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The optical properties of *anthocyanin*-doped nanocrystalline-TiO_2 and the photovoltaic efficiency on DSSC

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ABSTRACT

This research work is an investigation of the optical characteristics of nanocrystalline titanium dioxide doped with anthocyanin local dye. Anthocyanin local dye was extracted from hibiscus sabdariffa which is an edible plant called zobo by Nigerians. The sensitized nanocrystalline titanium (iv) oxide was discovered to have a reduced band gap energy and hence could absorb incident solar radiation beyond the ultraviolet region. Avaspec 2.1 Spectrophotometer was employed to determine the optical spectrum, while the Tauc model was used to obtain the optical band gap. The transmittance spectrum was shown, while the nature of the refractive index was studied using the Moss Rule. The behaviour of the extinction coefficient was also investigated. The current-voltage characteristics of a dye sensitized solar cell fabricated with the sensitized nc-TiO_2 working electrode was analyzed. The optical band gap of the sensitized nanocrystalline titanium dioxide was 2.59eV, while the conversion efficiency of the dye sensitized solar cell was 0.58%.

Key words: titanium dioxide, optical properties, dye sensitized solar cell, band gap.

INTRODUCTION

In the past decade, nanostructured materials have been of great interest as catalysts and other applications because of their unique textural and structural characteristics. Much interest has concentrated on the important metal oxides such as TiO_2, SnO_2, VO_2 andZnO[1]. Titania is a well known and well researched material due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties [1,2]. Titanium (iv) oxide exists in three mineral forms: anatase, rutile and brookite [1,3-5]. Anatase type TiO_2 has a crystalline structure that corresponds to the tetragonal system (with dipyramidal habit) and is used mainly as a photocatalyst under UV irradiation. Rutile type TiO_2 also has a tetragonal crystal structure (with prismatic habit). This type of titania is mainly used as white pigment in paint. Brookite type TiO_2 has an orthorhombic crystalline structure. Titanium dioxide, therefore is a versatile material that has applications in various products such as paint pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells, and even as a food coloring agent and in toothpastes [1,3,6].

The absorption spectrum of a semiconductor defines its possible uses. The useful semiconductors for photocatalysis have a bandgap comparable to the energy of the photons of visible or ultraviolet light, having a value below 3.5eV [7]. The bandgap values for the three crystalline forms of TiO_2 can be seen in Table 1 [3,4,8]. The surface as well as intrinsic properties of TiO_2 plays an important role in influencing the course of a photochemical reaction.

Table 1. Properties of the three crystal structures in TiO_2

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

Various doping methods have been extensively utilized for modifying the electronic structures of TiO_2 nanoparticles to achieve new or improved catalytic activities and the other chemical and physical properties [9-14].

The present energy and environment crisis has stimulated the interest in exploring renewable energy sources. Dye sensitized solar cells based on nanocrystalline TiO_2 certainly appear as one of the most promising candidate as low cost alternative to conventional semiconductor solar cells [15-17]. Since their invention in 1991 as reported by Gratzel *et al* [18], the DSSCs have been attracting a significant attention of the researchers due to their substantial possibilities to fabricate low-cost, environmental friendly, large-area photovoltaic devices [15].

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 [3,16,19]. 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 [16,20]. Although highly effective, with current maximum efficiency of 11% [20-22], 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 [15,20,23,24].

In this work we investigated the optical properties of a nc-TiO_2 film doped with *anthocyanin* natural dye. *Anthocyanin* local dye was extracted from hibiscus sabdariffa which is an edible plant called *zobo* by Nigerians. Avaspec 2.1 spectrophotometer was used to obtain the optical absorption spectrum of the doped film, while the Tauc model was employed to determine the optical band gap. The transmittance spectrum was shown while the variation of the refractive index was studied using the Moss Rule. The behaviour of the extinction coefficient was also investigated. The current voltage characteristics of a DSSC fabricated with the sensitized TiO_2 electrode was also presented.

MATERIALS AND METHODS

2.1 Preparation of the local dye

The *anthocianin* local dye used in sensitizing the nanocrystalline TiO_2 film was extracted from hibiscus sabdariffa which is a common edible plant in Nigeria. The grass was well blended and the green pigment was extracted with 90% ethanol [9].

2.2 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 fluorine-doped tin oxide (FTO) glass substrate 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.

2.3 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 [9].

