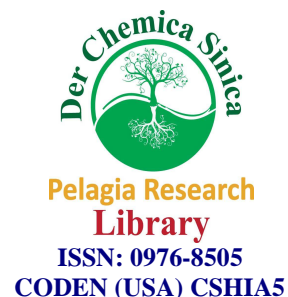




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Natural dyes adsorbed on nanocrystalline TiO₂ for photovoltaic applications

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ABSTRACT

We investigated the optical and photovoltaic performance of a nanocrystalline TiO₂ sensitized with chlorin dye. Chlorin is a natural dye extracted from bahama grass. The chlorin-stained titanium dioxide was found to have a reduced band gap energy and could absorb light beyond the ultraviolet region. Avaspec 2.1 spectrophotometer was used to obtain the optical absorption spectrum, while the well-known Tauc model was employed to determine the optical band gap. A dye sensitized solar cell fabricated with the chlorin-doped TiO₂ showed a photo-conversion efficiency of 1.008%.

Key words: Titanium dioxide, energy gap, photovoltaic performance, optical properties.

INTRODUCTION

Titanium dioxide occurs in nature as well-known minerals rutile, anatase and brookite, and additionally as two high pressure forms, a monoclinic baddeleyite-like form and an orthorhombic α -PbO₂-like form, both found recently at the Ries crater in Bavaria [1-4].

Table 1. Properties of the three crystal structures in TiO₂ [1,2,5]

Form	Crystal system	Band gap (eV)
rutile	tetragonal	3.02
anatase	tetragonal	3.20
brookite	orthorhombic	2.96

Titanium dioxide, particularly in the anatase form, is a photocatalyst under ultraviolet (UV) light [4,6]. Recently it has been found that titanium dioxide, when spiked with nitrogen ions or doped with metal oxide like tungsten trioxide, is also a photocatalyst under either visible or UV light. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly. Titanium dioxide is thus added to paints, cements, windows, tiles, or other products for its sterilizing, deodorizing and anti-fouling properties and is used as a hydrolysis catalyst. It is also used in the fabrication of dye-sensitized solar cells.

Dye-sensitized solar cell (DSSC) which was invented by Gratzel in 1991 is expected to be one of the next-generation photovoltaics because of its environment friendly properties, low manufacturing cost and low manufacturing energy consumption [7-12]. The central idea in DSSC fabrication is to separate the light absorption process from the charge collection process, mimicking natural light harvesting procedures in photosynthesis, by

combining dye sensitizers with semiconductors [11,13-15]. This enables the use of wide-gap but cheap oxide semiconductors such as TiO_2 . Early DSSC designs involved transition metal coordinated compounds (e.g. ruthenium polypyridyl complexes) as sensitizers because of their strong visible absorption, long excitation lifetime, and efficient metal to ligand charge transfer [11,14,16,]. Although highly effective, with current maximum efficiency of 11% [7,10,12,14], the costly synthesis and undesired environmental impact of those prototypes call for cheaper, simpler, and safer dyes as alternatives. Natural pigments, including chlorophyll, carotene, and cyanin, are freely available in plant leaves, flowers, and fruits and fulfill these requirements [14,15,17].

Undoped TiO_2 is active only under ultraviolet (UV) light because of its wide band gap rendering it inactive under visible light (Figure 1) [2,14], which causes most of the solar spectrum to go unutilized [3,4,18]. Extending the optical absorption of titanium dioxide to the visible region, therefore, is one of the important subjects for its increased utility in the fields of photocatalysis. Impurities doping induces substantial modifications in electrical and optical properties of semiconductor materials.

