous and $TiO_2$ nanoparticle based solar cells (Law et al. 2005). Also, metal complex and novel man made dyes have been proposed (Hasselmann & Meyer 1999; Isalm et al. 2000; Yang et al. 2000). However, their processing and synthesization is a complicated and costly process (Amano & Komori 2004; Garcia et al. 2003; Hao et al. 2006; Polo & Iha 2006; Kumara et al. 2006; Smestad 1998; Yanagida et al. 2004). Moreover, development or extraction of photosensitizes whose absorption extends to the near IR is

greatly desired. We found that our environment provides natural, non toxic and low cost dyes sources with high absorbance level of UV, visible and near IR. Examples of such dye sources are Bahraini Henna (*Lawsonia inermis* L.), Bahraini raspberries (Rubus spp.), pomegranate, and cherries.

In this work we characterize the optical and electrical properties of the dyes extracted from Bahraini and Yemeni Henna at different concentrations, Bahraini raspberries (*Rubus* spp.), pomegranate juice, and cherries. This work provides further investigation on the reported operation of Henna (*Lawsonia inermis* L.) as a dye sensitizer of nanostructured solar cell for the first time (Jasim & Hassan 2009).

## Experimental Method

The nanocrystalline $TiO_2$ film was prepared by following the preparation methodology detailed in (Hara & Arakawa 2003; Nazerruddin et al. 1993; O'Regan & Gratzel 1991; Smestad 1998). A suspension of $TiO_2$ was prepared by adding 9 mL of nitric acid solution of PH 3-4 (1 mL increment) to 6 g of colloidal P25 $TiO_2$ powder in mortar and pestle. While grinding, 8 mL of distilled water (in 1 mL increment) was added to get a white- free flow- paste. Finally, a drop of transparent surfactant was added in 1 mL of distilled water to ensure coating uniformity and adhesion to the transparent conducting glass electrode. The ratio of the nitric acid solution to the colloidal P25 $TiO_2$ powder is a critical factor for the cell performance. If the ratio exceeds a certain threshold value the resulting film becomes too thick and has a tendency to peel off. On the other hand, a low ratio reduces appreciably the efficiency of light absorption.

Soxhlet Extractor was used in the extraction of dyes from 80 g of Bahraini Henna (powder), 87 g of Yemeni Henna (powder) in 100 mL of methanol, 97 g of dried and grounded cherries in methanol, 97 g of dried and grounded cherries in methanol with 1% HCL, 32 g of Bahraini Raspberries in 100 mL of methanol, and pomegranate juice (from a 100 g pomegranate seeds). The light harvesting efficiency for each extract has been calculated from the measured absorbance. The extracted cherries of concentration 97 g in 100 mL methanol with 1% of HCl yield bright red solution suggesting that the presence of 1% HCL enhanced the extraction of the dye molecule. On the other hand the extracted cherries with methanol only yield pale-red solution. The addition of 1% HCL affected the absorbance of the dye molecule as well the electrical characteristic of the assembled solar cells as presented in Table 1. Although the extraction of Cherries with 1% HCL enhanced the absorption band at 500 nm, the absorbance of the extract beyond wavelength of 600 nm deteriorated.

Doctor blade method was employed in deposition of $TiO_2$ suspension which was applied uniformly on a cleaned (rinsed with ethanol) electrode plate. The $TiO_2$ film was allowed to dry and then annealed at approximately 450°C (in a well ventilated zone) for about 15 min to form a porous, large surface area $TiO_2$ film. The film must be allowed to cool down slowly to room temperature. This is a necessary condition to remove thermal stresses and avoid cracking of the glass or peeling off the $TiO_2$ film. Investigation of the formation of nanocrystalline $TiO_2$ film was confirmed by scanning electron micrograph SEM. $TiO_2$ nanocrystalline layer was stained with the dye for approximately a day, and then washed with distilled water and ethanol to ensure the absence of water in the film after removal of the residual dye. The counter electrode was coated with graphite (sooth) that acts as a catalyst in redoxing the dye. Both the photo- and the counter electrode were clamped together and drops of electrolyte were applied to fill the clamped cell. The electrolyte used consists of an organic solvent containing a redox couple (traditionally the iodide/triiodide [$I^-/I^-_3$] couple). The measurements of open-circuit voltage and short-circuit current have been performed under direct sun illumination at the noon time. Neither UV or IR cutoff filters nor AR coatings on the photoelectrode have been used.

