Research Journal of Physical Sciences ISSN 2320–4796
Vol. **1(10),** 6-10, November **(2013)** *Res. J. Physical Sci.*

Influence of Local Dye on the Optical band-gap of Titanium Dioxide and its performance as a DSSC Material

Okoli L. U. [1], Ozuomba J. O[2] and Ekpunobi A. J.[3]
[1]Department of Physics, Federal College of Education, Technical, Umunze, Anambra, NIGERIA
[2]Faculty of Science, Madonna University, Elele, Rivers State, NIGERIA
[3]Department of Physics and Industrial Physics, Nnamdi Azikiwe University, Awka, NIGERIA

Available online at: www.isca.in
Received 23rd September 2013, revised 5th October 2013, accepted 31st October 2013

Abstract

Titanium dioxide has been extensively studied in recent decades for its important applications including pigments, protective coatings and thin film optical devices such as photovoltaics. Dye sensitized solar cell is a photoelectrochemical cell which utilizes the property of nanocrystalline wide band-gap metal oxide semiconductor porous electrode. The search for a method to narrow the optical band-gap of TiO_2 plays a key role for enhancing its photocatalytic applications. The optical band-gap of a nanocrystalline titanium dioxide sensitized with anthocyanin local dye is determined in this work. Anthocyanin dye is a natural dye extracted from hibiscus sabdariffa which is an edible plant called zobo by Nigerians. A comparative study of the photovoltaic performance of anthocyanin-doped TiO_2 is also shown in this work.

Keywords: Titanium dioxide, dye sensitized solar cell, natural dye, optical band gap.

Introduction

Dye sensitized solar cells (DSSCs) show a very promising future in the field of photovoltaic cells, for their outstanding performance in light harvesting and relatively low manufacturing cost[1-6]. Dye sensitized solar cells have drawn great attention since O'Regan and Gratzel announced the first high-performance DSSC in 1991[3, 7-10]. Since then, not only the overall conversion efficiencies of the DSSCs have been improved to over 10%, but other aspects that limit the use of the cells like lifetime of dyes, case of operation, and material have been improved.

In traditional photovoltaic cells, the semiconductor functions to simultaneously absorb visible light and mediate electrons[1]. In contrast, DSSCs are not limited by the light harvesting ability of the semiconductor; in fact, most are optically transparent[3, 11]. The sensitization of these semiconductors to visible light involves interfacial electron transfer following selective excitation of a surface-bound molecular chromophore[1]. Such a photoinduced charge-separation process is a key step for solar energy conversion. A typical DSSC contains five components: a transparent conducting oxide substrate, a nanocrystalline network of a wide band gap semiconductor (usually TiO_2), a sensitizer, an electrolyte, and a counter electyrode[2,4,12,13].

Titanium dioxide is a common wide band gap semiconductor that is used in many applications. TiO_2 can exist as an amorphous layer and also in three crystalline phases: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic)[14,15]. TiO_2 displays excellent chemical stability and oxidation ability and can be considered as the most investigated material among metal oxides because it is used in a wide range of applications including photocatalysis and photovoltaics[4,16,17]. Titanium dioxide is characterized by the band gap of 3.0 eV (the rutile phase) and 3.2 eV (the anatase phase)[15,16,18,19] indicating that only a small fraction of the sun's energy (mainly ultraviolet region) will be utilized in solar energy conversion (figures 1 and 2)[20-21] and water splitting processes[3,14,18]. TiO_2 is usually doped or sensitized to enable it absorb visible light[12,16].

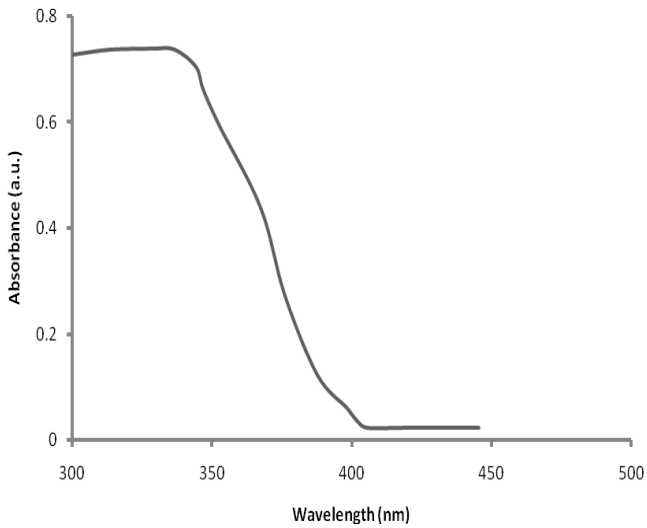

Figure-1
Diffused UV absorption spectrum of commercial polycrystalline titanium dioxide