2.4 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 vapour 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.

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-TiO_2 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 was employed [7,25].

$$\alpha hv = A(hv - E_g)^{\gamma} \quad (1)$$

where α is the absorption coefficient, hv is the photon energy, E_g is the optical band-gap, A is a constant that depends on the properties of the material and γ is a constant that can take different values depending on the type of electronic transition, for a permitted direct transition γ = ½, a prohibited direct transition γ = 3/2, a permitted indirect transition γ = 2 and for a prohibited indirect transition γ = 3[7,26]. In this work, the direct transition band gap of the doped TiO_2 electrode was determined by plotting a graph of $(\alpha hv)^2$ versus hv where the value of the band gap is obtained by extrapolating the linear part of the graphics to the axis of the abscissa.

The transmittance spectrum was determined while the variation of the refractive index was studied using the Moss Rule [26]. Occasionally the sum of absorption and scattering is also called extinction . The absorption coefficient (β) is given by:

$$\beta = 4\pi k/\lambda \quad (2)$$

where k is the extinction coefficient and λ is the wavelength of the radiation.

RESULTS AND DISCUSSION

The optical absorption spectrum (Figure 1) shows that the *anthocianin*-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 gag titanium (iv) oxide which alone cannot absorb visible light.

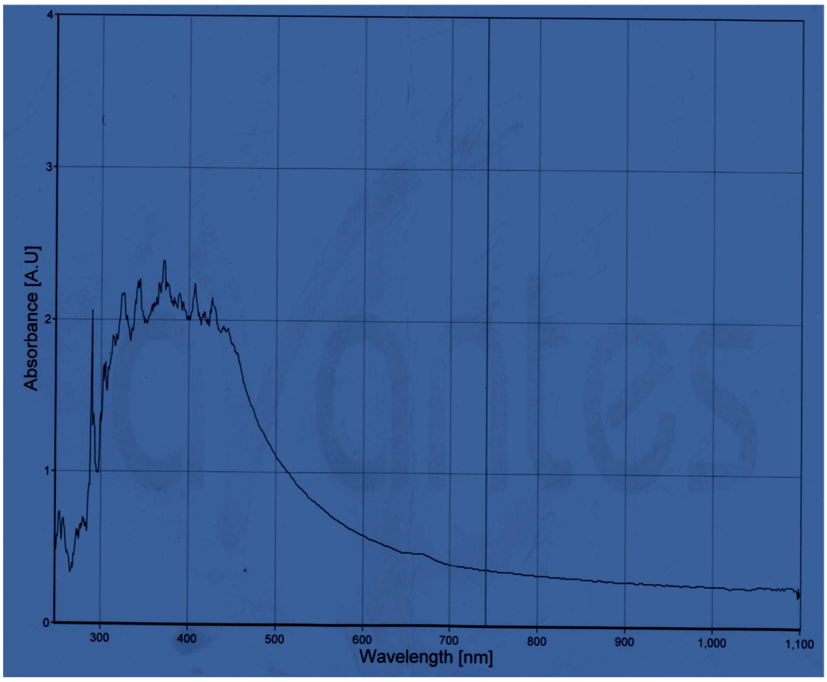

Figure 1. Optical absorption spectrum of *anthocyanin*-dyed nc-TiO_2

Figure 2 illustrates the plot of $(\alpha hv)^2$ vs. hv 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 gap 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 visible light as represented in Figure 1.