## Results and Discussion

Dyes extracts have been optically characterized by measuring their absorbance using dual beam UV-VIS spectrophotometer (Shimadzu, model UV-3101). Typical example of light harvesting efficiency (LHE = $1\text{-}10^{-A}$, where A is the absorbance) measurements are shown in Figures 2 and 4(a). In Figure 2, Yemeni Henna extract shows a remarkable level of absorbance as its concentration

TABLE 1. Measured and calculated parameters of the assembled photovoltaic cells with different dye sensitizers

| Dye | $V_{oc}$(V) | $I_{sc}$(mA) | FF % | η % |
|---|---|---|---|---|
| Bahraini Henna (80 g) | 0.426 | 0.368 | 24.6 | 0.128 |
| Yemeni Henna (87 g) | 0.306 | 0.407 | 28.1 | 0.117 |
| Cherries (97 g) | 0.305 | 0.466 | 38.3 | 0.181 |
| Cherries (97 g) + 1% HCL | 0.301 | 0.463 | 28.8 | 0.134 |
| Pomegranate juice (100 g) | 0.395 | 1.700 | 48.1 | 1.076 |
| Raspberries (32 g) | 0.360 | 0.566 | 45.5 | 0.309 |

increases. Similar behaviour has been observed with extracts from raspberries, cherries without HCL, and pomegranate juice. Bahraini Henna absorbance and LHE have been presented in (Jasim & Hassan 2009; Jasim et al. 2011).

The incident photon to current conversion efficiency IPCE is defined as:

$$IPCE = LHE\ \Phi_{inj}\ \eta_c \qquad (6)$$

where $\Phi_{inj}$ is the quantum yield of electron injection and $\eta_c$ is the collection efficiency of the injected electrons at the back contact. Therefore, the IPCE equals the LHE if both $\Phi_{inj}$ and $\eta_c$ are close to 100%. Thus, the investigated dye extracts are suggested to be a promising natural dye sensitizer for single junction DSSC.

SEM measurements have been performed before and after the annealing process to quantify the formation of nanocrystalline $TiO_2$ structure. Figure 3 shows the SEM image of the annealed $TiO_2$ layer. X-ray diffraction measurements confirmed the formation of nanocrystalline $TiO_2$ particles of sizes less than 50 nm (Jasim & Hassan 2009). The formation of nanocrystalline $TiO_2$ particles is greatly affected by $TiO_2$ suspension preparation procedures as well as by the annealing temperature. The porosity of the $TiO_2$ is an essential not only to ensure high roughness factor, but also to enhance the penetration of the redoxing ions into the film. It was found that a sintered $TiO_2$ film at temperatures lower than the recommended 450°C resulted in cells that generate unnoticeable electric current even in the $\mu$A level. Moreover, $TiO_2$ film degradation in this case was fast and cracks form after a short period of time when the cell is exposed to illumination.