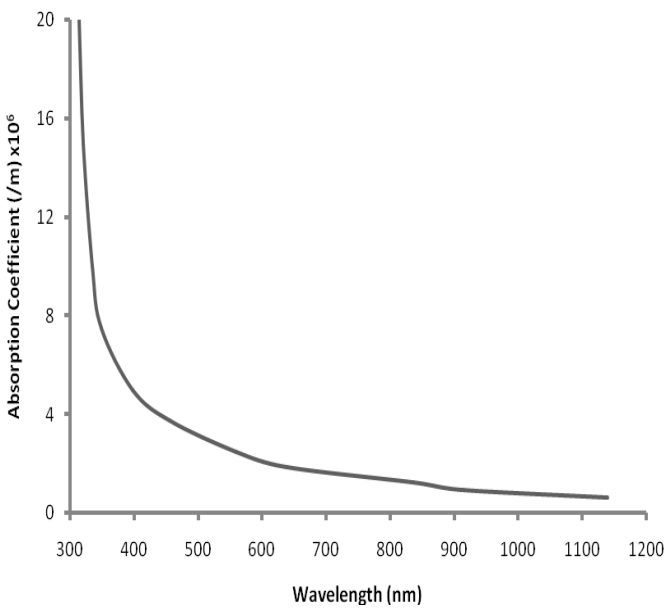

Figure-2
Dependence of absorption coefficient on the wavelenth of undoped titanium dioxide thin film of thickness 400 nm (After Ayieko *et al*, 2012)

In this work, we used the Tauc Model to determine the direct band gap of a nanocrystalline (nc)-TiO_2 anode electrode sensitized with *anthocyanin* dye. *Anthocyanin* dye is a natural dye extracted from hibiscus sabdariffa which is a popular plant in the northern part of Nigeria[22]. The photovoltaic performance of a dye-sensitized solar cell fabricated with the *anthocyanin*-dyed TiO_2 electrode was presented. Also, the current-voltage characteristics of a DSSC fabricated with undoped TiO_2 photo-electrode was displayed for the sake of comparison.

Material and Methods

Preparation of the local dye: The *anthocianin* dye used in sensitizing the mesoporous TiO_2 film was extracted from hibiscus sabdariffa which is a common edible plant called zobo by Nigerians. The grass was well blended and the green pigment was extracted with 90% ethanol[22].

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 fluorine-doped tin oxide (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 TiO_2 film. Before deposition, the glass substrate was cleaned with acetone, then methanol and etched through plasma treatment for 1min. The nc-TiO_2 was applied at one of the edges of the conducting glass and distributed with a squeegee sliding over the tape-covered edges.

Thermal Treatment: The nc-TiO_2 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 200^0C for 10 minutes. Immediately after annealing, the electrode was sintered for about 30 minutes at 400^oC using carbolite 201 tubular furnace[5,23].

Sensitizer Impregnation: The thermally treated electrode was immersed overnight into a solution of the *anthocyanin* dye. The electrode was preheated at 80^oC for 15 minutes before it was dipped into the dye solution. This process helps in the prevention of rehydration of the TiO_2 surface or capillary condensation of water vapours from ambient air inside the nanopores of the film. 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.

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 nc-TiO_2 electrode. 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 was employed[14,15,21,24,27].

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

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 TiO_2 electrode was determined by plotting $(\alpha h\nu)^2$ versus $h\nu$ curve with the extrapolation of the linear region to $(\alpha h\nu)^2 = 0$[14,18,21,28].

Results and Discussion

The optical absorption spectrum (figure 3) shows that the *anthocyanin*-dyed nc-TiO_2 working electrode noticeably absorbed 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 TiO_2 film. The optical band gap estimated from the intercept of the tangent to the plot was 2.59 eV which is lower than the band gaps for the crystal structures in titanium dioxide. This implies that the process of dye sensitization has led to band gap narrowing which was necessary for the doped TiO_2 to respond to the visible light as represented in figure 2.

