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Anthocyanin-dyed TiO_2 Electrode and its Performance on Dye-sensitized Solar Cell

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Abstract

The dye-sensitized solar cell, often called the "gratzel cell" 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. Recently, dye-sensitized solar cells based on natural pigments have been demonstrated. The performance of anthocyanin local dye as photosensitizer for dye-sensitized solar cell has been successfully studied. Anthocyanin dye is an extract from hibiscus sabdariffa which is an edible plant called zobo by Nigerians. Anthocyanin-stained TiO_2 electrode showed an outstanding optical absorbance within wavelength range of 283 nm – 516 nm. Peak absorbance of 2.16A.U. 2.26A.U. and 2.38A.U. were recorded in the UV region at 324.45nm, 344.87nm and 369.35nm respectively. Appreciable absorbance was recorded in the visible region with two outstanding peaks; 2.26A.U. and 2.16A.U., occurring at 405.99nm and 426.47nm respectively. The photovoltaic parameters of a second cell fabricated with unstained TiO_2 photo-electrode was studied for comparison of results. The overall conversion efficiency of the stained and unstained cells were 0.58% and 0.03% respectively.

Keywords: Gratzel cell, dye-sensitized, zobo, titanium (IV) oxide.

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 a modern photovoltaic system 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[5,6]. Thin films used in these photovoltaics are porous and thick, on the order of 10µm, and usually are prepared by coating a dispersion of commercial nanoparticles onto a conductive transparent oxide[1].

Titanium dioxide, particularly in the anatase form, is a photocatalyst under ultraviolet (UV) light[1,7]. The degradation of organic pollutants in water and gaseous formaldehyde by TiO_2 photocatalysis has attracted extensive attention during the most recent decade due to its optical and electronic properties, low cost, chemical stability and non-toxicity[7,8]. 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[10].

There are many deposition methods that can be used to prepare TiO_2 thin films, such as electron beam evaporation, ion-beam assisted deposition, DC reactive magnetron sputtering, RF reactive magnetron sputtering, sol-gel methods, chemical vapor deposition[1,10]. Among the different methods for the preparation of thin titania layer, sol-gel method has many advantages, particularly the possibility of producing large surfaces[11]. 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)[3,7]. 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[7-9]. Thus light of wavelength less than 385 nm, will excite electron from the valence band to the conduction band, producing an electron-hole pair. The refractive indices at 500 nm for anatase and rutile bulk titania are about 2.5 and 2.7, respectively[3]. The rutile phase is thermodynamically stable at all temperatures up to the melting point, while both anatase and brookite phases can be transformed into the rutile phase irreversibly by thermal treatment at certain temperature which depends on the preparation method, dopant concentration, and atmospheric conditions[5]. For many of above mentioned applications, the anatase-to-rutile phase transformation is not favoured since anatase has distinctly high catalytic activity than rutile. Also, this transformation results in a dense rutile phase, which is a disadvantage to photocatalysis. Undoped anatase TiO_2 is active only under ultraviolet (UV) light because of its wide band gap rendering it inactive under visible light, which

causes most of the solar spectrum to go unutilized. Extending the optical absorption of anatase to the visible region, therefore, is one of the important subjects for the increased utility of TiO_2 in the fields of photocatalysis. Impurities doping induces substantial modifications in electrical and optical properties of semiconductor materials. By doping with different impurities, the structural properties of titania thin films can be modified and consequently its optical constants and absorption spectrum.

Dye-sensitized solar cells (DSSCs) show a very promising future in the field of photovoltaic cells[4,12]. DSSCs differ from conventional semiconductor devices in that they separate the light absorption process from the charge collection process, mimicking natural light harvesting procedures in photosynthesis, by combining dye sensitizers with semiconductors[13,14]. This enables the use of wide band gap but cheap oxide semiconductors such as TiO_2[2,4,15,16]. A DSSC typically consists of a monolayer of photoactive dye molecules anchored onto the nanoparticles of a wide band gap semiconductor, an electrolyte and a counter electrode[2,17].

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[4,14]. Although highly effective, with current maximum efficiency of 11%, the costly synthesis and undesired environmental impact of those prototypes call for cheaper, simpler, and safer dyes as alternatives[14,18,19]. Natural pigments, including chlorophyll, carotene, and cyanin, are freely available in plant leaves, flowers, and fruits and fulfill these requirements. Experimentally, natural-dye sensitized TiO_2 solar cells have reached an efficiency of 7.1% and high stability[14,20]. Higher efficiency over 8.0% has been obtained using similar synthetic organic dyes[14]. This research work studies the photovoltaic performance of a DSSC fabricated with *anthocyanin*-dyed TiO_2 electrode by comparing its characteristics with those of un-dyed TiO_2 electrode. *Anthocyanin* dye is a local dye extracted from hibiscus sabdariffa which is a popular plant in the Northern part of Nigeria.

