

Curcumin Dye-Sensitized Solar Cell

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Abstract: DSSCs (dye sensitized solar cells) are expected to be one of the efficient third generation solar cells that are generating green energy at low production cost since no vacuum systems or expensive equipment are required in their fabrication. In this paper, review of the structure, and operation principles of the dye sensitized solar cell DSSC is outlined. Extraction and optical characterization of Curcumin dye are detailed. Preparation procedures, optical and electrical characterization of the DSSC using Curcumin dye, as well as factors limiting the operation of the DSSC are discussed. Open circuit voltage $V_{oc} = 430$ mV and short circuit current $I_{sc} = 0.72$ mA from a 3 cm^2 curcumin sensitized solar cell is achievable under solar illumination.

Key words: Curcumin dye, DSSC, photovoltaic, nanoporous TiO_2 .

1. 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 coworkers [1-4] 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 [4]. Extensive review of DSSC (dye sensitized solar cell) can be found in Refs. [1, 2] and references cited therein. It might be possible in the near future to achieve commercial DSSC production for indoor applications such as calculators [1].

Fig. 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 HOMO (highest occupied molecular orbitals) to the LUMO (lowest unoccupied molecular orbitals) state as presented in Eq. (1). Once an electron injected into the conduction band of the wide bandgap semiconductor nanostructured TiO_2 film, the dye molecule (photosensitizer) become oxidized, Eq. (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, Eq. (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)

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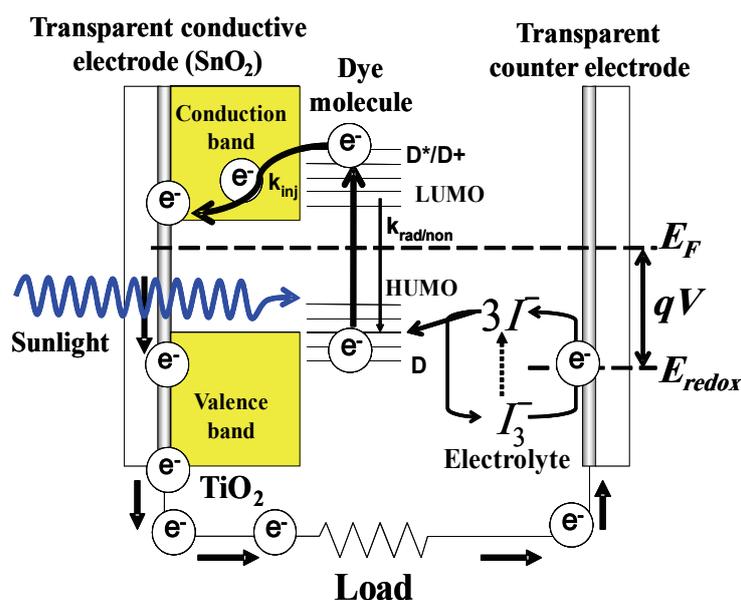
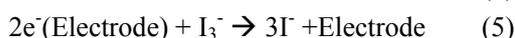
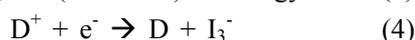
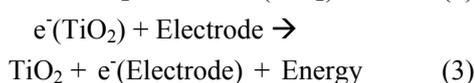
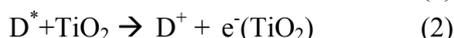


Fig. 1 Schematic diagram illustrating the structure and operation principle of dye-sensitized cell.

are regenerated by receiving electrons from the Γ ion redox mediator that will oxidized to I_3^- (Tri-iodide ions), Eq. (4). The I_3^- substitutes the donated electron internally with that from the external load and gets reduced back to Γ ion, Eq. (5). Therefore, generation of electric power in DSSC causes no permanent chemical change or transformation.



The conducting electrodes are prepared such that they possess 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 (soot) just before assembling the cell.

Also illustrated in Fig. 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 [1].

