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Comparative study of N719 dye on two different photo-anodes

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Abstract. Nano-composites of TiO_2 and ZnO were successfully prepared using the doctor blade application and high temperature sintering on indium-doped tin oxide (ITO) glass substrate. They were used as efficient photo anode in high performance dye-sensitized solar cells (DSSCs) assembled with N719 dye. The high-density frameworks of TiO_2 and ZnO were synthesized on separate ITO conducting glass using a facile and cost-effective two-step approach to compare the output efficiency. We report on the interfacial boundary relationships, charge – collection conversion efficiency and I-V characteristics of the DSSCs with different electrolytes. The TiO_2 photo anode demonstrated an enhanced solar-to-electrical energy conversion of approximately 5.41 % with KCl electrolyte which was far less than that of a ZnO photo anode with KCl electrolyte which had about 21 % increase under conditions of 1.5 AM. Because of the enhanced solar energy conversion of the ZnO photo anode, *l.arboreus* with KI sensitizer records 9.78 % is a promising candidate for large manufacture of high performance DSSCs modules.

1. Introduction

In the present day, photovoltaic technologies based on inorganic materials dominate the commercial sphere. They are however very expensive and require high temperature and specified environmental conditions for their preparation. Furthermore, materials like CdTe, are scarce, toxic and poisonous. Dye-sensitized solar cells (DSSCs) or organic photovoltaic conversely, are not susceptible to these problems. Although, the efficiencies of DSSCs is still presently less than pure inorganic based photovoltaic technologies, DSSC based on nano-structured electrodes has been subject of intensive research in the last decade. This is due to their special hybrid design which uses the phenomenon of photo electrics, a prospect for low cost electricity from the corresponding synthesis procedure and use of sunlight harvest [1]. Several elements in the intricate DSSC architecture can limit their performance and require an improvement simultaneously to obtain an optimal performance. Precisely, increased dye loading of internal surfaces of the photo-anode and improved conduction of the electrons through 2D metal oxide nano-structures are the specific objectives [2]. Nano-phase anatase TiO_2 is the most popular photo anode material in the DSSC context, but in most studies this material is used in spherical morphology or as faceted nanoparticles (NPs). It is to be noted that unlike ZnO, the crystal habit of TiO_2 does not produce normal progression of regular structures. Recent study has revealed that the photosensitizer is one of the most important materials in DSSCs, which is responsible in determining the performance of the solar cells. Basically, this framework consists of a TiO_2 nanoparticle film that offers a large surface area for adsorption of dye sensitizers, which absorbs light and transfers photo electrons into the conduction band of the TiO_2 after excitation. Law et al. compared the ZnO nanoparticle electron diffusion coefficient to that of TiO_2 nanoparticle film and obtained different efficiencies [3].

Presently, ruthenium dye complexes have power conversion efficiencies of over 11% under standard global air mass 1.5 and also show promising result in stability [4]. Nonetheless, their application is constrained by the high cost and scarcity of ruthenium. In recent times, interest in metal-free organic dyes as alternatives for noble metal complexes has been aroused due to their low cost, ease of manufacture, facile molecular design and high molar extinction coefficient. A large number of researches have been carried out on the molecular engineering of chromophores for higher capability of panchromatic light-harvesting. A variety of organic dyes, such as carbazole, cyanine, coumarin, thiophene, indoline, and fluorine based dyes have reportedly shown positive results [5].

Generally organic dyes used for efficient solar cells are required to possess broad and intense spectral absorption in the visible light region. Overall, DSSC is considered as a low cost and promising solution to solve the energy problem. The authors have shown that the output efficiency for DSSCs depends on the electrolytes used for sensitizing the solar cell and the choice of photo anode determines the photo electrochemical properties of composite films [6] .We therefore present, analyse and discuss these data in this paper.

