



OPTICAL CHARACTERIZATION OF NANOCRYSTALLINE TITANIUM DIOXIDE (TiO₂) SENSITIZED WITH NATURAL DYES IN THE APPLICATION OF DYE SENSITIZED SOLAR CELLS (DSSCs)

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ABSTRACT

This paper optically characterized nanocrystalline titanium dioxide (TiO₂) using natural dyes obtained from *dacryodes edulis*, *mimosa pudica*, *delonyx regia* and *xanthosoma sagittifolium* leaves to function as dye sensitizers in dye-sensitized solar cell (DSSC). Solvent extraction method was employed, UV-VIS spectrophotometer was used to obtain the optical absorbance spectra of the sensitized films while Tauc model was employed to determine the optical band gaps. From UV-Vis absorption spectra, nc-TiO₂ sensitized with these natural dyes have absorbance at wavelength 200-720nm but low transmittance and reflectance in the visible region. This indicated that the dyes absorb visible light, which improves the optical properties of TiO₂ when sensitized with these natural dyes and have been found to be suitable for the use as sensitizers in solar cells. Also, their optical band gaps were obtained using Tauc relation, result showed approximate value of $1.30 \times 10^{-9} eV$.

Keywords: DSSC, Titanium dioxide, efficient sensitizers, optical band gap.

1.0 INTRODUCTION

Dye-sensitized solar cells was invented by Micheal Gratzel in 1991 as an alternative in solar cell development because of its specialty on simple fabrication, low cost and clean to the environment because used safer material in fabricating. Visible spectrum, which is near to ultraviolet and infrared can be captured and generate electricity (Gomesh et al., 2014). Dyes are important parameters in absorption of a photon of sunlight to generate electricity and its dye molecules will sensitize the wide-bandgap semiconductor (TiO₂) to the visible radiation (Hemalatha et al., 2012).

Natural dye which was extracted from various fruits and plant contained anthocyanin, chlorophyll, carotenoid and xanthophyll pigments and have been used in DSSC (Kim 2013). Generally, dye sensitizer from Ru-containing complex will result in efficiency up to 11-12 % (Zhou et al. 2011) but due to high cost and long term unavailability, natural based dyes from fruits and leaves is proposed as an alternative to reduce the cost, high light harvesting, simple fabrication, but at the same time is friendly to nature because it is free from contamination and natural dyes from fruits, plants and leaves have been used as an alternative to overcome this problem.

In this work, the optical properties of nc-TiO₂ films sensitized with natural dyes obtained from extracts of *mimosa pudica* (touch me not/ sensitive plant), *xanthosoma sagittifolium* (cassava leaf), *dacryodes edulis* (African pear) and *delonyx regia* (flame of the forest) which are locally sourced in Nigeria was investigated using a Uv-Vis spectrophotometer to obtain

the optical absorption spectra of the sensitized films, while the Tauc model was employed to determine its optical bandgap.

2.0 MATERIALS AND METHODS

2.1 Preparation of Mesoporous TiO₂.

TiO₂ mesoporous layers were prepared by screen printing method. A layer of TiO₂ paste (Titanium nanoxide D /Sp, Ti-20, solaronic) was coated on to the as-deposited layer of TiO₂ / FTO glass using screen printer (MESH COUNT = 70). This was done by spreading the TiO₂ paste evenly on the MESH surface of the printer with glass rod, the glass slide was carefully removed without perturbing the TiO₂ layer. Followed by a heat treatment at 450°C for 30 mins until the dried TiO₂ turns brown, at this point we cover the glass with foil and continue heating at 5000C when it turns white again. This shows the film deposited was purely TiO₂, no impurity was present. The TiO₂ films was allowed to cool at room temperature, removed from the hot plate.

2.2 Extraction of the Natural Dyes

Dye sensitizers were prepared using natural dyes from *mimosa pudica*, *delonyx regia*, *dacryodes edulis* and *xanthosoma sagittifolium* leaves which are common in Nigeria. Solvent extraction method was employed. First, fresh leaves of these plants were cut into small pieces. Afterwards, they were weighed using an electronic weighing balance (METLAR analytical balance, MTL-200) and then ground thoroughly in a mortar, homogenous was achieved. The extracts inserted into a glass beaker were mixed with 80 ml of water as the extracting solvent, and let to stand for 30 mins. They were covered with aluminum foil to prevent evaporation.

The soaked extracts were filtered using filter paper and kept in sealed transparent bottle. The resulting filtrate will serve as natural sensitizers for DSSC.

