

Optical Studies and Photovoltaic Performance of Nanocrystalline Titanium Dioxide Sensitized with Local Dye

Jude O. Ozuomba^a, Azubuike J. Ekpunobi^b

^a Faculty of Science, Madonna University, P.M.B. 48, Elele, Nigeria .

^b Department of Physics and Industrial Physics, Nnamdi Azikiwe University, P.M.B. 5025, Awka, Nigeria.

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**Corresponding author:*

E-mail address:

okanandu@yahoo.com

phone: +2348033267967

Abstract

Nanocrystalline titanium (iv) oxide paste has been deposited on Fluorine doped tin oxide glass substrate by the blade method. The deposited film was subjected to thermal treatment to obtain an electrode for a photo-electrochemical cell. The electrode was sensitized with prophyrin dye which was a local dye extracted from carica papaya leaves. Avaspec 2.1 spectrophotometer was used to obtain the absorbance data, while the Tauc Model was employed to estimate the optical band gap of the sensitized film. The sensitization process led to band gap narrowing and, hence, the prophyrin-dyed electrode could absorb light beyond the ultraviolet region. Also, the current-voltage characteristics of a dye sensitized solar cell based on the prophyrin dye revealed that the natural dye is a good photosensitizer.

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1. Introduction

Titanium dioxide is a common wide band gap semiconductor that is used in many applications including pigments, protective coatings and thin film optical devices such as photovoltaics [1, 2]. For example dye sensitized solar cells are modern photovoltaic systems that utilize a wide band gap semiconductor as charge carrier [3, 4]. Titania has become the prominent semiconductor in these systems because of its stability as well as its electronic properties. Thin films used in these photovoltaics are porous and thick, on the order of

10 μ m, and usually are prepared by coating a dispersion of commercial nanoparticles onto a conductive transparent oxide [1].

Moreover, one particular area of interest is the photocatalytic activity of titania for environmental protection. The degradation of organic pollutants in water and gaseous formaldehyde by TiO₂ photocatalysis has attracted extensive attention during the most recent decade due to its optical and electronic properties, low cost, chemical stability and non-toxicity [5, 6]. The photocatalytic activity of TiO₂ is dependent on crystal structure, surface

area, size distribution, porosity, surface hydroxyl group density, etc. The highly transparent TiO_2 films have also been widely used as anti-reflection coatings for increasing the visible transmittance in heat mirrors. As a dielectric, TiO_2 is one of the most popular materials for the purpose of anti-reflection coatings [7].

The properties of the titanium oxide films depend not only on the preparation techniques but also on the deposition method, substrate and annealing temperature. TiO_2 can exist as an amorphous layer and also in three crystalline phases: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [7, 8]. The band gap value for the anatase type is 3.2 eV, for the rutile type is 3.02 eV and for the brookite type 2.96 eV [5, 6, 8].

Dye-sensitized solar cell (DSSC), often called the “gratzel cell” [4] after its inventor, is a promising route toward harvesting solar energy in the effort to address the daunting global energy and environment challenges of the 21st century. DSSC is a new type of photoelectrochemical solar cell which effectively utilizes a property of nanocrystalline wide band gap metal oxide semiconductor porous electrode [2, 4]. Generally, a DSSC consists of an indium-tin oxide (ITO) or fluorine-doped tin oxide (FTO), dye modified electrode, electrolyte and a counter electrode. Unlike standard silicon-based solar cells, DSSCs are photoelectrochemical in nature, making the manner by which they convert solar energy into electrical energy resemble photosynthesis [9-11]. The reaction taking place within the cells closely mirrors that of the photosynthesis reaction in

plants. Like chlorophyll in plants, the light absorbing dyes used in thin-film based solar cells absorb incoming sunlight and use that energy to perform chemical reactions.

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 [2, 4, 16]. Although highly effective, with current maximum efficiency of 11% [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 [10, 11, 15].

In recent years, impurity doping has been widely performed by chemical synthesis and ion implantation in order to create photocatalysis operating under visible light irradiation [8]. Impurity doping induces substantial modifications in electrical and optical properties of semiconductor materials. Undoped TiO_2 is active only under ultraviolet (UV) light because of its wide band gap rendering it inactive under visible light (Figure 1) [10, 16, 19, 20], which causes most of the solar spectrum to go unutilized [8, 17, 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.

