



Evaluation of the Internal Resistance, Generate of Photocurrent in the DSSC and Cyclic Voltametric Measurements from Gautankura (*Solanum incanum*) Plant

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Abstract The use of natural dyes in solar cells offers promising prospects for the advancement of this technology, because fabrication of cost effective solar cells is a scientific challenge. The use of natural pigments cut down the cost of chemical synthesis and high cost of rare metals need for metal organic dye sensitizers. Therefore lot of interest has been drawn on natural dyes extracted from plant materials. Several natural pigments have been utilized as sensitizers in photovoltaic cells due to their capability of injecting electron from excited pigments to the conduction band of the semiconductor material. The natural dye extracted from the fruits of *Solanum incanum* plant shows good quality for sensitization of photoelectrochemical solar cell. The dye sensitized solar cell fabricated shows a good photoelectric effect as a maximum voltage of 0.31 V was obtained when the sun was at 11.40 am on exposure to the sun. . It was also observed that the voltammetric response of Pt/TiO₂/Dye electrode has higher magnitude of current compared to Pt/TiO₂ electrode which is almost half the magnitude of current response of Pt/TiO₂/Dye electrode.

Keywords Internal Resistance, DSSC, Cyclic Voltametric Measurements, Gautankura, *Solanum incanum*

Introduction

Photosynthesis requires the light harvesting complex of chlorophyll to shuttle photon energy from a light source into chemical energy. It has been demonstrated that a thin film coating of titanium (iv) oxide (TiO₂) on conductive glass, impregnated with dye molecules, and placed in contact with a suitable redox mediator, can facilitate an electron transfer process that parallels photosynthesis [1]. In this process, TiO₂ acts as the electron acceptor and an iodine solution replaces water as the electron donor (redox mediator). The use of natural dyes in solar cells offers promising prospects for the advancement of this technology, because fabrication of cost effective solar cells is a scientific challenge. The use of natural pigments cut down the cost of chemical synthesis and high cost of rare metals need for metal organic dye sensitizers. Therefore lot of interest has been drawn on natural dyes extracted from plant materials. Several natural pigments have been utilized as sensitizers in photovoltaic cells due to their capability of injecting electron from excited pigments to the conduction band of the semiconductor material. Most natural pigments that can be utilized in dye sensitized solar cells undergo rapid photo degradation. Cyanidin is an organic dye of the flavonoid class found in leaves and fruits of plants and responsible for the colours of various vegetable tissues, which have been studied as a sensitizer in solar cells that found to be photo stable [2]. Natural pigments have also demonstrated a capacity of functioning as the pigment in DSSCs [3]. Dye-sensitized nanocrystalline solar cell is a nonconventional solar electric technology that gained the attention of the photovoltaic community. Its foundations are in photochemistry rather than in solid state physics, the discipline underlying today's conventional solar cells. Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism (Gratzel, 2003). The dominance of photovoltaic field by inorganic solid state junction devices is now being challenged by



the emergence of a third generation of cells which is based on nanocrystalline conducting polymer films [4]. This offers the prospective of very low cost fabrication and presents attractive features that facilitate market entry. It can now be possible to move away from the classical solid-state junction devices by replacing the contacting phase to the semiconductor by an electrolyte, liquid, gel or solid thereby forming a photochemical cell. A progress has recently being realized in the fabrication and characterization of nanocrystalline materials and this has opened up vast new opportunities for this systems.

The dye-sensitized nanocrystalline solar cell therefore realizes the optimal absorption and charge separation processes by association of a sensitizer as light absorbing material with a wide band gap semiconductor of nanocrystalline morphology. To date this field has been dominated by solid-state junction devices usually made of silicon and profiting from the experience and material availability resulting from the semiconductor industry [1]. Since the development of dye-sensitized solar cells, these have attracted considerable attention due to their environmental friendliness and low cost of production. In dye sensitized solar cells, 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. By far, the highest efficiency of dye sensitized solar cells sensitized by Ruthenium containing compounds adsorbed on nanocrystalline TiO₂ reached 11–12% [5]. Although such dye sensitized solar cells have provided a relatively high efficiency, there are several disadvantages of using noble metals in them since noble metals are considered as resources that are limited in amount, hence their costly production.

