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The optical properties of chlorin-doped nc-TiO_2 and the photovoltaic efficiency on DSSC

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ABSTRACT

This study investigated the optical characterization of a chlorin-doped nanocrystalline titanium dioxide (nc-TiO_2) and its application to dye-sensitized solar cells. Chlorin local dye was extracted from bahama grass.The dye-sensitized nc-TiO_2 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. 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 energy conversion efficiency of a dye-sensitized solar cell fabricated from chlorin-doped nanocrystalline titanium dioxide was 1.008%.

Key words: Titanium dioxide, local dye, refractive index, optical properties.

INTRODUCTION

Titanium dioxide (TiO_2) is a material with wide application due to its optical and electronic properties [1]. TiO_2 is used as an ingredient in sunscreen lotions and food products, as a pigment in paints and as semiconductors in the photocatalytic degradation of organic compounds [1-5]. It is also used in the fabrication of dye-sensitized solar cells (DSSCs) [4]. In TiO_2, the crystalline phase, the composition and the surface states strongly affect the electronic structure and the charge properties [1,6]. Among semiconductor metal oxides, titanium (iv) oxide has been the focus of photocatalysis under ultraviolet irradiation due to its superiority in the oxidation capacity, non-toxicity, and long-term stability [7-9]. There are three crystalline forms of TiO_2; anatase, rutile and brookite [1,10]. Anatase phase is metastable and has the greater photocatalytic activity; rutile has a high chemical stability but is less active [11,12]. Besides, some TiO_2 with a large quantity of anatase and a small quantity of rutile exhibits a higher photocatalytic activity than in the pure anatase or rutile phases [1,6,13].

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 [1]. The bandgap values for the three crystalline forms of TiO_2 can be seen in Table 1 [14-16]. 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 [7,18-26].

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 [17,27,28]. Since their invention in 1991 as reported by Gratzel *et al* [27,28], 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 [17]. These cells are composed of a wide band gap semiconductor (like TiO_2, ZnO) deposited on a transparent conducting substrate, an anchored molecular sensitizer, a redox electrolyte (I / I couple) and a counter electrode [27,29-32]. DSSCs based on Ruthenium-complex photo sensitizers, such as N_3, N_{719} and black dyes have shown high photo-conversion efficiency [17, 33-35]. In recent years, metal free organic dyes have been explored as an alternative to Ruthenium-complexes because of low material costs, ease of synthesis and high molar extinction coefficients [17,36-39].

Herein we investigated the optical properties of a nc-TiO_2 film doped with *chlorin* local dye. *Chlorin* dye was extracted from bahama grass. 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 *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 [40].

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 TiO_2 film. Before deposition, the glass substrate was cleaned with acetone, then methanol and etched through plasma treatment for 1minute. 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.

1.3 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 ^{o}C using carbolite 201 tubular furnace.

1.4 Sensitizer Impregnation

The thermally treated electrode was immersed overnight into a solution of the *chlorin* dye. The electrode was preheated at 80 ^{o}C 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 [4,40]. 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.

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 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 [1,41].

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

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band-gap, A is a constant 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. In 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[1,42]. In this work, the direct transition band gap of the doped TiO_2 electrode was determined by plotting a graph of $(\alpha h\nu)^2$ versus $h\nu$ where the value of the band gap was obtained by extrapolating the linear part of the graphics to the axis of the abscissa[1,35].

The transmittance spectrum was determined while the variation of the refractive index was studied using the Moss Rule [43].

$$n^4E_g = 77 \quad (2)$$

Where n is refractive index and E_g is the energy gap.

Occasionally the sum of absorption and scattering is also called extinction [44]. The absorption coefficient (α) is given by:

$$\alpha = 4\pi k/\lambda \quad (3)$$

Where k is the extinction coefficient and λ is the wavelength of the radiation [44,45].

RESULTS AND DISCUSSION

The optical absorption spectrum (Figure 1) shows that the *chlorin*-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 2 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 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 TiO_2 to respond to the visible light as represented in Figure 1.