Since the overall DSSC efficiency is proportional to electron injection efficiency in the wide bandgap nanostructured semiconductor, investigations have been escalated over the past decade where ZnO nanowires, for example, have been developed to replace both porous and TiO_2 nanoparticles based solar cells [5]. Also, metal complex and novel man made dyes have been proposed [6-8]. However, their processing and synthesis is a complicated and costly process [9-15]. In this paper, we report for the first time the sensitization of nanoporous TiO_2 layer using Curcumin solutions. Details of the preparation of Curcumin dye, characterization of its optical properties, and investigation of photovoltaic action via sensitizing nanoporous TiO_2 are stated.

2. Experimental Method

The nanoporous TiO₂ film was prepared by following the preparation methodology detailed in Refs. [1, 3, 4, 14, 16]. A suspension of TiO₂ was prepared by adding 9 mL of nitric acid solution of pH 3-4 (1 mL increment) to 6 g of colloidal P25 TiO₂ 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 TiO₂ 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.

As detailed in Ref. [17] curcumin is a yellow pigment. It is a natural component of rhizome called turmeric, of the plant *Curcuma Longa L.* The powdered rhizome of this plant, called turmeric. In addition to its use in curries, flavoring and coloring of the diet, Curcumin has been used as a medicine for treatments of inflammation, skin wound and cough, however its anticancer properties have generated a great interest and results in many publications. Chemical analysis of the extraction products of this powder by a variety of solvent mixtures has shown the principal components to be curcumin [1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione], demethoxycurcumin [1-(4-hydroxyphenyl)-7-(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione] and bisdemethoxycurcumin [1,7-bis(4-hydroxyphenyl)-1,6-heptadiene-3,5-dione] [18]. The structures of the above molecules are shown in Fig. 2. In fact, the curcumin has a β -diketone group which equilibrates to a more stable keto enol tautomeric conformation which can exist in cis and trans isomers [19-21]. Fig. 3 shows typical structures of different keto and keto enol forms [22].

For the purposes of this investigation, turmeric was extracted using acetonitrile as in the following procedures: Turmeric (20 g) was added to acetonitrile (100 mL) and stirred for 6 hours. The yellow solution was filtered under vacuum through a bed of charcoal and silica gel in a 1 : 1 mixture. The solvent was evaporated at ambient temperature to give a glass like residue with a yield of 0.62 g. A homogenous solution is prepared by dissolving 0.255 g in 100 mL of methanol grade 99.9%.

Doctor blade method was employed in deposition of TiO₂ suspension which was applied uniformly on a cleaned (rinsed with ethanol) electrode plate. The TiO₂ film was allowed to dry and then annealed at approximately 450 °C (in a well ventilated zone) for about 15 minutes to form a porous, large surface area TiO₂ 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 TiO₂ film. Investigation of the formation of nanocrystalline TiO₂ film was confirmed by scanning electron micrograph SEM. TiO₂ 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 (soot) 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

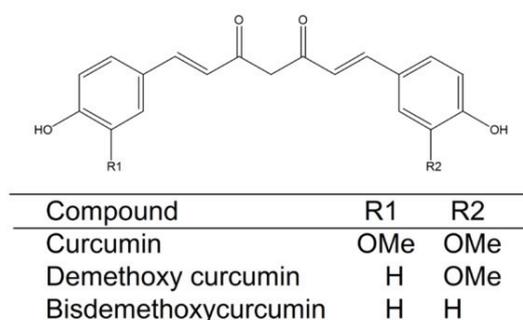
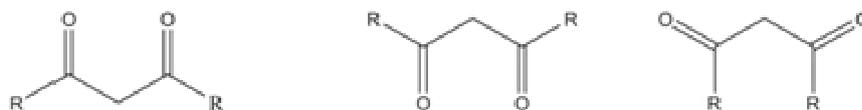
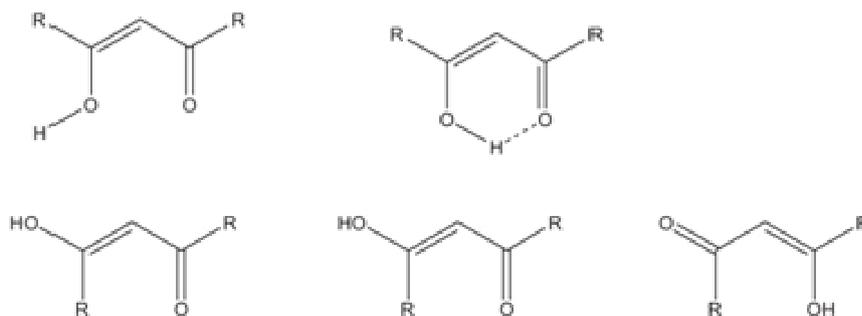