Material and Methods

Electrode preparation: In this work, an equal amount of well blended powdered activated carbon (PAC) and a kind of natural graphite powder (NGP) was used as counter electrode for both cells[21]. Carboxy ethyl cellulose (natrosol) and tin II chloride were used in a sol-gel process to produce our binder. The well blended carbon mixture was mixed with the binder in the ratio of 3g/ml to obtain our carbon paste for the counter electrode. The active area of a 2.5cm x 2.5cm fluorine-doped tin oxide conducting glass substrate (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 film. Before deposition, the glass substrate was cleaned with acetone, then methanol and etched through plasma treatment for 1min. The carbon paste was applied at one of the edges of the conducting glass and distributed with a squeegee sliding over the tape-covered edges. A hot air blower was used to dry the electrode for about 3 minutes before removing the adhesive tapes. The edges were cleaned with ethanol. The carbon electrode was sintered at 150^0C in a furnace (carbolite 201 tubular furnace) for about 15 minutes.

Nanocrystalline titanium (IV) oxide (Ti-nanoxide T/sp, Solaronix SA, Rue de e' duriette 128) was used as photo-electrode. The same blade method used in depositing the counter electrode was adopted in depositing the TiO_2 layer. The film was allowed to dry naturally without blowing before removing the adhesive tapes. The edges were also cleaned with ethanol. The electrode was sintered for 30 min at 400 ^{o}C using the same carbolite 201tubular furnace.

Dye sensitization: The *anthocianin* dye used in sensitizing the mesoporous TiO_2 film was extracted from hibiscus sabdariffa which a common edible plant is called zobo by Nigerians. Extraction of the pigment from hibiscus sabdariffa was achieved through this simple process: i. Blend the hibiscus sabdariffa using electric blender. ii. Add 90% ethanol and continue blending. iii. Use sieve to extract the pigment which forms our dye.

The TiO_2 photo-electrode was immersed into a solution of the local dye overnight. The electrode was preheated at 80^0C for 15 minutes before it was dipped into the dye solution. Another photo-electrode was sensitized using ruthenium-620 organic dye.

Cell fabrication: Sealing gasket (SX 1170 – 60 PF, Solaronix SA) brings the ease of using a 60µm thick hot melt foil for sealing the cells. The sealing gasket was cleaned in ethanol before placing it on top of the dyed working electrode. The counter electrode was gently placed on top of the frame and held in position with a clamp with the conducting carbonized side towards the working electrode. The set up was held over a hot plate for 1 min at 150 ^{o}C before allowing it to cool for a few minutes. A few drops of the electrolyte (Iodolyte R-150, BN408/071008SN, solaronix SA) were introduced in between the electrodes and the cell was sealed using Amosil 4R sealant (BN011008SN, Solaronix SA). Electrical contacts were made by applying silver paint along one of the edges on the conducting side of each electrode. A second cell was assembled using un-dyed TiO_2.The active surface area of the *anthocianin*-dyed and un-dyed cells was 1.54cm^2 and 2.25cm^2 respectively.

Measurements: The thickness of both electrodes was measured using Dektak stylus 7.0 surface profiler. The sheet resistance of the carbon counter electrode was measured using dual-Pro 301 (auto calculating 4 pt. Probe resistivity test system). The optical absorbance of the *anthocianin*-stained TiO_2 was measured using Avaspec 2.1 spectrophotometer. The I-V characteristics was

measured using an Oriel class A solar simulator (AM 1.5, 100mW/cm^2).

Results and Discussion

The thickness and sheet resistance of the carbon counter electrode were 4.2µm and 15.4ohms/square respectively. The thickness of the photo-electrode deposited using the same blade method was 6.2µm. *Anthocyanin*-stained TiO_2 electrode showed an outstanding optical absorbance within the wavelength range of 283nm – 516nm. Peak absorbance of 2.16A.U., 2.26A.U. and 2.38A.U. were recorded in the UV region at 324.45nm, 344.87nm and 369.35nm respectively(figure-1).

Appreciable absorbance was recorded in the visible region with two outstanding peaks; 2.26A.U. and 2.16A.U. at the wavelength of 405.99nm and 426.47nm respectively.