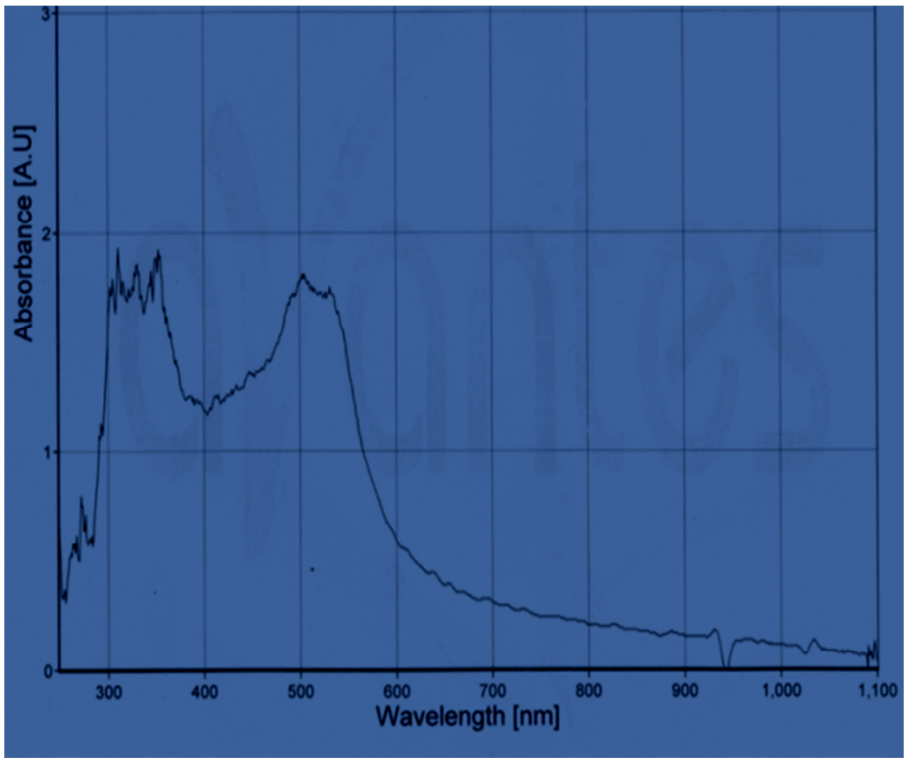

Figure 1. Optical absorption spectrum of *chlorin*-dyed nc-TiO_2

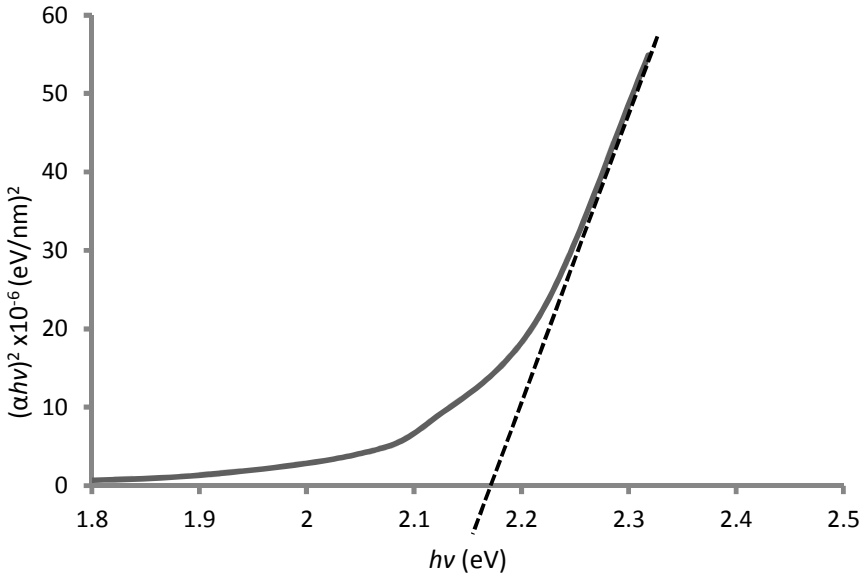

Figure 2. Optical band gap for *chlorin-doped* titanium dioxide

Figure 3 represents the transmittance spectrum while Figure 4 is the variation of refractive index with wavelength. The transmittance of the doped titanium dioxide was very low between 300 nm to 560 nm, meanwhile, it increased from 7% at 560 nm to 70% at 909 nm. 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 [43]. Figure 5 shows the extinction coefficients plotted against wavelength. The extinction coefficient has peak of 0.15 at 355 nm and 505 nm and decreased to 0.01 at 909 nm.