2. The general components and function of a dye-sensitized solar cell

A dye-sensitized solar cell consists of five main parts: the conducting glass substrate usually fluorine or indium doped a photo anode, a dye which will be sensitized, an electrolyte and a platinum coated counter electrode. Ruthenium dyes have been used and are presently used as sensitizer, titanium oxide because of being readily available, non-toxic and cheap has become a preferred choice of photo anode, other materials such as zinc oxide, aluminium oxide are also suitable candidates for photo anode. Lastly the most common redox mediator used is the iodide/triiodide. In the initial process, the sensitizer D (equation (1)), absorbs quantized energy from the sun. This excites the sensitizer and causes it to inject an electron into the conduction band of the semiconductor thus, leaving the sensitizer in an oxidized state D^+ (equation (2)). The electron circuits the pathway provided by the semiconductor lattice to reach the back contact and the counter electrode through the external load to reduce the redox couple (equation (3)) which subsequently completes the circuit as it revitalizes the sensitizer (equation (4)).

$$D + \hbar\nu \rightarrow D* \tag{1}$$

$$D* \rightarrow D + e^- \tag{2}$$

$$I_{3^-} + 2e^- \rightarrow 3I^- \tag{3}$$

$$2D * + 3I^- \rightarrow 2S + I^{3-} \tag{4}$$

Some limitations to the favourable reactions above are illustrated by the following equations:

$$D * + e^- \rightarrow D \tag{5}$$

$$I^{3-} + 2e^- \rightarrow 3I^- \tag{6}$$

Equation (5) and (6) show undesirable reactions in which an injected electron either combines with the oxidized redox mediator or semiconductor. The output efficiency of a DSSC is determined by a harmonious blend of all the individual components, especially the spectral responses of the dye film on the semiconductor film [7].

The incident photon to current conversion efficiency (IPCE) is a vital factor for distinguishing a photovoltaic device. Specifically where the same architecture is employed with different devices, it is used to relate the performance of sensitizers. It is described as the integral sum of electrons produced per amount of incident photons expressed as a function of wavelength as shown in Equation (7).

$$IPCE(\lambda) = \frac{Photocurrent}{\lambda \times photonflux} \tag{7}$$

The total efficiency (ŋ) of the DSSC is determined by the photocurrent density (J_{sc}), open circuit voltage (V_{oc}), fill factor (ff) and intensity of light (I_s).

$$\eta_{global} = \frac{J_{sc} \times V_{oc}}{I_s} \tag{8}$$

The energy difference between the Nernst potential of the redox mediator in the electrolyte and the Fermi energy level of the photo anode is the open circuit voltage [8]. This is because of the differential discharge or kinetics arising from charge transfer and recombination path. An understanding of these devices and rates of reactions is crucial for upgrading and in the choice of efficient sensitizers for high efficiency DSSCs [2]. The fill factor (ff) is defined as the quality of the device expressed as the ratio of maximum power P_{max} output of the device to the theoretical maximum power. The value of ff lies between 0 and 1 and indicates electrochemical and electrical losses that may occur during the DSSC operation. Thus, the sensitizer delineates the performances of the device.

3. Materials and method

L.arboreus leaves were harvested and air dried until they assumed constant weight. The dried leaf was milled, weighed and allowed to aerate overnight. A 450 g of *L.arboreus* was soaked in 1000 ml of methanol to extract the dye according to established standard laboratory procedures. The conducting sides of glass substrate of FTO variety and resistivity 18 Ω/m^2 was coated with TiO_2 using the doctor blade method, following a hydrothermal method using a mixture of concentrated nitric acid, isopropyl alcohol and titanium oxide in a ratio of 5:3 respectively, a smooth paste was obtained. The coat was allowed to harden under conditions of 1.5 AM. Then the TiO_2 framework was sintered with Vecstar furnace at 300 ^{o}C for 90 min. The area of exposure was 2.5 mm X 2.5 mm, the characteristic colour change from brown to white indicated the process was complete [9].

4. Results and discussion

4.1. The absorbance, comparative efficiency of L.arboreus on different electrodes and microstructure of L.arboreus are discussed below.

4.1.1. Phytochemical Analysis. A qualitative phyto-screening reveals the presence of flavonoids, glycosides, saponins, steroids and terpenes in abundance. Proteins, tannins and resins are only moderately present while carbohydrates and alkaloids are in traces.