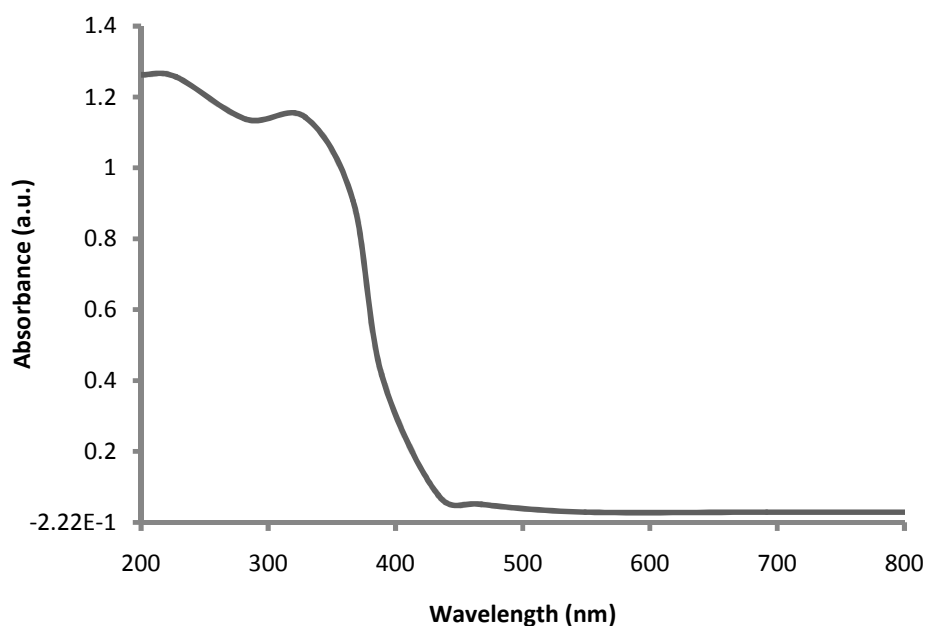


Figure 1(a). UV-vis spectra of nanoporous titanium dioxide [2]

In this research work, the blade method was used to deposit a sol-gel derived nanocrystalline TiO_2 (n- TiO_2) onto an FTO glass substrate. The titanium (iv) oxide film was subjected to annealing treatment to enable it serve as a photo-electrode for DSSC [11,16,19,20]. The film was then doped with *chlorin* dye which is a natural dye extracted from bahama grass. Optical characterization of the sensitized TiO_2 film was carried out. The current-voltage characteristics of a dye-sensitized solar cell fabricated with the doped electrode are presented in this work.

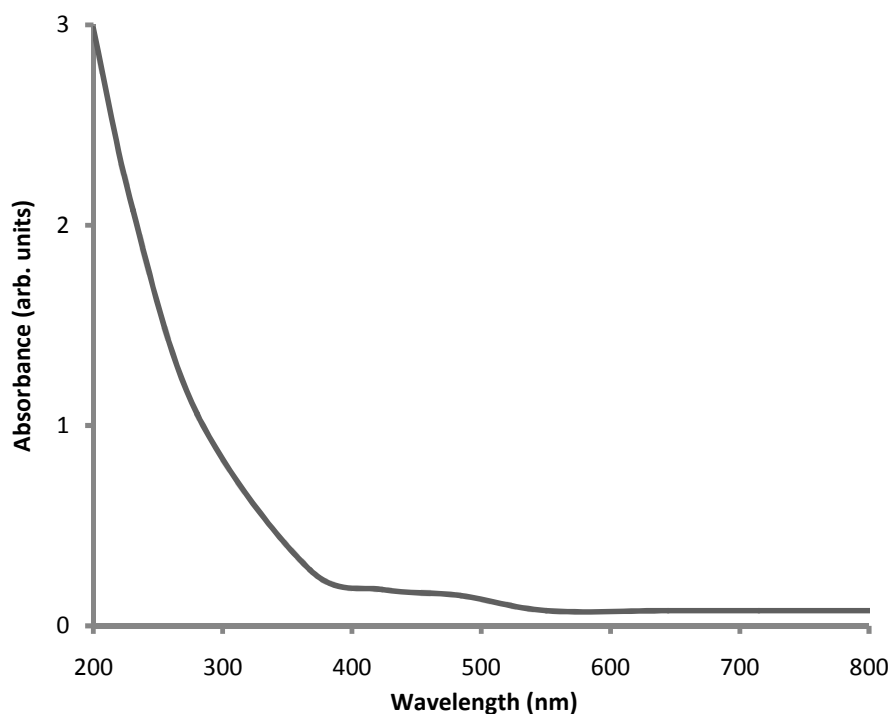


Figure 1(b). Optical absorption spectra of a finite segment of titanium dioxide nanowire [14]

MATERIALS AND METHODS

The *chlorin* local dye was extracted from the popular bahama grass. The grass was blended and the green pigment extracted with 90% ethanol. The extract was purified by column chromatography and some copper ions were introduced into the extract [21].