Fig. 2 Chemical structure of the curcumin molecules.

Different keto forms



Different enol forms



Different R groups that may exist.

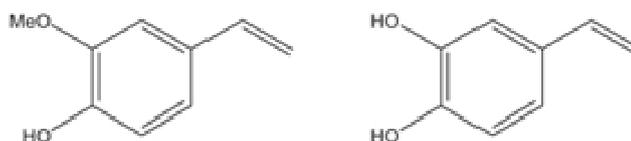


Fig. 3 Keto-enol tautomerism of Curcumin.

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 using solar simulator. UV and IR cutoff filters but no AR coatings on the photoelectrode have been used.

3. Results and Discussions

The extracted curcumin dye solutions have been optically characterized by measuring its absorbance using dual beam UV-VIS spectrophotometer (Shimadzu, model UV-3101). Typical example of light harvesting efficiency ($LHE = 1 - 10^{-A}$, where A is the absorbance) measurements is shown in Fig. 4. In this figure, curcumin solution exhibits 100% LHE for photons with wavelength between 300 nm to 500 nm,

and it sharply drops less than 10% beyond 600 nm. Hence, red and near infrared portion of the solar spectrum is not absorbed by curcumin molecules. The

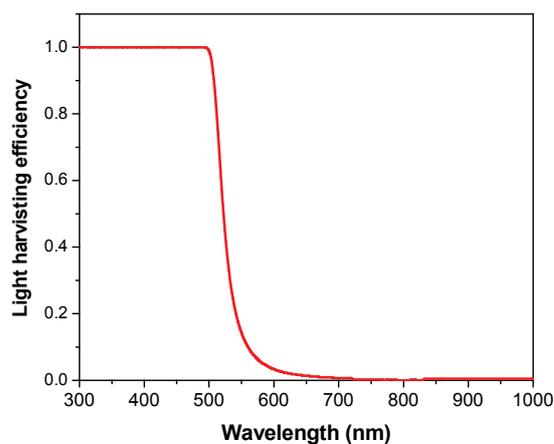


Fig. 4 Light harvesting efficiency vs. wavelength for curcumin dye.

incident photon to current conversion efficiency IPCE is defined as:

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

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

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 μA level. Moreover, TiO_2 layer degradation in this case was fast and cracks form after a short period of time when the cell is exposed to illumination.

Table 1 presents some of the measured and calculated parameters of the assembled photovoltaic cells. 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 simulator spectrum (AM 1.5) is allowed. On the average, the active area of the photovoltaic cell is 3 cm^2 .

The I - V characteristics shown in Fig. 5 indicate the presences of a noticeable series resistance. Such series resistance affects cell performance. Capacitive effect is

also existed due to nature of cell layer structure.

Generally speaking, the performance of the studied photovoltaic cells is affected by many factors. Firstly, the dye structure must possess several carbonyl ($\text{C}=\text{O}$) or hydroxyl ($-\text{OH}$) groups capable of complexing to the Ti (IV) sites on the TiO_2 surface [23]. 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 [14, 24].