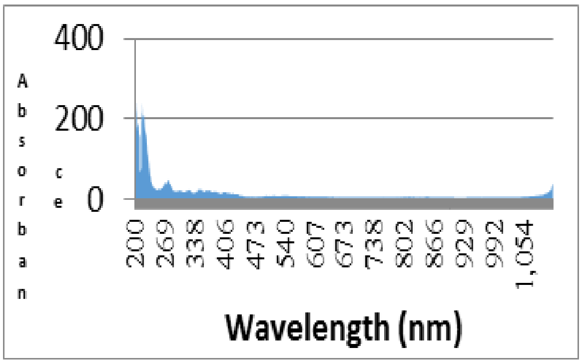

Figure 1. UV/Vis of *L.arboreus*.

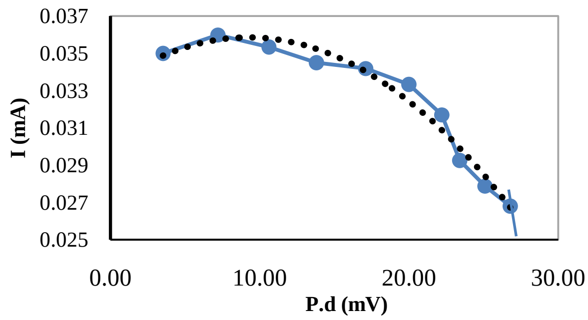

Figure 2. I-V of *L.arboreus* on ZnO with $HgCl_2$.

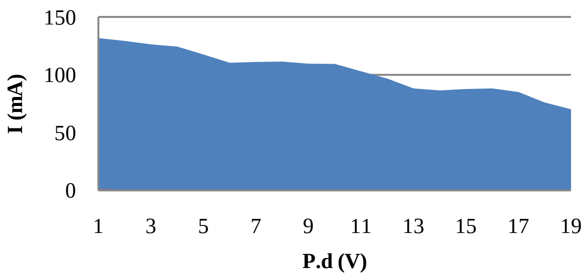

Figure 3. I-V of *L.arboreus* on ZnO with KI.

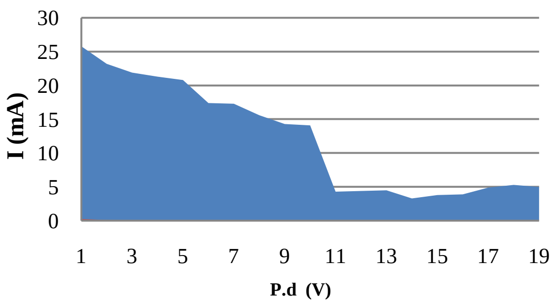

Figure 4. UV/Vis of *L.arboreus* on TiO_2 with KCl.

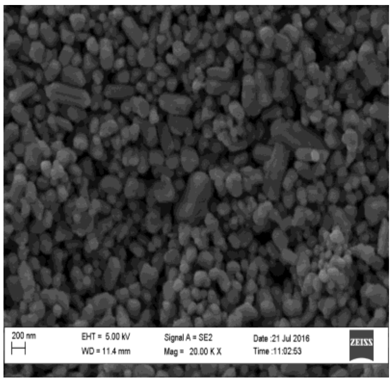

Figure 5. SEM of *L.arboreus* on TiO_2 with KBr.

4.1.2. UV/Vis spectroscopy. A function of absorbance between 200-1100 nm for *L.arboreus* reveals a peak absorbance at about 220 nm. This is a ruthenium dye characteristic. The absorbance has a value 2.0 a.u (on a scale of 100) in the blue region of the electromagnetic spectrum. The absorbance trend is least in the visible region and continues in this same pattern to the near infrared region. At the far infrared region, there is a marginal increase in absorbance as shown in figure 1.