Meanwhile, Lee and Kang, 2010 studied an unstained nanoporous TiO_2 and obtained optical absorbance of 1.3A.U. and 1.2A.U. at 200nm and 350nm respectively but no absorption was recorded beyond UV region[22]. Also, a bare TiO_2 nanowire studied by Meng et al, 2008 showed no optical absorption beyond 400nm[14]. Hence, the *anthocyanin* dye greatly improved the optical absorption capacity of the TiO_2 electrode. figure 2 and figure 3 are the photocurrent-voltage characteristics of DSSCs fabricated with the *anthocyanin*-dyed and un-dyed working electrodes respectively.

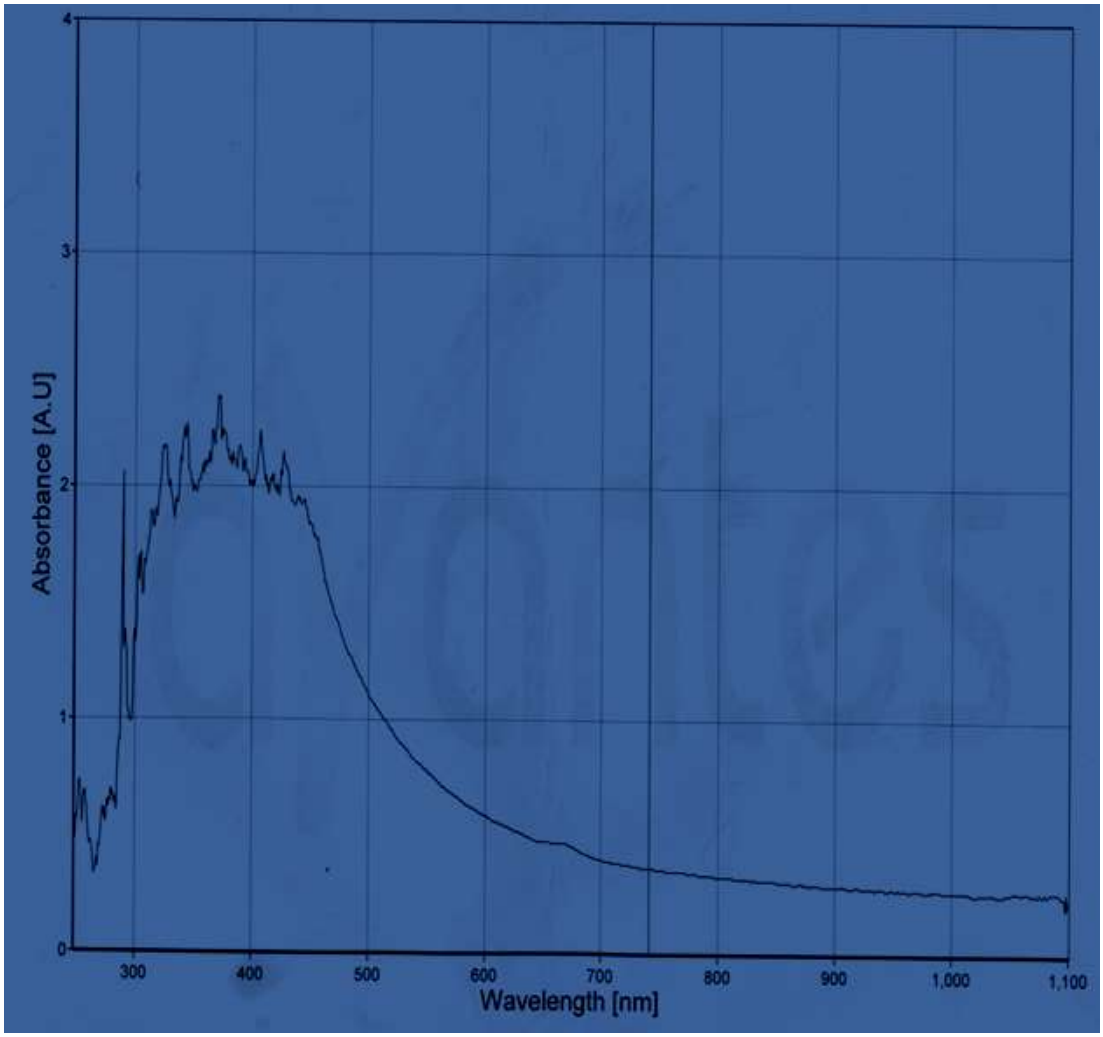

Figure – 1
Optical absorbance of *anthocyanin*-stained TiO_2

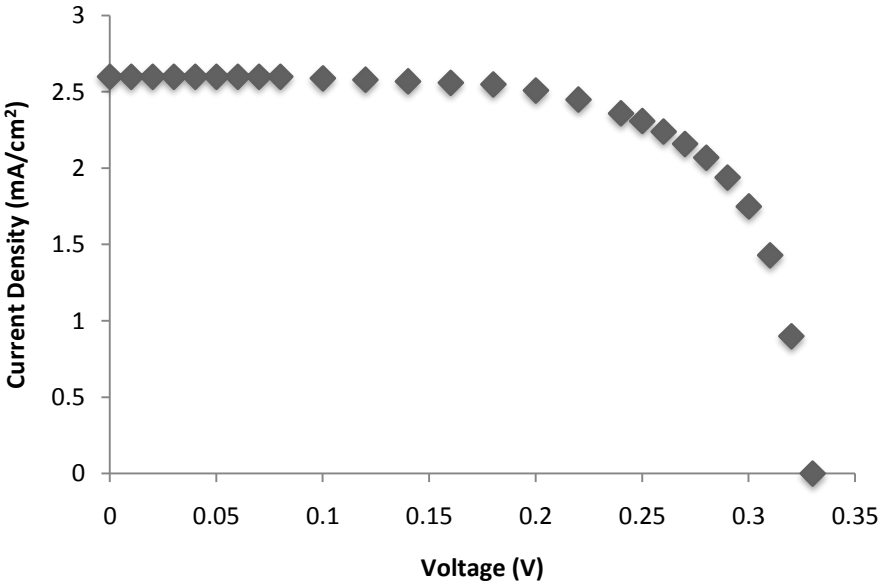

Figure - 2
The I-V curve for the cell sensitized with *anthocyanin* dye

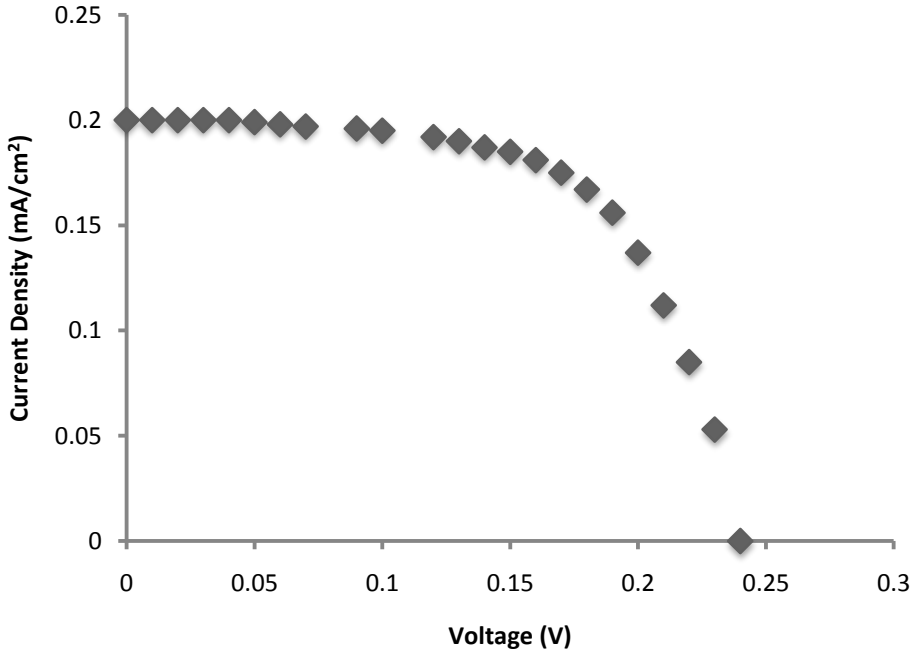

Figure - 3

The I-V curve for the plain cell

The cell parameters obtained for the *anthocyanin*-dyed electrode 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 un-dyed 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 photovoltaic performance of the *anthcyanin*-dyed cell was outstandingly great when compared with the performance of the un-stained cell.

Conclusion

Natural pigment from hibiscus sabdariffa will have a promising future as alternative photo-sensitizer for the wide band gap titanium (iv) oxide electrode. Even though the *anthocyanin*-dyed cell showed a lower light to electricity conversion efficiency than the current maximum DSSC efficiency, the local dye is considerably cheaper than the ruthenium complexes. Also, comparison of results shows that the photo-conversion efficiency of the *anthocyanin*-dyed cell was about twenty times higher than that of the un-dyed cell. The poor absorption of solar radiation by the plain cell despite comparable high surface area reduces the injection efficiency of carriers, and thus leads to poor photovoltaic performance.

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