Figure 4(b) presents an example of the I-V characteristics of NDSSC sensitized with pomegranate juice. To asses the stability of the assembled cells, they have been wrapped in tissue and left for few months. Then, just after adding a drop or two of electrolyte to the dry cell, photovoltaic action happened, but values of the $I_{sc}$ and $V_{oc}$ are lower than what have been recorded when

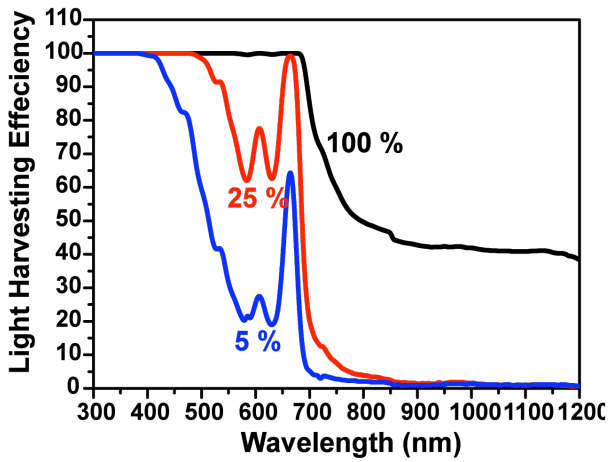


FIGURE 2. Light harvesting efficiency vs. wavelength for Yemeni Henna extracts at different concentration

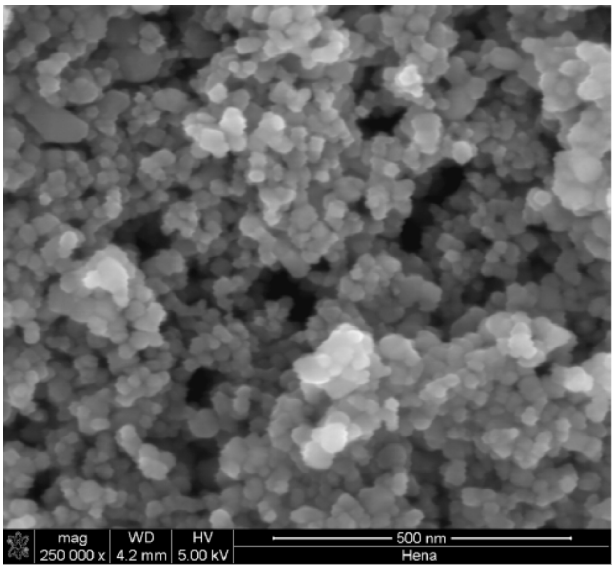


FIGURE 3. SEM image of $TiO_2$ film after annealing

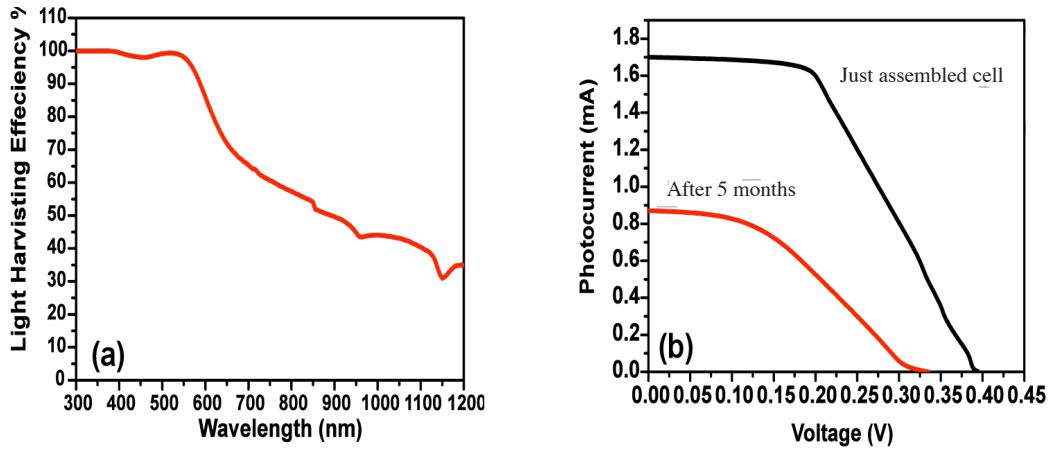


FIGURE 4(a). Light harvesting efficiency vs. wavelength for pomegranate juice and (b) I-V characteristics for an assembled solar cell

the cell just has been assembled. Figure 4(a) presents the measured light harvesting efficiency (LHE) of pomegranate juice.