4.1.3. Photoelectric Characteristics. The DSSC was connected in parallel to a variable load supply and a Voltcraft digital multimeter to obtain the photoelectric values. The result is shown on table 1 and the I-V curve illustrated in figure 2. *L.arboreus* based on TiO_2 and sensitized with $HgCl_2$ shows a close approximation to the theoretical value; a fill factor of about 0.8 was recorded. The chemical kinetics is not as favourable, as indicated by the I_{sc}, V_{oc} and power output due to poor charge transport and many trap sites. The effect of using KI and KCl as sensitizer is shown in figures 3 and 4 respectively on ZnO and TiO_2 photo anodes. The ZnO nano-composite is approximately ten times more efficient; output voltage about 7 times more than that of the TiO_2 nano-composite and maximum power output is about 9.78 % more in the ZnO nano-composite. The pattern is recurrent for all electrolyte sensitizers however, KI records the highest power output with the largest I_{sc} and V_{oc} values, this is a result of a more efficient I/I_3^- redox system and an excellent interfacial bonding at the TiO_2/*L.arboreus*/KI interface. The least efficient sensitizer was $HgCl_2$ due to poor excitation, inhibited charge transport, oxidation and weak spectral responses. The most efficient sensitizer on the ZnO photo anode; KI collaborates with KI/TiO_2 (table 1) this is attributable to the chemical kinetics, surface morphology and the strong interfacial bond between the ZnO/*L.arboreus*/KI as shown in figure 3. The least efficient sensitizer is KCl; its spectral response in ZnO is comparative to the result obtained for $HgCl_2$ in table 2. A 60 % increase was recorded from ZnO photo anode relative to the TiO_2 photo anode.

Table 1. Photoelectric values of *L.arboreus* based on TiO_2 Photo anode.

Sensitizer	Isc (mA)	Voc (V)	P max (W)	η (%)
$HgCl_2$	0.128	0.176	5.2 X 10^{-6}	0.0003
KBr	0.506	0.525	5.4 X 10^{-4}	0.0027
KI	7.800	12.5	1.85	0.98
KCl	2.600	5.30	0.0216	0.14

Table 2. Photoelectric values of L.arboreus based on ZnO photo anode.

Sensitizer	I_{sc} (mA)	V_{oc} (V)	P max (W)	Ŋ (%)
$HgCl_2$	0.937	70.5	23.3	0.66
KBr	3.200	11.5	0.426	0.37
KI	1.143	0.285	82.8	9.7
KCl	0.037	0.009	1.2×10^{-5}	3.3×10^{-6}

4.1.4. SEM Microscopy. The thickness of the TiO_2 film in figure 5 is 200 nm. The Zeiss electron microscope reveals *L.arboreus* on TiO_2 with KI sensitizer in figure 5; at a resolution of W.D of 11.4, 5.00 KV and magnification of 20.00KX. The nanoparticles are similar and form clusters. The gap in the clusters is significant for recombination, thus, obstructing the interfacial transfer of electrons. This explains the low output efficiency and poor power output for KBr and $HgCl_2$. The micrograph in figure 5 shows many trap sites amongst the rod-like and spherical nanoparticles. The sizes are more varied which limits effective charge transport, this accounts for its poor efficiency. The efficiency output would therefore be greatly enhanced if the nanoparticles are symmetrical in arrangement. This would reduce the rate of charge recombination and decrease the band gap energy thus exhibiting a synergistic effect.

5. Conclusion

The poor efficiency observed for TiO_2 dye-sensitized solar cell is probably as a result of several unfavourable inter-boundary reactions between the interface of the counter electrode and the TiO_2 photo anode. Nevertheless, the KI sensitizer still shows a promising yield. The reaction kinetics does not seem to favour the displacement of Cl^- as illustrated by the weak J_{sc} recorded for both KCl and $HgCl_2$. The output efficiency for ZnO/*L.arboreus*/KI was 9.7 %, the least efficient was ZnO/*L.arboreus*/KCl with a value of 3.6 X 10^{-6} %. TiO_2/*L.arboreus*/KI had a value of 0.98 %, the most efficient DSSC on TiO_2 photo anode while the least efficient TiO_2/*L.arboreus*/$HgCl_2$ has 0.00023 %. This reveals ZnO/*L.arboreus*/ KI as a promising candidate (IPCE of 21 % and 9.7%) which with positive synergistic sensitizer effect could even still be improved upon for large scale production of DSSC modules.

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