On the other hand, organic dyes are not only cheaper but have also been reported to reach efficiency as high as 9.8% [6]. However, organic dyes have often presented problems such as complicated synthetic routes and low yields. Nonetheless, the natural dyes found in flowers, leaves, as fruits can be extracted by simple procedures. Due to their cost efficiency, non-toxicity and complete biodegradation, natural dyeshave been a popular subject of research. Thus far, several natural dyes have been utilized as sensitizers in dye sensitized solar cells, such as cyanin, carotene, tannin and chlorophyll [7]. Calogero and Marco [8] reported that a conversion efficiency of 0.66% was obtained using red Sicilian orange juice dye as sensitizer. Wongcharee *et al.*, [9] employed rosella as sensitizer in their dye sensitized solar cell, which achieved a conversion efficiency of 0.70%. Furthermore, they carried out structural modification of coumarin and used the coumarin derivation dye as sensitizer in their dye sensitized solar cell, which provided an efficiency of 7.6%. Thus, optimization of the structure of natural dyes to improve efficiency is promising aspect of the development of this type of cells. This piece of work includes an investigation of photosynthetic pigments rather than inorganic complexes.

Bioactivity of Gautan Kura (*Solanum incanum*)

Solanum genus species like potatoes, tomatoes and aubergines consists of a vast array of secondary metabolites such as alkaloids, phenolic compounds, lectins and glycoalkaloids. The presence of pharmacologically activeglycosidal alkaloids in Solanaceae has been known for centuries and in addition, spasmotic drug produced from this family were the only therapeutic agent alleviating Parkinsonism.

The glycosidal alkaloids in particular have been associated with antibiotic activity. Solanocapsine of *solanum pseudocapsicum* is antibacterial and the drug solanine from potatoes is toxic to various species of fungi. In addition to antimicrobial activity some glycoalkaloid display antitumor effects as well.

Electrochemical Characterization

All electrochemical measurements were performed with an Autolab PGSTAT 302N driven by NOVA software version 1.8. A three electrode system was employed for this study. The counter electrode was a platinum wire and aAg|AgCl 3M KCl was used as the reference electrode. Nitrogen was bubbled in the electrolyte solution at least for five minutes between the analyses to ensure there was no oxygen present in the solution. During the analyses nitrogen was conducted in the air above the solution surface to maintain non-oxygen conditions.

Photoelectrochemical Properties of the Solar cell

Upon exposing a metallic surface to electromagnetic radiation that is above the threshold frequency, the photons are absorbed and current is produced. In a broader sense, the radiant energy may be infrared, visible, or



ultraviolet light, X rays, or gamma rays; the material may be a solid, liquid, or gas; and the released particles may be ions (electrically charged atoms or molecules as well as electrons) [10]. It was observed that the maximum kinetic energy of the released electrons did not vary with the intensity of the light as expected, but was proportional instead to the frequency of the light. What the light intensity did determine was the number of electrons released, and that there was virtually no time lag between the arrival of radiation and the emission of electrons. A photon carries an energy E , and this energy $E = hf$, which can also be written as $E = hc/\lambda$. Where $h = \text{Planck's constant}$, $f = \text{frequency}$, $c = \text{speed of light}$ and $\lambda = \text{wavelength}$. As the electron moved through the material at high speed and finally emerged from the material, its kinetic energy would diminish by an amount ϕ called the work function, which represents the energy required for the electron to escape from the metal. By conservation of energy, this led to the photoelectric equation $E_k = hf - \phi$, where $E_k = \text{maximum kinetic energy of the ejected electron}$ [10].

Tables 1 and 2 show the photoelectric effect of the solar cell fabricated with decreasing coated area on the conductive glass. The surface area of the conductive glass is determined by measuring the required area using a meter rule. In Table 1, effect of photons of sunlight on the cell indicates increasing activity of photoelectrons emitted with increasing solar energy. Maximum voltage of 0.31 V measured with a volt-ohmmeter M832 was obtained when the sun was at 11.40 am. Photons of solar energy cause greater excitation of more electrons from dye molecule moving into the conduction band of the TiO_2 at this time. But this was observed to decrease at the same time in subsequent days. This is as a result of degradation and evaporation of volatile components of the electrolyte since the cell is not sealed. As the surface area of the conductive glass coated with TiO_2 is reduced, the maximum voltage observed in day 1 of Table 2 was 0.26 V at 12.00 noon, indicating direct proportion of the dye adsorbed with the surface area coated.