2.3. Sensitization Process

The already prepared samples (glass / FTO / ETL / porous TiO₂) films were soaked in the different dyes solution overnight. After which they were rinsed with the appropriate solvent (water) to remove excess non-adsorbed dye and dried on a magnetic stirrer hot plate 78.1 (PEC. MEDICAL USA) at 60°C for 20 mins.

Finally, they were stored in a dry dark container ready for analysis.

3.0. MEASUREMENT AND THEORITICAL ANALYSIS

3.1. Optical Measurement

The evaluation of the optical band gaps of the nc-TiO₂ films sensitized with the four different natural dyes extracted from mimosa pudica, solanium melongena, dacryodes edulis and delonyx regia were obtained. A UV-VIS spectrophotometer was used to obtain the optical absorbance spectra of the sensitized films while Tauc model was employed to determine the optical band gaps. These were determined by the extrapolation of the linear region to zero absorbance from a plot that was drawn according to the Tauc relation (see equation 1 and other relations).

$$\alpha = B/hv([hv - E_g])^2 \text{ ----- (1)}$$

where hv is the energy of incoming photons, and B is the Tauc coefficient describing the efficiency in light absorption (Tauc et al., 1966).

To have a quantitative estimation of the optical bandgap of the sensitized TiO₂, the Tauc equation will be employed.

Other relation employed include:

The Absorption coefficient (α) which determines how far into a material, light of a particular wavelength can penetrate before it is absorbed. This depend on the material and also on the wavelength which is being absorbed.

It can be calculated using the relation,

$$\alpha = A/\lambda \text{ ----- (2)}$$

Where α is the absorption coefficient, λ is the wavelength and A is the absorbance of the material.

Recall photon energy E=hv, ----- (3)

v is the frequency v=c/λ ----- (4)

Where c is the speed of light=3×10⁸m/s, 1eV = 1.60 x 10⁻¹⁹ J, h = Planck constant =6.626×10⁻³⁴ Js and E stands for photon energy.

These parameters can be used to obtain the bandgap of the sensitized TiO₂ by plotting the graph of absorption coefficient square vs photon energy (Arunachalan et al., 2016).

4.0. RESULTS AND DISCUSSION

4.1. Results On Optical Characterization

The representative UV–VIS absorption spectra for the sensitized films from extracts of *mimosa pudica*, *delonyx regia*, *dacryodes edulis* and *xanthosoma saggitifolium* leaves have been investigated. Figures 1-4 showed the UV–VIS absorption spectra of these sensitized films. The most striking feature that has been observed from these figures is that nc-TiO₂ sensitized with *mimosa pudica*, *delonyx regia*, *dacryodes edulis* and *xanthosoma saggitifolium* have absorbance at wavelength 200-720nm but low transmittance and reflectance in the visible region. It indicated that the dyes absorb visible light. This improves the optical properties of TiO₂ when sensitized with these natural dyes and have been found to be suitable for the use as sensitizers in solar cells. A similar result was found for extract dragon fruit which has been reported by Riyaz and Nayan, (2011).

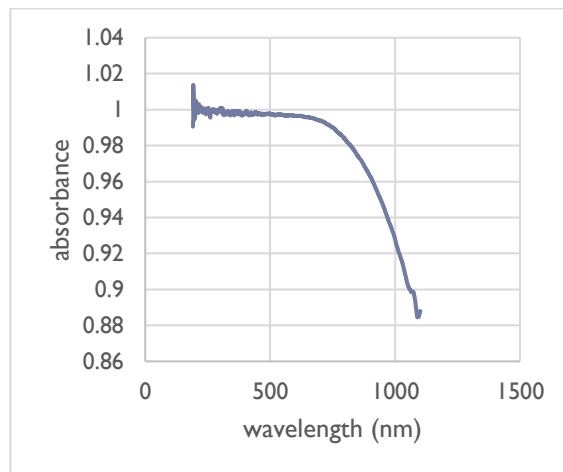


Figure 1: The spectra absorbance as a function of wavelength for TiO₂ sensitized with DE.