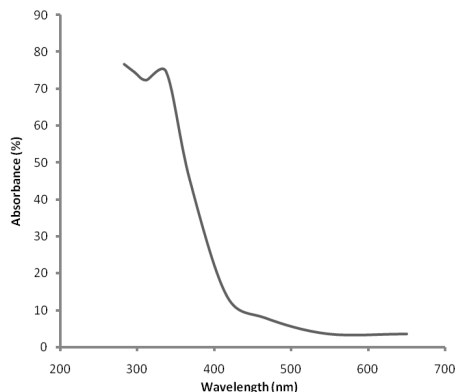


Figure 1(a): Absorbance vs Wavelength for commercially-available titanium iv oxide [19]

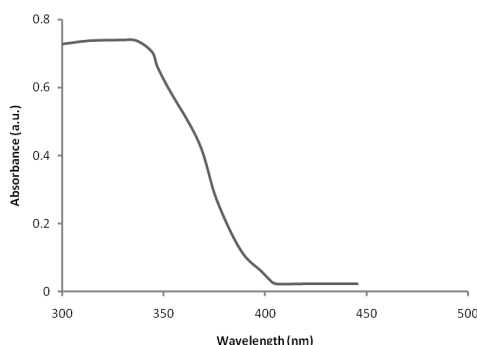


Figure 1(b): Diffused UV absorption spectrum of commercial polycrystalline titanium dioxide [20]

In this work, a nanocrystalline titanium (iv) oxidizer (nc-TiO₂) was deposited onto a Fluorine-doped tin oxide (FTO) glass substrate through the blade method. The deposited film was subjected to thermal treatment and sensitized with prophyrin local dye which was an extract from carica papaya leaves. The effect of prophyrin dye on the optical absorbance and band gap of the nc-TiO₂ is treated in discussed in this paper. The photovoltaic performance of the dyed nc-TiO₂ was evaluated from the current-voltage characteristics of a DSSC fabricated with the sensitized anode electrode.

2. Experimental

2.1 Dye Extraction

The prophyrin natural dye was extracted from carica-papaya leaves through the following process:

- (i) Blend the carica-papaya leaves using electric blender.
- (ii) Add 90% ethanol and continue blending.
- (iii) Use sieve to extract the pigment which forms our dye.

2.2 Electrode deposition

Nanocrystalline titanium (iv) oxide paste (Titanoxide 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 nc-TiO₂ paste was applied at one of the edges of the conducting glass and distributed with a squeegee sliding over the tape-covered edges [2, 11, 21].

2.3 Thermal Treatment

The nc-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 [EgRu 12, 26].

2.4 Sensitizer Impregnation

The thermally treated electrode was immersed into a solution of the dye prophyrin and allowed to stay overnight [11, 21]. Before dipping the photo-electrode into the dye solution, we preheated it at 80 °C for 15 minutes. This process helps in the prevention of rehydration of the TiO₂ surface or capillary condensation of water vapors from ambient air inside the nanopores of the film [2].

We undertook the following precautionary measures:

- (i) The presence of water in the pores decreases the injection efficiency of the dye, so, we rinsed dye-coated film in ethanol and dried using hot-air blower.
- (ii) The properly sensitized film was kept in dark in an air tight case till the solar cell assembly.
- (iii) The electrode was gently and slowly put into the dye to avoid cracking because of the difference in temperature.
- (iv) We ensured that the electrode was facing up for proper adsorption of the dye.
- (v) Dye-coated film was kept in dark in an air tight case till solar cell assembly.

2.5 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 nc-TiO₂ electrode. The spectrophotometer was computerized and so measurement was taken with the help of experts. The result was displayed as a graph of optical absorbance (arbitrary units) versus wavelength (nm).