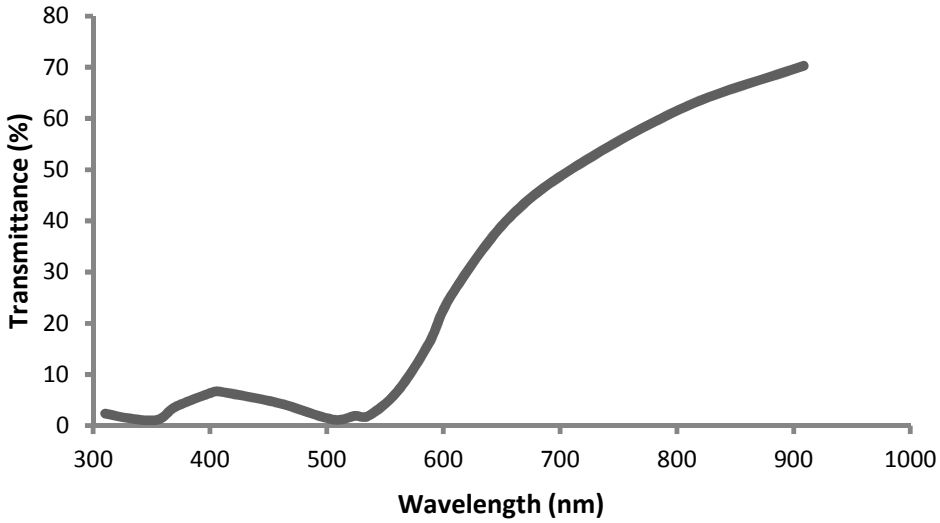

Figure 3. Transmittance spectrum of chlorin-doped nc-TiO_2

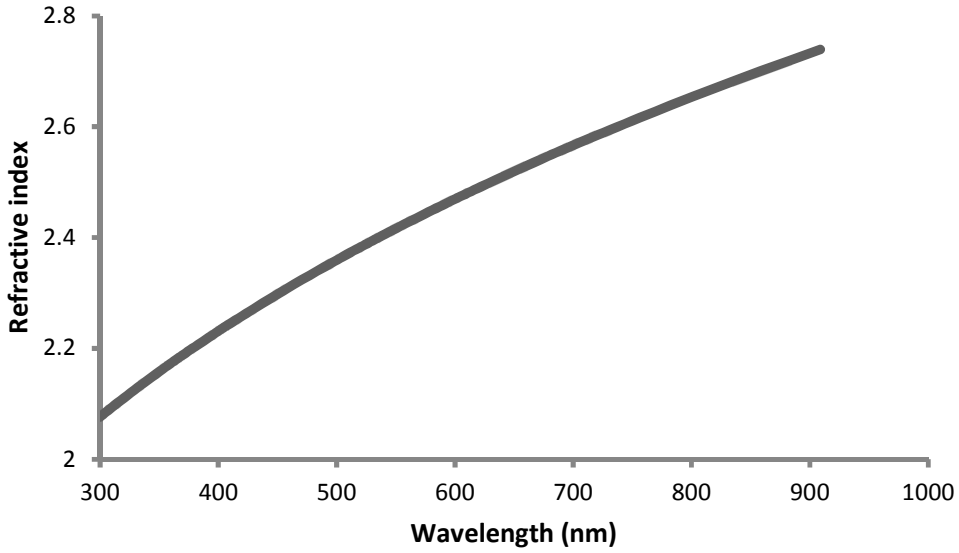

Figure 4. Changes in refractive index of the *chlorin*-dyed nc-TiO_2 vs. wavelength