1.2 Electrode deposition

A sol-gel derived nanocrystalline titanium (iv) oxide (Ti-nanoxide T/sp, Solaronix SA, Rue de e' duriette 128) was deposited onto an FTO glass substrate through the blade method. The active area of a 2.5cm x 2.5cm FTO was identified and covered on each of the two parallel edges with a double layer of masking tape to control the thickness of the TiO₂ film. Before deposition, the glass substrate was cleaned with acetone, then methanol and etched through plasma treatment for 1min. The n-TiO₂ was applied at one of the edges of the conducting glass and distributed with a squeegee sliding over the tape-covered edges [16,17,19,21].

1.3 Thermal Treatment

The n-TiO₂ electrode was allowed to dry naturally for about 15 minutes before removing the adhesive tapes. The edges were cleaned with ethanol. Using an electric hot plate, the film was subjected to thermal annealing at 200°C for 10 minutes. Immediately after annealing, the electrode was sintered for about 30 minutes at 400 °C using carbolite 201 tubular furnace [17,19,22].

1.4 Sensitizer Impregnation

The thermally treated electrode was immersed overnight into a solution of the *chlorin* dye [15,21]. The electrode was preheated at 80 °C for 15 minutes before it was dipped into the dye solution. This process helps in the prevention of rehydration of the TiO₂ surface or capillary condensation of water vapours from ambient air inside the nanopores of the film [16]. The presence of water in the pores decreases the injection efficiency of the dye. After dye sensitization, the dye-coated film was rinsed in ethanol, then dried using hot-air blower and kept in dark in an air tight case till solar cell assembly.