Secondly, the redoxing electrolyte needs to be chosen such that the reduction of I_3^- ions by injection of electrons is fast and efficient (see Fig. 1). This arise from the fact that the dependence of both hole transport and collection efficiency on the dye-cation reduction and I/I_3^- redox efficiency at counter electrodes are to be considered [25]. As a matter of fact, besides limiting cell stability due to evaporation, liquid electrolyte inhibits fabrication of multi-cell modules since module manufacturing requires cells be connected electrically yet separated chemically [26, 27]. To improve the performance of the cell we suggest replacing the liquid electrolyte with a solid state one that provides a better sealing of the cell [28, 29].

Thirdly, the thickness of nanocrystalline TiO_2 film must be few tens of micrometers ($< 30 \mu\text{m}$) to ensure that the diffusion length $L_n = \sqrt{D_n \tau_n}$ of the photoelectrons is greater than that of the nanoporous TiO_2 layer [1, 30]. To increase photogenerated electron diffusion length, 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 [5, 32-34].

Table 1 Measured and calculated parameters of the assembled solar cells using different natural dye sensitizers.

Dye	V_{oc} (V)	I_{sc} (mA)	FF (%)	η (%)
Curcumin	0.432	0.720	40	0.41
Bahraini Henna 8 g ^a	0.410	0.906	36.3	0.450
Yemeni Henna 4.2 g ^b	0.500	0.414	27.6	0.191
Raspberries ^a	0.360	0.566	45.5	0.309
Cherries in Methanol ^a	0.305	0.466	38.3	0.181

^a Ref. [16], ^b Ref. [31].

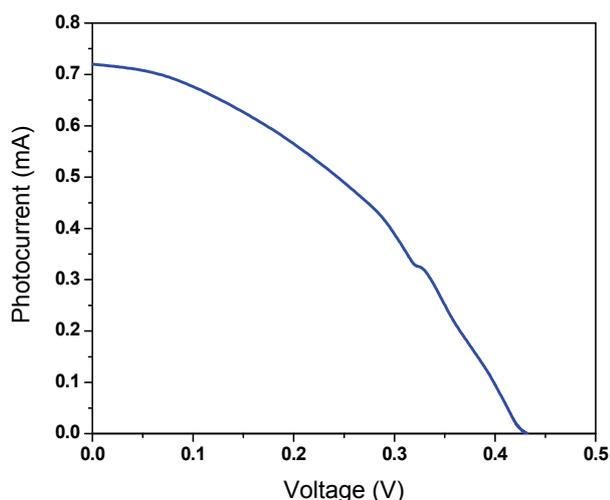


Fig. 5 Typical I - V characteristics for an assembled Curcumin sensitized nanoporous TiO_2 solar cell.

Finally, dark current in DSSC is mainly due to the loss of the injected electron from nanostructured TiO_2 to I_3^- (the hole carrier in solution electrolyte). Reduction of dark current enhances the open circuit voltage of the cell, and one successful way to suppress dark current is to use of coadsorbates on the nanostructured TiO_2 surface. Therefore, to achieve further improvement of the performance of DSSC cell many researchers have suggested replacing the liquid electrolyte with a solid state one that provides a better sealing of the cell [28, 29] and fabrication of large area modules with efficiency above 12%. The success of Sony in 2010 to present a DSSC module with efficiency close to 10% is one of the driving achievements toward fabrication of outdoor larger area modules that can be integrated in green buildings. Also, as presented for example by Dyesol™, development of flexible transparent substrate (polymer-based) will transform DSSCs industry toward mass production and commercialization of single cell or mini modules for indoor and personal appliances.

4. Conclusions

In summary, we have demonstrated the sensitization of nanoporous TiO_2 with Curcumin dye extract. Dye extract showed a high level of absorbance in the UV, and visible 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 factors during dye extraction such as solvent choice and temperature of extraction 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 will facilitate mass production and commercialization of DSSC.

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