Table 1 presents some of the measured and calculated parameters of the assembled photovoltaic cells. The sensitized cell with pomegranate juice resulted in the highest conversion efficiency compared with other extracts. Although both the open circuit voltage and short circuit current of cells sensitized with cherries and 1% HCl treated cherries extracts do not show any noticeable difference, the overall conversion efficiencies and fill factors reflect clear variations. Similarly, Henna brand must be considered when chosen as sensitizer. Due to light reflection and absorption by the conductive photoelectrode and scattering nature of the nanostructured $TiO_2$, the measured transmittance of the photoelectrode shows on the average 10% of the solar spectrum (AM 1.5) is allowed. On the average, the active area of the photovoltaic cell is about 3 $cm^2$.

Generally speaking, the performance of the studied photovoltaic cells is affected by many factors. Firstly, the dye structure must possess several carbonyl (C = O) or hydroxyl (-OH) groups capable of complexing to the Ti (IV) sites on the $TiO_2$ surface (Tennakone et al. 1997). This in fact explains why dyes from grapes are not good sensitizer, while the California blackberries (Rubus ursinus) are excellent source of dye for sensitization (Cherpy et al. 1997; Smestad 1998).

Secondly, the redoxing electrolyte must be efficient and fast in regenerating oxidized dye molecules. Since both hole transport and collection efficiency on the dye-cation reduction and $I^-/I^-_3$ redox efficiency at counter electrodes must considered (Yanagida et al. 2006). Besides limiting cell stability due to evaporation, liquid electrolyte inhibits fabrication of multi-cell modules because module manufacturing requires solar cells be connected electrically yet separated chemically (Matsumoto et al. 2001; Tennakone et al. 1999). Therefore, to improve the performance of the solar cell we suggest replacing the liquid electrolyte with a solid state that provides a better sealing of the cell (Kruger et al. 2003; Stthatos et al. 2004).

Thirdly, the thickness of nanocrystalline $TiO_2$ film must not be more than 30 $\mu$m to ensure a diffusion length of photoelectrons greater than that of the nanostructured $TiO_2$ layer. Thus, many studies suggest replacing the nanoparticles film with an array of single crystalline nanowires or nanosheets in which the electron transport increases by several orders of magnitude (Kopidakis et al. 2003; Law et al. 2005; Noack et al. 2002; Xiang et al. 2006).

## Conclusion

In summary, we have demonstrated the sensitization of nanocrystalline $TiO_2$ using some local natural dyes extracts. Both Henna (*Lawsonia inermis* L.) dye extracts showed a high level of absorbance in the UV, visible, and NIR regions of the solar spectrum; a similar behavior is possessed by pomegranate and Bahraini raspberries. Therefore, these natural dyes extracts are potentially capable of replacing some of the man made dyes used as sensitizer in nanocrystalline $TiO_2$ photovoltaic cells. Both the preparation of nanocrystalline $TiO_2$ layer and the nature of redoxing electrolyte must be optimized to enhance collection efficiency of the cell. We do suggest other nanostructure configurations such as nanocrystalline rods or dendrimers structures. Other large bandgap semiconductors such a $ZO_2$ might be used instead $TiO_2$. Other factors during dye extraction such as solvent choice, temperature of extraction, and pH of the extracted dye solution must be investigated.

Due to the following advantages of DSSC over semiconductor based solar cells: bifacial configuration, efficiency less sensitive to angle of incidence, transparency for power windows, and color variation by selection of the dye; DSSC are expected to be a choice in building integrated photovoltaics BIPV. Also, success in fabrication of flexible substrate and screen printing of wide bandgap nanostructured semiconductor materials will facilitate mass production and commercialization of DSSC.

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Department of Physics
College of Science
University of Bahrain
Po Box 32038, Kingdom of Bahrain

*Corresponding author; email: khalilej@gmail.com

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