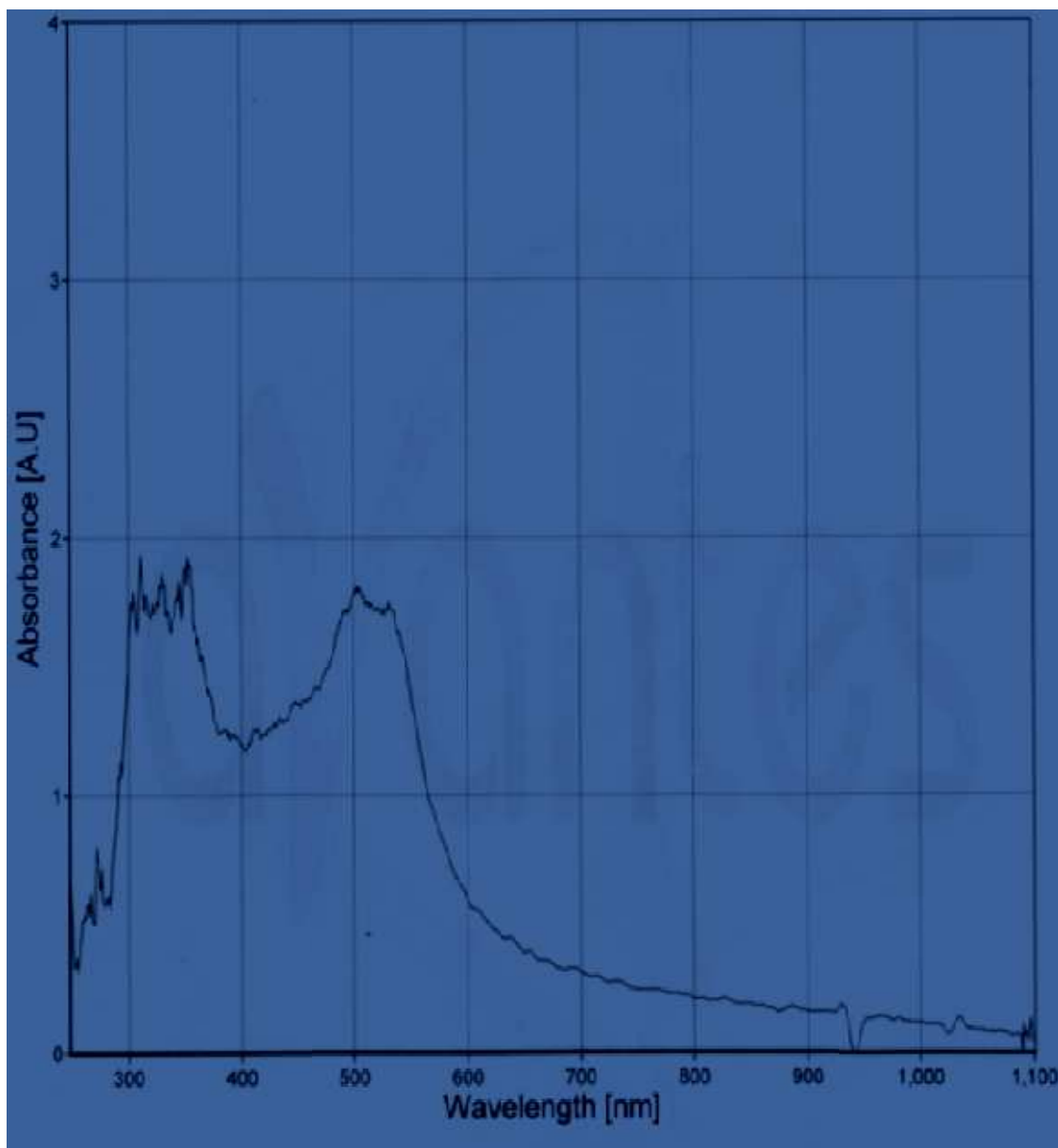


Figure 2. Optical absorption spectrum of chlorin-dyed n-TiO₂

1.5 Optical Measurements

Avaspec 2.1 spectrophotometer was used to obtain the optical absorption spectrum for the dyed working electrode. This measurement was carried out at room temperature before storing the dyed n-TiO₂ electrode. The spectrophotometer was computerized and so measurement was taken with the help of experts. The result was displayed as graph of optical absorbance (arbitrary units) versus wavelength (nm).

To have a quantitative estimate of the optical band gap of the film, the Tauc equation is employed [4,23-28].

$$\alpha h\nu = A(h\nu - E_g)^\gamma \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band-gap, A is a constant which does not depend on photon energy and γ has four numeric values ($\frac{1}{2}$ for allowed direct transitions, 2 for allowed indirect, 3

for forbidden direct and $\frac{3}{2}$ for forbidden indirect optical transitions. In this work, the direct transition band gap of the doped TiO₂ electrode was determined by plotting $(\alpha h\nu)^2$ versus $h\nu$ curve with the extrapolation of the linear region to $(\alpha h\nu)^2 = 0$ [1,23,28,29].

RESULTS AND DISCUSSION

The optical absorption spectrum (Figure 2) shows that the *chlorin*-dyed n-TiO₂ working electrode noticeably absorbs light beyond the UV region. Hence, the natural dye greatly improved the absorbance of the wide-band gap titanium (iv) oxide which alone cannot absorb visible light.

Figure 3 illustrates the plot of $(\alpha h\nu)^2$ vs. $h\nu$ for the doped TiO₂ film. The optical band gap estimated from the intercept of the tangent to the plot is 2.16eV which is lower than band gaps for the three crystal structures in titanium dioxide (see Table 1). This implies that the process of dye sensitization has led to band gap narrowing which is necessary for the doped TiO₂ to respond to the visible light as represented in Figure 2 [4].