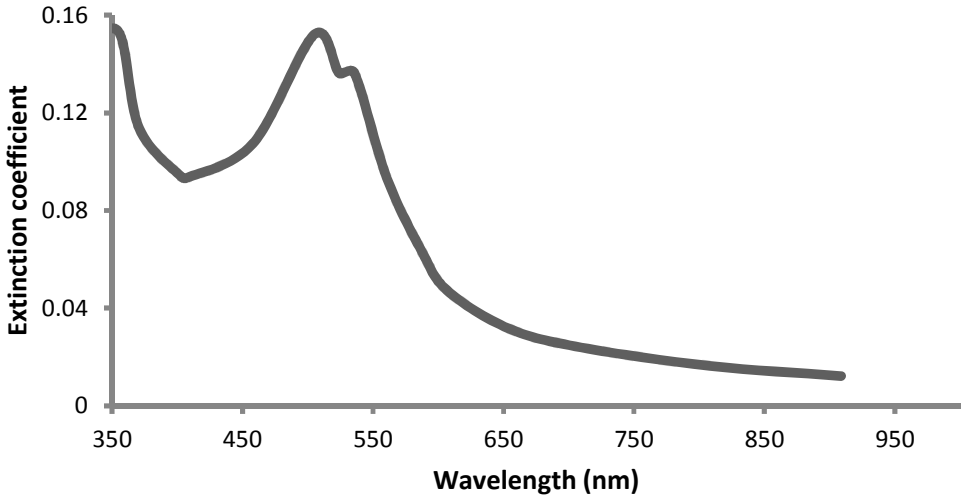

Figure 5. The values of extinction coefficient for *chlorin*-doped nc-TiO_2

Figure 6 represents the photocurrent-voltage characteristics of a DSSC based on the *Chlorin*-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:

$$n = \frac{\textit{maximum power output}}{\textit{maximum power input}} = \frac{I_m V_m}{A \text{ x } E} \quad (4)$$

$$FF = \frac{I_m V_m}{V_{oc} \text{ x } I_{sc}} \quad (5)$$

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/cm^2, 0.44 V, 0.59 and 1.008% respectively.

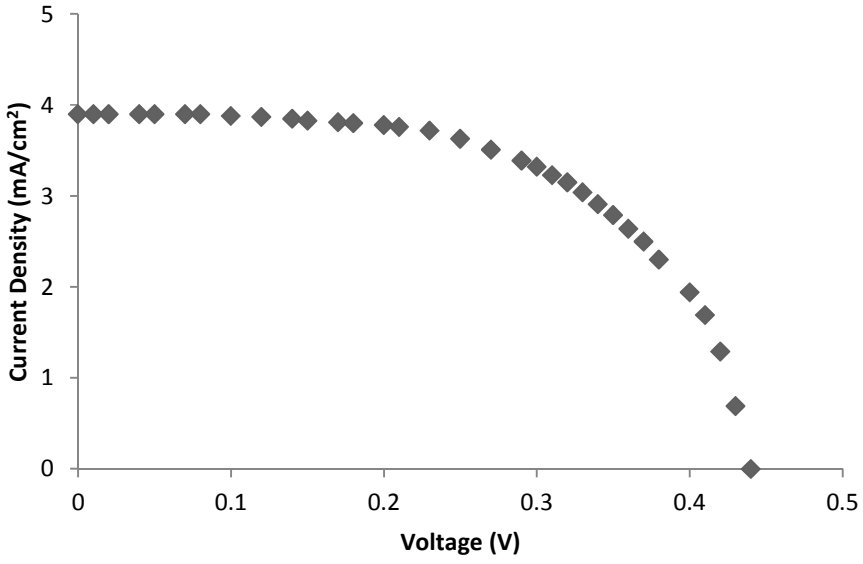

Figure 6. The I-V curve for solar cell sensitized with *chlorin* dye

CONCLUSION

Thin film of sol-gel derived nc-TiO_2 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 TiO_2 was found to be 2.16eV which is lower than the band-gap of the three crystal structures in TiO_2. Hence, the *chlorin* 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 1.008%.

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