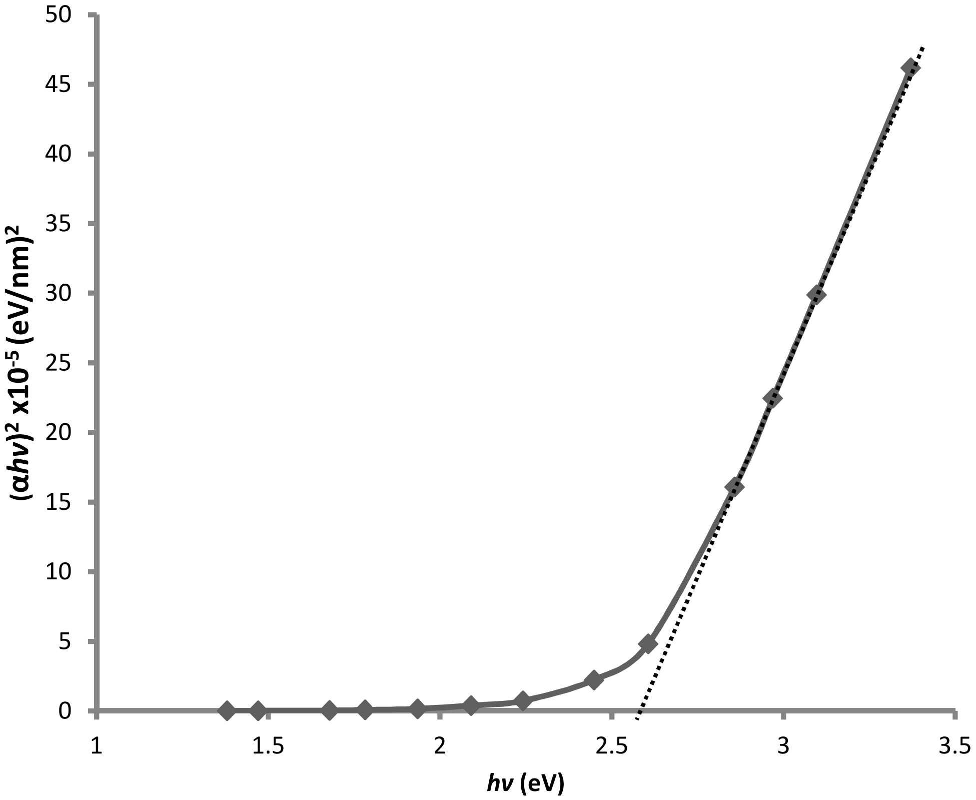

Figure 2. Optical band gap for *anthocyanin-doped* TiO_2

Figure 3 represents the transmittance spectrum while Figure 4 is the variation of refractive index with wavelength. The transmittance of the *anthocianin*-doped titanium dioxide was almost zero between 300nm and 440nm. It increased from 5% at 477nm to 46% at 700nm wavelength. The transmittance further increased to 59% at 900nm. The high refractive index of 2.7 as can be seen in Figure 4 makes the film to be very applicable in solar cell and anti-dazzling coating [27]. Figure 5 shows the extinction coefficient plotted against wavelength. The extinction coefficient has peak of 0.19 at 369 nm and decreased to 0.02 at 740 nm.

Figure 6 represents the photocurrent-voltage characteristics of a DSSC based on the *anthocianin*-dyed electrode under solar illumination of 100 mW/cm^2. The energy conversion efficiency (n) and fill factor (FF) were evaluated using the following relations:

$$n = \frac{\textit{maximum power output}}{\textit{maximum power input}} = \frac{I_m V_m}{A \times E} \quad (3)$$

$$FF = \frac{I_m V_m}{V_{oc} \times I_{sc}} \quad (4)$$

A is the active surface area of the solar cell while E is the illumination intensity. The cell parameters obtained were; open circuit voltage (0.33V), short circuit photocurrent (2.60mA/cm^2), fill factor (0.68) and photoelectric conversion efficiency (0.58%).