Table 1: Photoelectric effect with active surface area of 2.5cm^2

Time (min)	Day 1 (volts)	Day 2 (volts)	Day 3 (volts)	Day 4 (volts)	Day 5 (volts)	Day 6 (volts)	Average (volts)
8.00 am	0.17	0.15	0.14	0.13	0.12	0.14	0.1417
8.20 am	0.18	0.17	0.15	0.14	0.14	0.14	0.1533
8.40 am	0.20	0.18	0.17	0.16	0.15	0.16	0.1700
9.00 am	0.21	0.19	0.18	0.18	0.16	0.17	0.1817
9.20 am	0.23	0.20	0.19	0.17	0.17	0.18	0.1900
9.40 am	0.24	0.22	0.20	0.19	0.18	0.19	0.2033
10.00 am	0.26	0.25	0.25	0.20	0.19	0.20	0.2250
10.20 am	0.28	0.25	0.25	0.21	0.20	0.21	0.2317
10.40 am	0.29	0.26	0.26	0.22	0.21	0.20	0.2400
11.00 am	0.30	0.28	0.26	0.24	0.22	0.18	0.2467
11.20 am	0.31	0.29	0.24	0.22	0.21	0.19	0.2433
11.40 am	0.31	0.29	0.26	0.23	0.20	0.19	0.2467
12.00 pm	0.30	0.28	0.26	0.21	0.20	0.20	0.2417
12.20 pm	0.30	0.26	0.24	0.20	0.19	0.19	0.2300
12.40 pm	0.28	0.25	0.23	0.19	0.18	0.18	0.2183
1.00 pm	0.24	0.24	0.23	0.18	0.16	0.17	0.2033
1.20 pm	0.23	0.23	0.22	0.17	0.15	0.15	0.1917
1.40 pm	0.22	0.22	0.21	0.18	0.15	0.14	0.1867
2.00 pm	0.20	0.21	0.20	0.16	0.14	0.13	0.1733
2.20 pm	0.20	0.20	0.21	0.15	0.13	0.12	0.1683
2.40 pm	0.18	0.20	0.20	0.14	0.12	0.11	0.1583
3.00 pm	0.16	0.18	0.19	0.13	0.12	0.10	0.1467
3.20 pm	0.15	0.15	0.14	0.12	0.11	0.08	0.1250
3.40 pm	0.15	0.14	0.13	0.11	0.10	0.06	0.1150
4.00 pm	0.14	0.13	0.12	0.09	0.07	0.06	0.1017
4.20 pm	0.13	0.10	0.10	0.08	0.06	0.05	0.0867
4.40 pm	0.12	0.10	0.09	0.06	0.06	0.04	0.0783
5.00 pm	0.12	0.10	0.08	0.06	0.04	0.04	0.0733



Cyclic Voltammetric (CV) Studies

Cyclic voltammetry is the method used to study the electrochemical properties of the dye in solution. Figure 1 compares a typical cyclic voltammetric evolutions of bare Pt and Pt/TiO₂/Dye recorded in 0.005 M [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ solution containing 0.2 M NaOH. Note that [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ is an important redox probe known to exhibit 1- electron reversible process. The choice of this redox probe in this work is to answer the question: to what extent can the modifying species permit the electron transfer of the [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ species to the underlying Pt electrode?

In Fig. 1 the bare Pt shows a pair of oxidation (E_{ox}) and reduction (E_{red}) peak potentials at 250 mV and 203 mV ascribed to Fe³⁺/Fe²⁺ while the Pt/TiO₂/Dye modified electrode shows two pair of oxidation peaks at 256 and 474 mV which is ascribed to Fe³⁺/Fe²⁺, and a reduction peak of 210 mV which is ascribed to TiO₂/Dye. The high voltage is as a result of the impregnation of the dye on the TiO₂. All the four electrodes gave a formal potential (E_{1/2} = E_{ox} + E_{red}) of 220mV, 222mV, 227mV and 225mV respectively.