The theory of the interband absorption shows that at the optical absorption edge, the absorption coefficient α varies with the photon energy $h\nu$ according to the equation below:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (1)$$

where: A is a constant that depends on the properties of the material, $h\nu$ is the photon energy, E_g is the optical band gap. Thus a plot of $(\alpha h\nu)^2$ versus $h\nu$ is a curve line whose intercept on the energy axis gives the energy gap. The band gap energy of the film have been determined by the extrapolation of the linear regions on the energy

axis $h\nu$ [7, 8, 22-30] EgRu17, 27-31, EgProph03 Also Ref. 26, 27 of EgRuth01 and EgRuth01].

3. Results and Discussion

The optical absorption spectrum (Figure 2) shows that the porphyrin-dyed nc-TiO₂ working electrode noticeably absorbs light beyond the UV region. Hence, there was a great improvement in the optical absorbance of the wide-band gap titanium (iv) oxide which alone cannot absorb visible light.

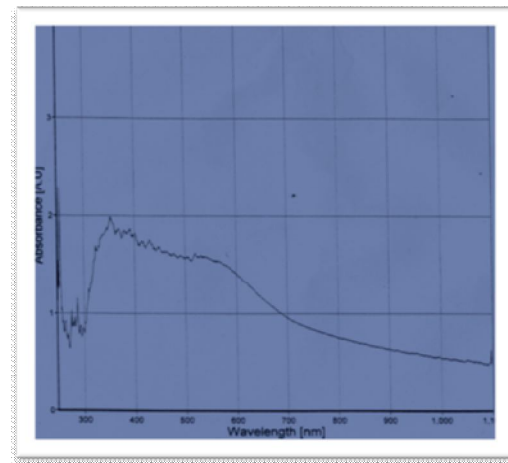


Fig. 2. Optical absorbance of porphyrin-stained TiO₂ electrode

Fig. 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 2.46 eV which is lower than the established band gap for the different crystal structures in titanium dioxide. 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 Fig. 3 [27].

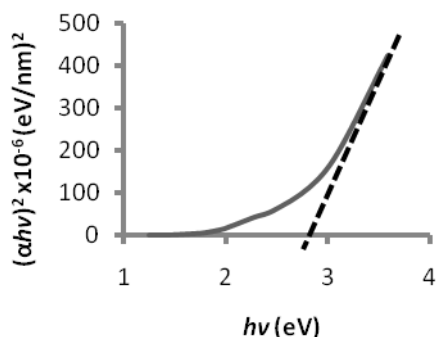


Fig. 3. Optical band gap for prophyrin-doped TiO₂

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

$$\eta = \frac{\text{maximum power output}}{\text{maximum power input}} = \frac{I_m V_m}{A * E} \quad (2)$$

$$FF = \frac{I_m V_m}{V_{oc} * I_{sc}} \quad (3)$$

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 η for the ruthenium-stained solar cell were found to be 0.26 mA/cm², 0.60 V, 0.71 and 0.11%, respectively

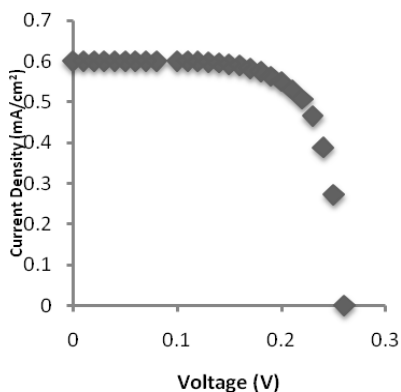


Fig. 4. The I-V curve for solar cell sensitized with prophyrin dye

4. Conclusions

Nanocrystalline TiO₂ paste was successfully deposited onto fluorine-doped tin oxide glass substrate through the blade method. The deposited film was subjected to thermal treatment to obtain a photo-electrode for dye sensitized solar cell. The electrode was doped with prophyrin local dye to enhance its solar energy conversion efficiency. Analysis of the optical performance of the dyed TiO₂ showed that the band gap was reduced and, thus, the electrode could absorb incident solar radiation beyond the UV region. The photovoltaic parameters of a DSSC fabricated with the doped nc-TiO₂ were as follows: open circuit voltage = 0.60V, short circuit current = 0.26mA, fill factor = 0.71 and photo-conversion efficiency = 0.11%. This study is the first to explain the optical and photovoltaic behavior of prophyrin-dyed titanium dioxide.

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