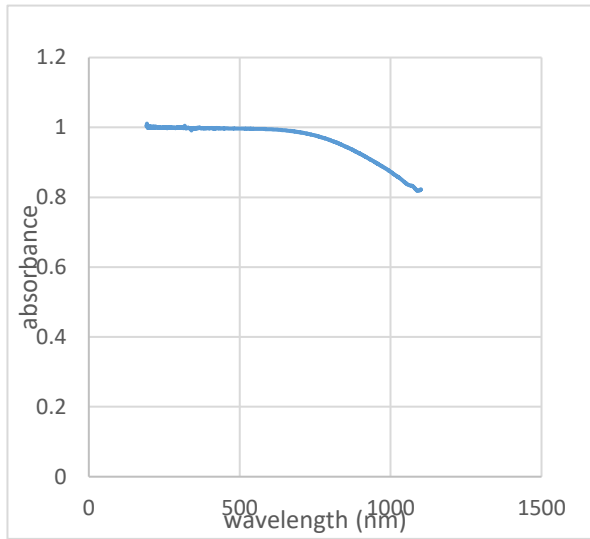


Figure 2: The spectra absorbance as a function of wavelength for TiO₂ sensitized with MP.

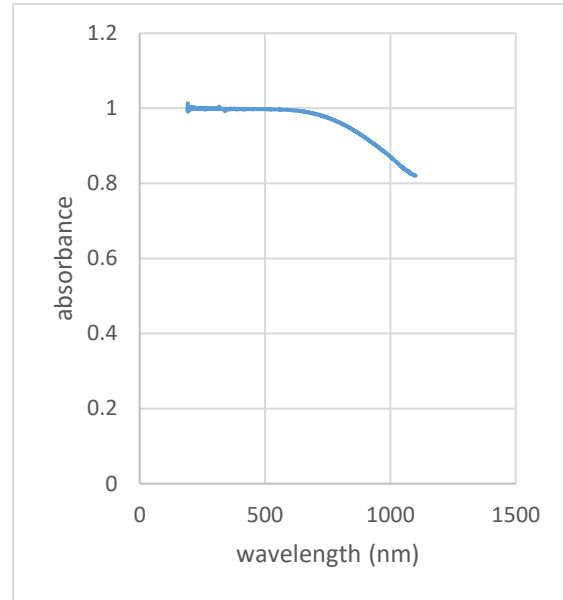


Figure 4: The spectra absorbance as a function of wavelength for TiO₂ sensitized with SX.

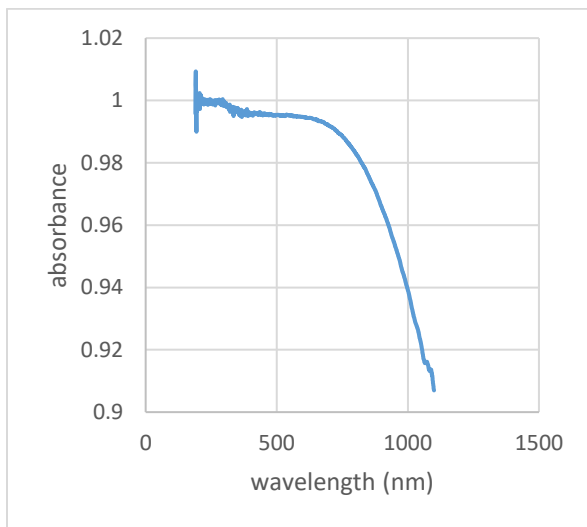


Figure 3: The spectra absorbance as a function of wavelength for TiO₂ sensitized with DR.

4.2. RESULTS FROM OPTICAL BAND GAPS

As already reported, once the absorption spectra are calculated, the optical band gaps can be extracted by using the linear fit performed on Tauc plots.

Figure 5 – 8 showed the extracted optical band gaps and energy ranges of linear fit for Tauc plots. These were determined by extrapolating the linear part of the graphics to the axis of the abscissa from the plots that was drawn according to the Tauc relation (see equation 1). The band gaps were found to be approximately $1.30 \times 10^{-9} eV$ which implies a reduction in the band gap of the semiconductor as a result of dye sensitizer. The semiconductor (nc-TiO₂) with wide band gap $\sim 3.2 eV$ can only absorb light in the ultraviolet region, but when sensitized with natural dye, its low band gap enables the semiconductor to absorb photon in the visible region. This agrees well with In Chung *et al.*, (2012) that materials with low band gap generate extra current by absorbing more photons, but the charge carriers are swept away by the smaller built-in potential.