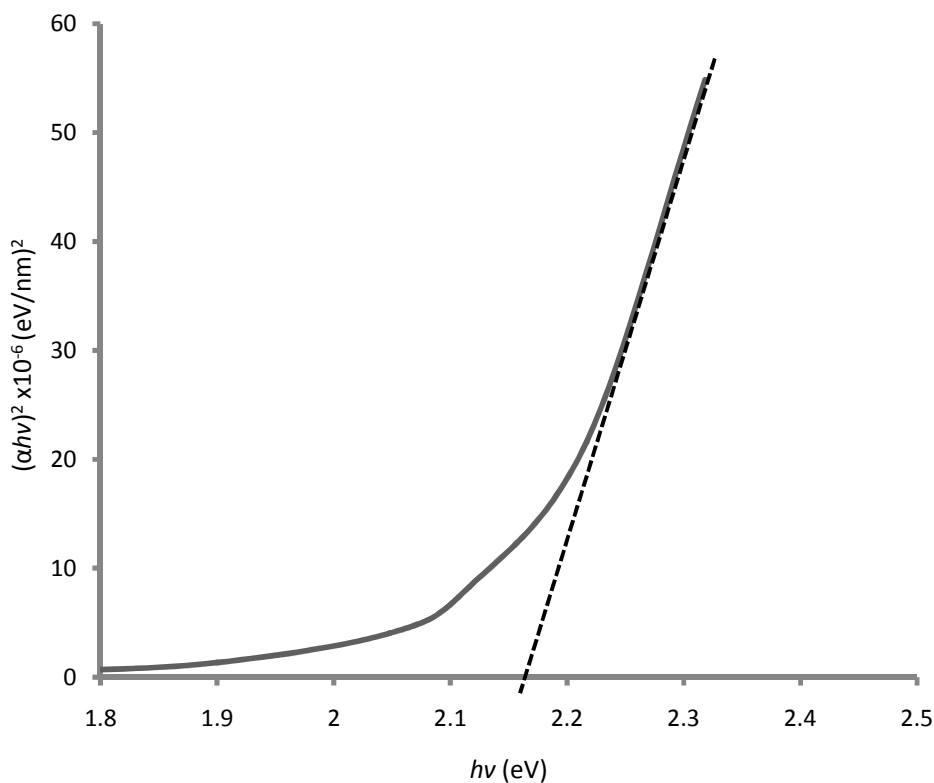


Figure 3. Optical band gap for *chlorin*-doped titanium dioxide

Figure 4 represents the photocurrent-voltage characteristics of a DSSC based on the *Chlorin*-dyed electrode under solar illumination of 100 mW/cm². The energy conversion efficiency (*n*) and fill factor (FF) were evaluated using the following relations:

$$n = \frac{\text{maximum power output}}{\text{maximum power input}} = \frac{I_m V_m}{A \times E} \tag{2}$$

$$FF = \frac{I_m V_m}{V_{oc} \times I_{sc}} \tag{3}$$

A is the active surface area of the solar cell while E is the illumination intensity. The short circuit photocurrent (I_{sc}), the open circuit voltage (V_{oc}), FF, and n for the *chlorin*-stained solar cell were found to be 3.9 mA/cm², 0.44 V, 0.59 and 1.008% respectively.