The type of diffusion process that could be occurring at the Pt/TiO₂/Dye electrode was interrogated by using the “diffusion domain approximation” theory developed by Davies and Compton for the voltammetric responses at spatially heterogeneous electrodes/partially blocked electrodes [11-12] which can also be applied to a 3-dimensional electrochemically heterogeneous electrode. It can be seen in Fig. 1 that the voltammetric response by the Pt/TiO₂/Dye electrode is lower in magnitude of the current of the bare Pt electrode, suggesting that the size of the electroactive zones are micro in size but are separated with sufficiently large inert blocking materials such that the electrode as a whole behaves as a collection of isolated microelectrodes, each of which experiences convergent diffusion where there is partial depletion in the concentration of the redox couple to the surface of the Pt/TiO₂/Dye electrode hence a reduced current response.

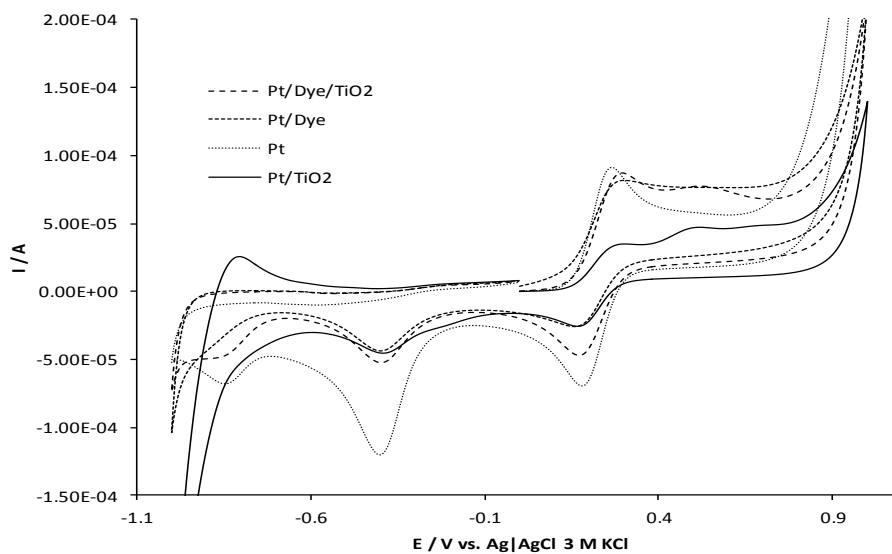


Figure 1: Comparative Cyclic voltammograms of the electrodes in 0.005 M [Fe(CN)₆]³⁻/[Fe(CN)₆]⁴⁻ 0.2 M NaOH solution. Scan rate: 100 mV/s.

Table 2: Results of the impedance analysis for DSCs using four kinds of electrodes with *Solanum incanum* natural dye as sensitizer

Electrode	Rs (Ω)	Rct (Ω)	W (Ω)	Circuit	χ ²
Pt	47.887	261.6	-	[R(C[RW])]	0.3198
Pt/Dye	47.337	524.8	6.522	[R(C[R(RQ)](RQ))]	0.0268
Pt/TiO ₂	48.024	2.383 E -5	-9459.2	[R(Q[R(RQ)]W)]	0.0362
Pt/Dye/TiO ₂	60.097	-3456.6	1.5963 E +5	[R(Q[R(RQ)]W)]	0.2611



Conclusion

The natural dye extracted from the fruits of *Solanum incanum* plant shows good quality for sensitization of photoelectrochemical solar cell. The dye sensitized solar cell fabricated shows a good photoelectric effect as a maximum voltage of 0.31 V was obtained when the sun was at 11.40 am on exposure to the sun. It was also observed that the voltammetric response of Pt/TiO₂/Dye electrode has higher magnitude of current compared to Pt/TiO₂ electrode which is almost half the magnitude of current response of Pt/TiO₂/Dye electrode. This is because the diffusion domain of every electrode differs due to the degree of blockage of platinum. Investigation into the internal resistance of the DSSC shows the dye can be strongly adsorbed to the surface of TiO₂, therefore Pt/TiO₂/Dye electrode transfers electron with very minimal resistance making the dye a good sensitizer material for DSSCs.

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