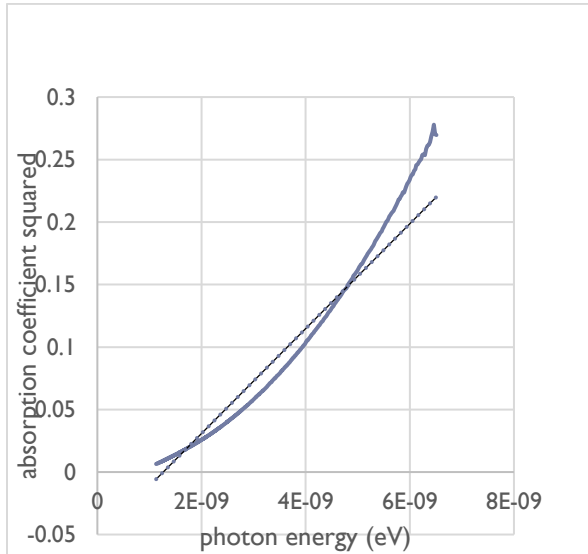


Figure 5: a plot of absorption coefficient squared vs photon energy for TiO₂ sensitized with DE.

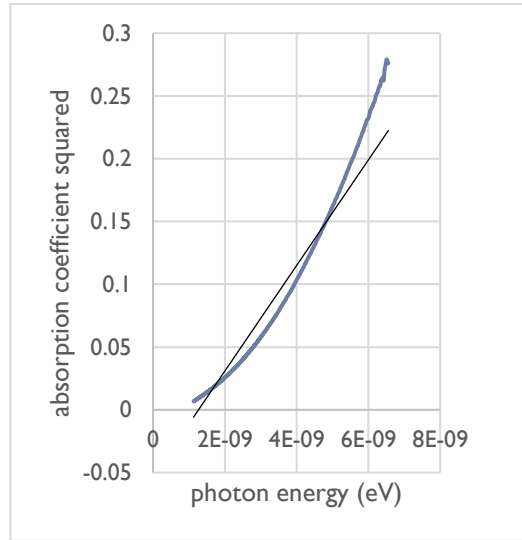


Figure 7: A plot of absorption coefficient squared vs photon energy for TiO₂ sensitized with DR.

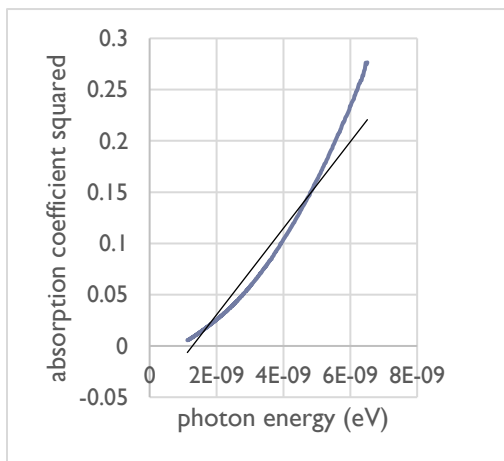


Figure 6: A plot of absorption coefficient squared vs photon energy for TiO₂ sensitized with MP.

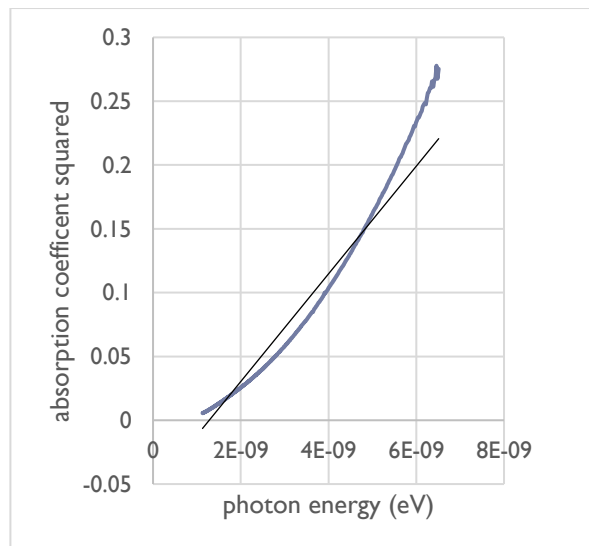


Figure 8: A plot of absorption coefficient squared vs photon energy for TiO₂ sensitized with SX.

5.0. CONCLUSIONS

The optical band gap of the sensitized TiO₂ were calculated and determined using Tauc model based on data obtained from UV-VIS absorption spectra. It was revealed that the energy band gaps of the natural dye were approximately 1.30×10^{-9} eV resulting in improved energy harvesting capability of the film. The band gap of a solar cell

simultaneously determines the strength (voltage) of the electric field as well as the amount (current) of photons to be absorbed.

The dye gives the absorbance at wavelength 200-720 nm but low transmittance and reflectance in the visible region. It indicated that the dyes absorb visible light and have been found to be suitable for the use as sensitizer in solar cells.

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