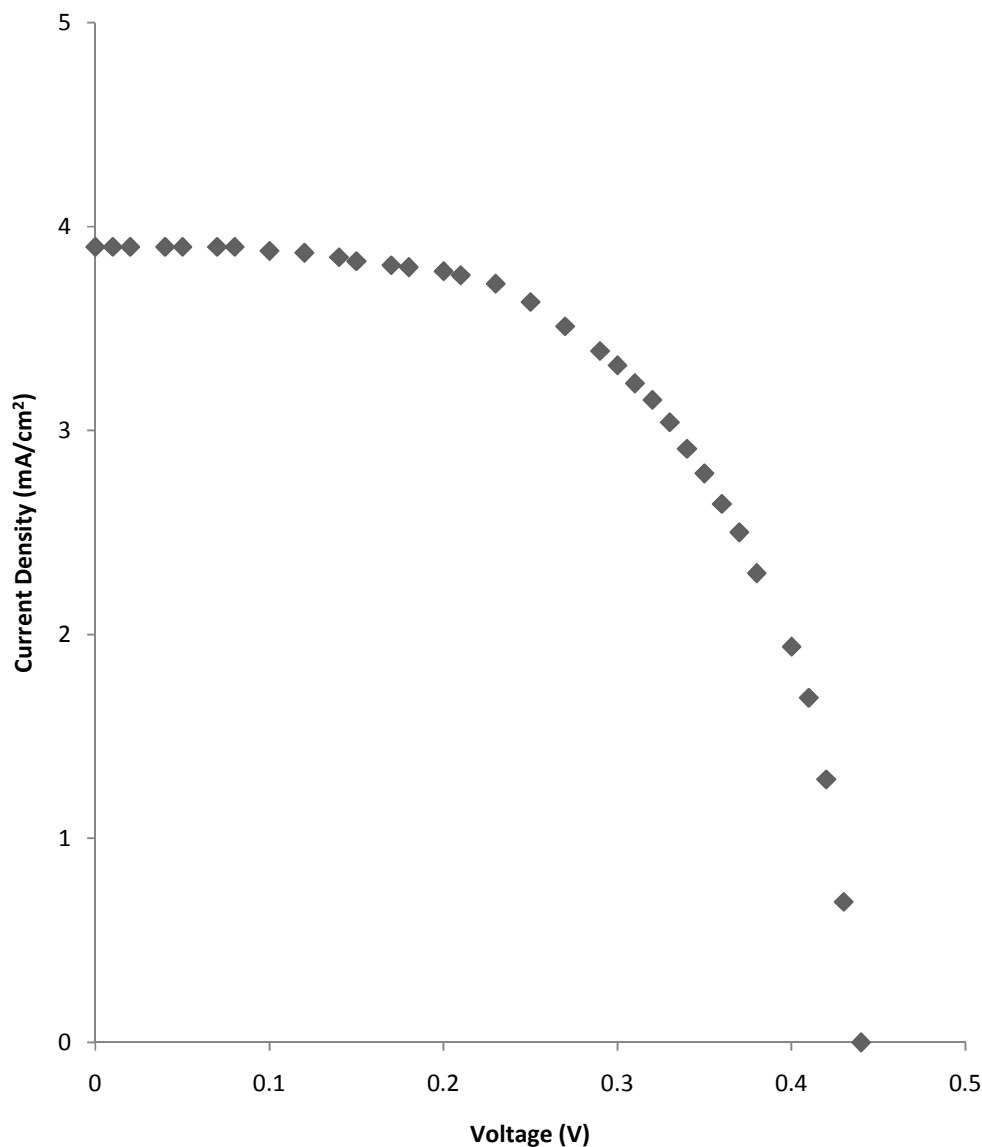


Figure 4. The I-V curve for solar cell sensitized with *chlorin* dye

CONCLUSION

Thin film of sol-gel derived n-TiO₂ was successfully deposited on an FTO substrate through the blade method. The film was subjected to thermal treatment and then doped with a natural dye extracted from bahama grass. Optical characterization using Avaspec 2.1 spectrophotometer shows that the sensitized titanium dioxide electrode could absorb light both in the ultraviolet and visible region. Using the Tauc model, the optical band gap of the dyed TiO₂ was found to be 2.16eV which is lower than the band-gap of the three crystal structures in TiO₂. Hence, the *chlorin* dye can be used as photo-sensitizer for wide-band gap semiconductors such as TiO₂ which alone cannot absorb

visible light. The photo-conversion efficiency of a dye sensitized solar cell fabricated with the doped nanocrystalline titanium (iv) oxide was 1.008%.