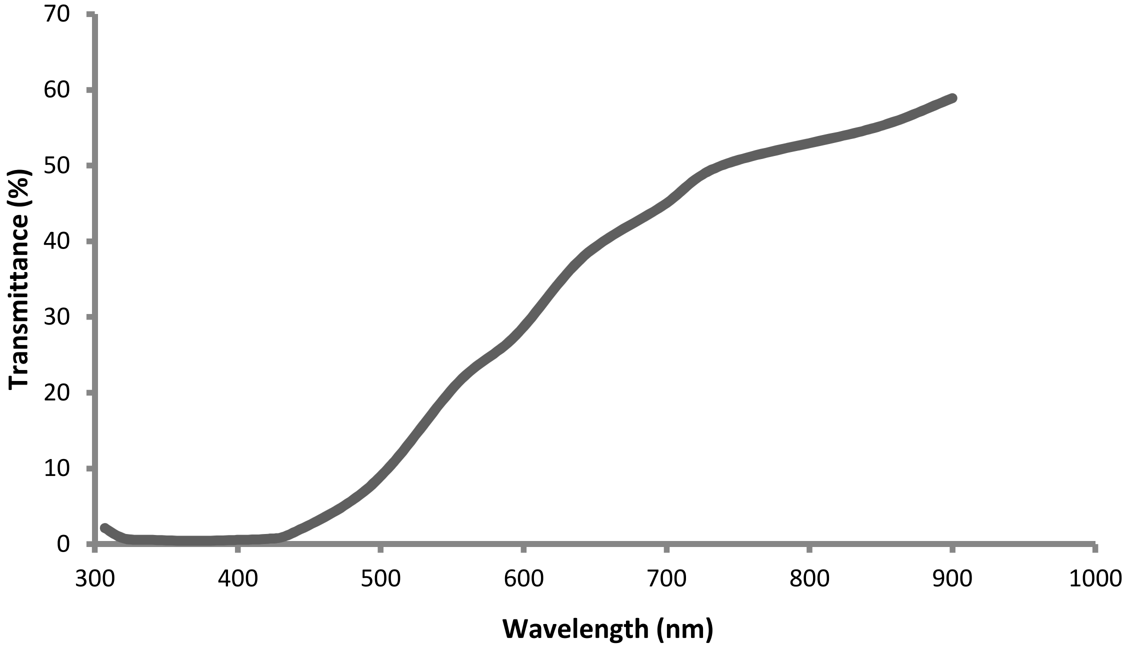

Figure 3. Transmittance spectrum of anthocianin-doped nc-TiO_2

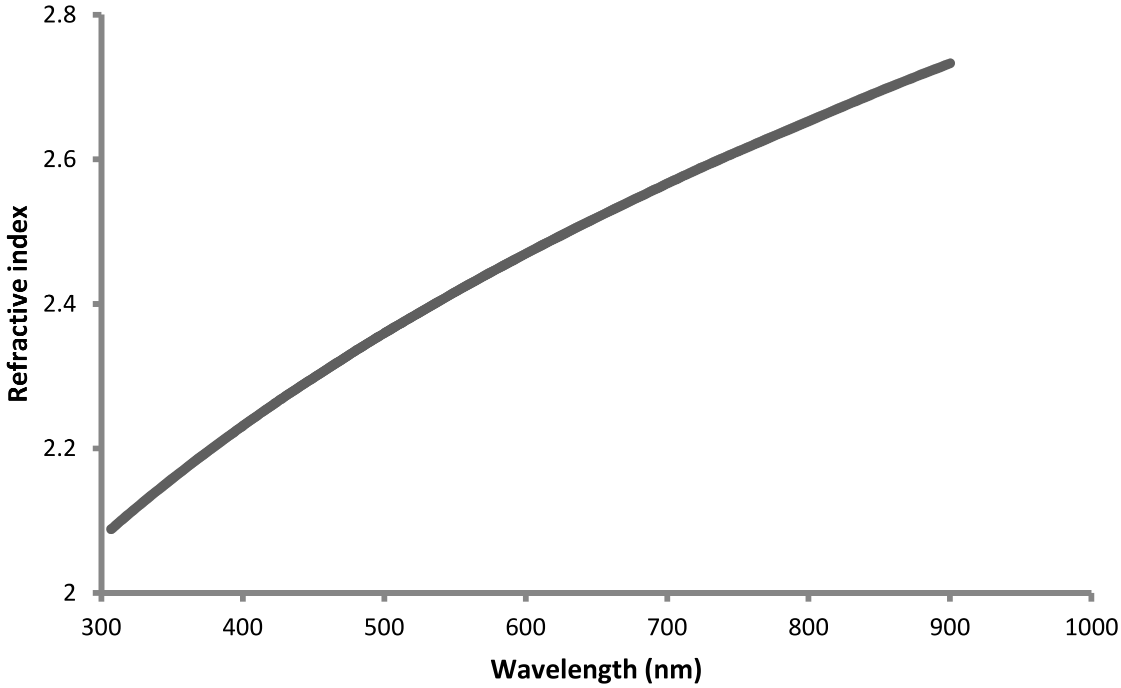

Figure 4. Refractive index of the *anthocyanin*-dyed nc-TiO_2 vs. wavelength

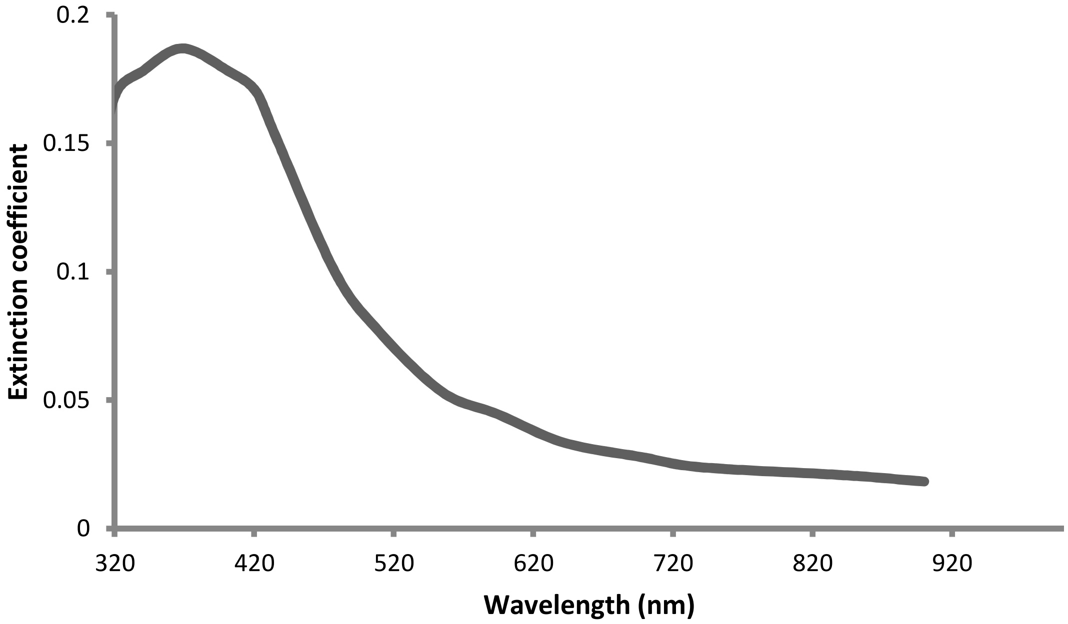

Figure 5. The values of extinction coefficient for *anthocyanin*-doped nc-TiO_2

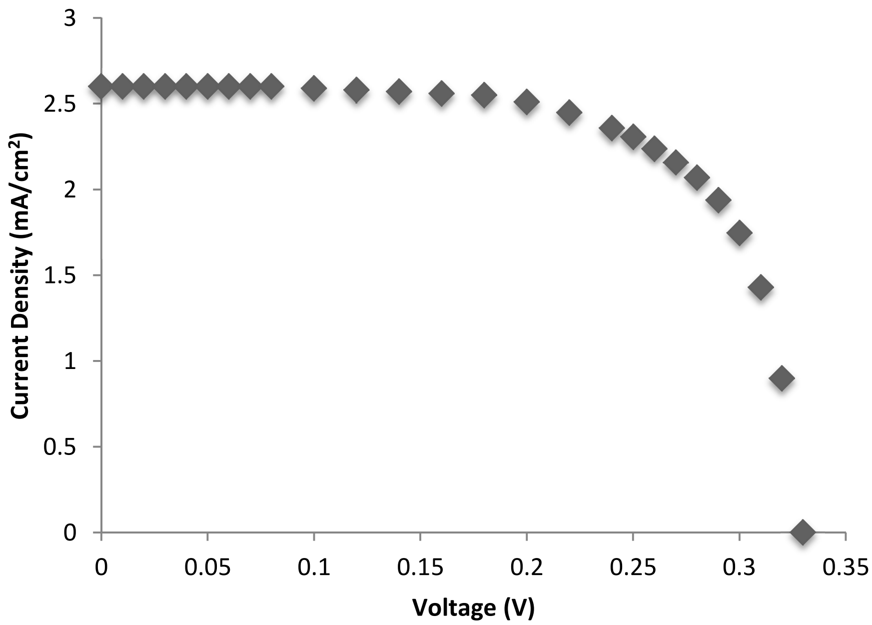

Fig ure 6. The I-V curve of the cell sensitized with *anthocyanin* dye

CONCLUSION

Thin film of sol-gel derived n-TiO_2 was successfully deposited onto an FTO substrate through the blade method. The film was subjected to thermal treatment and then doped with a local dye extracted from hibiscus sabdariffa. 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 TiO_2 was found to be 2.59eV which is lower than the band-gap of the three crystal structures in TiO_2. Hence, the *anthocianin* dye can be used as photo-sensitizer for wide-band gap semiconductors such as TiO_2 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 0.58%.

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