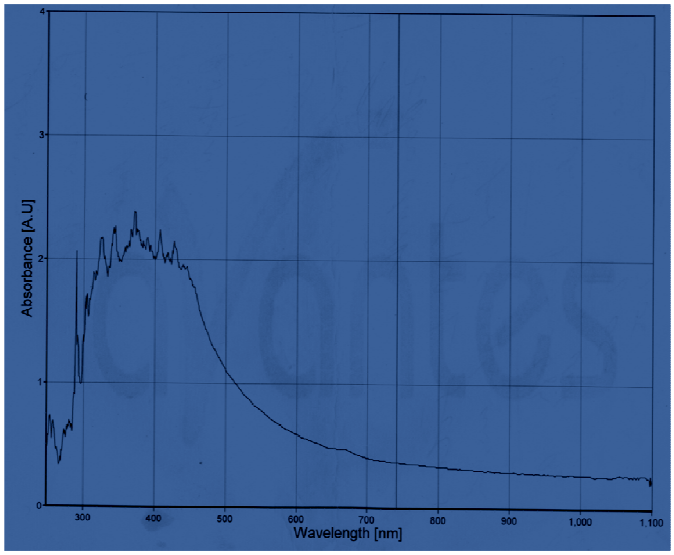

Figure-2
Optical absorption spectrum of *anthocyanin*-dyed nc-TiO_2

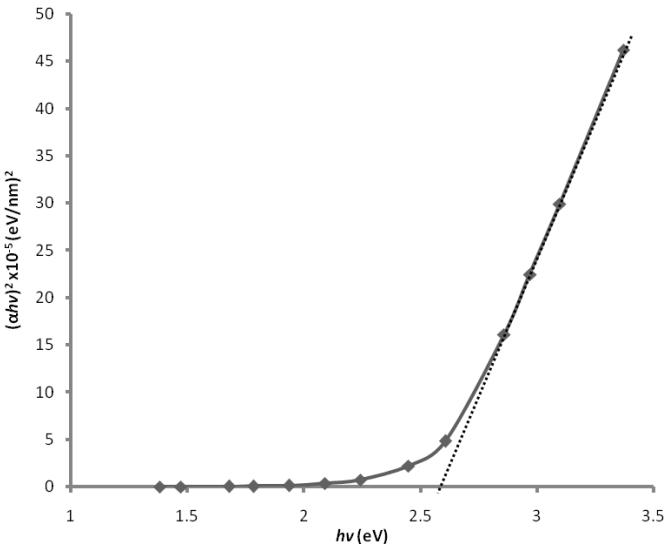

Figure-3
Optical band gap for *anthocyanin-doped* TiO_2

Figure 5 and figure 6 are the photocurrent-voltage characteristics of DSSCs fabricated with the *anthocyanin*-dyed and un-dyed electrodes respectively. The cell parameters obtained for the *anthocyanin*-dyed cell were; open circuit voltage (0.33V), short circuit photocurrent (2.60mA/cm^2), fill factor (0.68) and photoelectric conversion efficiency (0.58%); while the results obtained for the plain cell were; open circuit voltage (0.24V), short circuit photocurrent (0.20mA/cm^2), fill factor (0.63) and photoelectric conversion efficiency (0.03%). The performance of the dyed cell could be compared to the results obtained by Sirimanne *et al*, 2008 and Waita *et al* 2006[4,29,30].

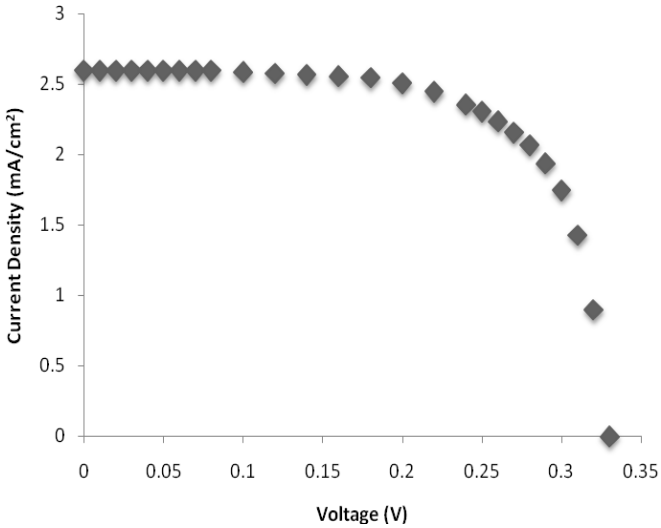

Figure-5
The I-V curve of the cell sensitized with *anthocyanin* dye

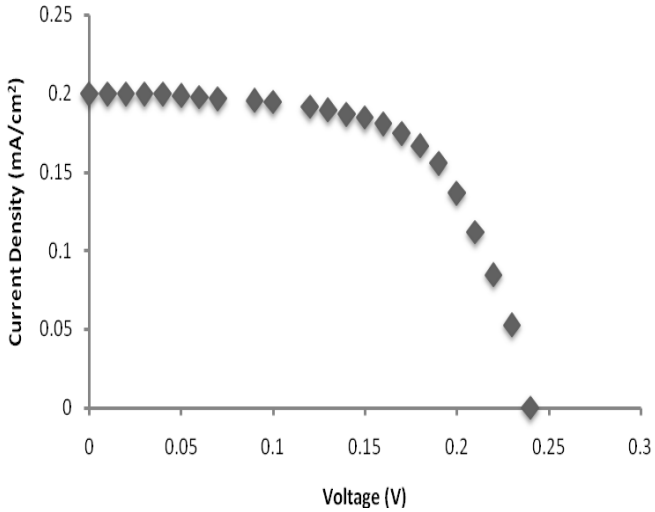

Figure-6
The I-V curve for the plain cell

Conclusion

An investigation of the optical band gap and photovoltaic performance of nc-TiO_2 sensitized with *anthocyanin* local dye was carried out. The local dye was extracted from hibiscus sabdariffa. The Tauc model was employed to estimate the direct optical band gap of the doped-TiO_2 electrode. Our results revealed that TiO_2 sensitized with *anthocyanin* dye has a reduced band gap and can absorb light both in the ultraviolet and visible region. The current-voltage characterization of a DSSC fabricated with the *anthocyanin*-dyed TiO_2 electrode and another DSSC fabricated with un-doped TiO_2 electrode were presented and it was observed that the dyed nc-TiO_2 is a better photo-electrode.

Acknowledgement

The authors are grateful to Mrs. Nkah, Bessie C. of Federal College of Education, (Technical), Umunze, Anambra State, Nigeria and Engr. Simeon Ozuomba of University of Uyo, Nigeria for stimulating discussion on the presented results.

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