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REFERENCES

- [1] M.C. Wang, H.J. Lin and T.S. Yang, *J. Alloys and Compounds*, **2009**, 473, 394-400.
- [2] Y. Lee and M. Kang, *Mat. Chem. Phys.*, **2010**, 122, 284-289.
- [3] K. Kamada, M. Mukai, Y. Matsumoto, *Electrochimica Acta*, **2002**, 47, 3309-3313.
- [4] L. Mai., C. Huang, D. Wang, Z. Zhang and Y. Wang, *Appl. Surface Sci.*, **255**, 9285-9289 (2009).
- [5] S. Banerjee, J. Gopal, P. Murakedharan, A. K. Tyagi and B. Raj, *Current Sci.*, **2006**, 90, 1378-1383.
- [6] S. Phadke, J. D. Sorge, S. Hachtmann and D. P. Birnie, *Thin Solid Films*, **2010**, 518, 5467-5470.
- [7] M. Adachi, J. Jiu and S. Isoda, *Current Nanosci.*, **2007**, 3, 285-295.
- [8] H. Arakawa, T. Yamaguchi, K. Okada, H. Matsui, T. Kitamura and N. Tanabe, *Fujikura Tech. Rev.*, **2009**, 3, 55-60.
- [9] J. Bisquert, J.G. Canadas, I.M. Sero and E. Palomares, *SPIE USE*, **2003**, V, 5215-5226.
- [10] L. Zhifeng, L. Chengcheng, Y. Jing and E. Lei, *Solid State Sciences*, **2009**, 12(1), 111-114.
- [11] B. O'Regan and M. Gratzel, *Nature*, **1991**, 353, 737-740.
- [12] G. Wang, L. Wang, W. Xing and S. Zhuo, *Mat. Chem. Phys.*, **2010**, 123, 690-694.
- [13] P. M. Sirimanne and V. P. S. Perera, *Phys. Stat. Sol. (b)*, **2008**, 245, 1828-1833.
- [14] S. Meng, J. Ren and E. Kaxiras, *Nano Letters*, **2008**, 8, 3266-3272.
- [15] J. O. Ozuomba, A. J. Ekpunobi and P. I. Ekwo, *Chalcogenide Letters*, **2011**, 8, 155 – 161.
- [16] S. M. Waita, J. M. Mwabora, B. O. Aduda, G. A. Niklasson, S. Lindquist and C. Granqvist, *Afr. J. of Sci. Tech.*, **2006**, 7, 106-119.
- [17] J. O. Ozuomba, A. J. Ekpunobi and P. I. Ekwo, *Digest J. Nanomaterials and Biostructures*, **2011**, 6, 1043 – 1051.
- [18] M.J. Pawar and V.B. Nimbalkar, *Research Journal of Chemical Sciences*, **2012**, 2(1), 32-37.
- [19] L. U. Okoli, A. J. Ekpunobi and J. O. Ozuomba, *Digest Journal of Nanomaterials and Biostructures*, **2011**, 6(4), 1929 – 1934.
- [20] P. Suri, M. Panwar and R. M. Wehra, *Mat. Sci. – Poland*, **2007**, 25, 137-144.
- [21] J.O. Ozuomba, A.J. Ekpunobi and P.I. Ekwo, *Moldavial Journal of the Physical Sciences*, **2011**, 10(2), 220-226.
- [22] J. O. Ozuomba, L. U. Okoli, A. J. Ekpunobi and P. I. Ekwo, *Moldavian J. Phy. Sci.*, **2012**, 11(1-2), 106-111.
- [23] M. M. Hasan, A. S. Haseeb, R. Saidur, H. H. Masjuki and M. Hamdi, *Optical Mat.*, **2010**, 32, 690-695.
- [24] N.A. Okereke and A.J. Ekpunobi, *Res. J. Chem. Sci.*, **2011**, 1(6), 64-70.
- [25] E.I. Ezema, P.U. Asogwa, A.B.C. Ekwealor, P.E. Ugwuoke and R.U. Osuji, *Journal of the University of Chemical Technology and Metallurgy*, **2007**, 42(2), 217-222.
- [26] T. Ivanova, A. Harizanova, M. Surtchev and Z. Nenova, *Sol. Ener. Mat. Sol. Cells*, **2003**, 76, 591-598.
- [27] I.E. Ottih, A.J. Ekpunobi and P.I. Ekwo, *The African Review of Physics*, **2011**, 6:0001, 1-6.
- [28] C.O. Ayieko, R.J. Musembi, S.M. Waita, B.O. Aduda and P. K. Jain, *International Journal of Energy Engineering*, **2012**, 2(3), 67-72.
- [29] M. Yuonesi, M. Izadifard, M.E. Ghazi and F.E. Ghodsi, *Chinese Journal of Physics*, **2011**, 49(4), 941-949.