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A Plasmonic Effect of Coelastrella sp Mediated Silver Nanoparticles Embedded in TiO_2 Photoanode for Dye-Sensitized Solar Cells

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ABSTRACT

Semiconductor oxide layer like ZnO and TiO_2 coated FTO glass act as photoelectrode for dye-sensitized solar cells; enhanced power conversion by DSSCs is achievable through the selection of the optimum conditions for the fabrication process. A plasmonic effect of bio-synthesized silver nanoparticles (AgNPs) embedded in TiO_2 photoanode was studied for performance improvement. Silver nanoparticles were synthesized using the cell-free extracts of Coelastrella sp MG257917, the properties of the nanoparticles were determined using UV-vis spectrophotometry, Fourier Transform Infrared Microscopy (FT-IR), Scanning Electron Microscopy (SEM), and Energy - Dispersive X-ray (EDX). The influence of the nanoparticles embedded at different quantity and different dye loading time on optical properties of the modified photoanode was carried out using UV-vis spectrophotometry. The fabricated cells were exposed to a dark and light intensity of 100 mW/cm^2 to evaluate the solar to electrical conversion efficiency. The nanoparticles were spherical and the particle size ranged from 21 -105 nm. The EDX examination revealed that silver was the element with the highest composition (97.96 %). The optimum quantity of CO-AgNPs to TiO2 was 1:1 while the dye loading time was 15 hours. The solar to electrical conversion efficiency of the biosynthesized CO-AgNPs cells was 1.09 % (light) and 0.95 % (dark) while conversion efficiency of the TiO_2 cell was 0.03 % (under light) and 0.004 % (dark).

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1.0 Introduction

Nanotechnology is a new area of research in science which involves the synthesis of nanomaterials from already existing materials ranging from living to non-living things. The resulting nanomaterials from the synthesis have been known to possess distinct optoelectronics and physical properties that have qualified them for application in wide areas (Castro *et al*. 2013). Nanoparticles (NPs) are very minute in terms of size but more reactive, this is because of the increased surface area of reaction which results in improved properties and reaction of the material (Vincy *et al*. 2017). Nanoparticles could either be naturally synthesized, engineered, or incidental (Vincy *et al*. 2017). Different methods exist through which metallic nanoparticles can be produced; these include physical and chemical methods. These methods are associated with the production of materials that are not easily biodegraded and it also has a deleterious effect on the immediate environment (Kumar *et al*. 2016). Biological Synthesis of nanoparticles using biologically based materials is recently encouraged because of low toxicity level, cost-effectiveness, and environment-friendliness (Singaraelu *et al*. 2007).

Nanoparticles have found wide applications in various fields which include: photography; production of fluorescent tubes, laser and sensor; biological labelling; photocatalysts in photoreactions, optoelectronics, production of cosmetics, photonics coatings, drug delivery, production of antimicrobial agents, textile engineering, wastewater treatment, biotechnology and bioengineering (Niemeyer et al. 2003; Lee and Jeung 2005; Wiley *et al*. 2007; Soloveve *et al*. 2007; Buzea et al. 2007; Cheng *et al*. 2008; Cao *et al*. 2010; Son *et al*. 2011; Vilela *et al*. 2012). Nanoparticles have been synthesized from different biological materials and these include bacteria, fungi, plant, yeast, actinomycetes (Kaushik *et al*. 2010; Huh 2011; Nayanayanan and Sakthivel 2000, 2011). From all the biomaterials that have been considered previously, synthesis of nanoparticles from algae has not been fully exploited to the best of our knowledge.

Synthesis of nanoparticles from algae has shown some advantages over other organisms equally used as bio-agent in synthesizing nanoparticles. These advantages include: reduction in time of synthesis (Thakkar *et al*. 2010; Rauwel *et al*. 2015) its application in scaling up of silver nanoparticles and absence of culture and maintaining process (Singh *et al*. 2012). Algae-based nanoparticles have been known for their antimicrobial activities against pathogenic organisms. Silver nanoparticles synthesized using *Scenedesmus abundans* (Aziz *et al*. 2014; *Caulerpa racemosa* (Kathiraven *et al*. 2014); *Synechococcus* sp, *Phormidium* sp, *Gleocapsa* sp, *Spirulina* sp, *Lyngbya* sp, (Sudha *et al*. 2012); *Chlorella vulgaris*, *Chaetoceros calcitranta* (Karthikeyan *et al*. 2015) and *Neodesmus pupukensis* (Omomowo *et al*. 2020) have been reported as potential antimicrobial agent against some pathogenic bacteria. The application of algal-based nanoparticles in optoelectronics especially in photovoltaic cells has been rarely reported.

Dye-sensitized solar cells (DSSCs) are photovoltaic cells which absorbs photon energy from sunlight and efficiently converts solar into electrical energy with the aid of different photoelectrochemical components which are inexpensive (Lim *et al*. 2014; Fan *et al*. 2017). Different components interact together in DSSCs for its effective performance. These components include an electrode, electrolyte, counter electrode, and light-absorbing dye. When the cell is exposed to light, the dye material absorbs photon energy of a known value resulting in excitation of an electron. This electron migrates from the positively charged dye and gets deposited on the metal oxide semiconductor which has a wide bandgap, it then moves through the electrode to an external circuit (Gallegos and Alvarado, 2015; Dumbrava *et al*. 2016).

A semiconductor or photoanode can effectively improve the performance of DSSCs if it has a large surface area and the thickness which can enhance the rate and impact of dye loading unto it (Rothenberger *et al*. 1999). The use of nanomaterials as photoanodes has been reported as the best choice in harvesting of light and extraction of charges thereby resulting in enhanced photovoltage, photocurrent, and fill factor (Panchal and Shah 2015). Titanium oxide has been commonly used as photoanodes because it is cheap, readily available, non-toxic and has a wide energy bandgap (Frank *et al*. 2004; Green *et al*. 2005; Nazeeruddin *et al*. 2011). Apart from TiO_2 as photoanodes, zinc oxide has also been adopted as photoanode having the second-best performance after TiO_2 (Keis *et al*. 2002; Longyue *et al*. 2006; El- Agez *et al*. 2012).

The performance of DSSC also depends on the morphology, phase compositions, and other properties (Alivov and Fan 2009; Li *et al*. 2009). Improving the performance of TiO_2 has been achieved by mixing

TiO_2 with different size, phase composition, and morphology (Zhang *et al*. 2008; Liu and Aydil 2009). Also, TiO_2 has been coated with metals to enhance its performance as photoanode, the challenge encountered using these metal coated photoanode was thermal instability (Mcevoy 2007; Yella 2011; Macaira 2013). In order to improve the performance of photoanodes without the use of toxic chemicals or metals which can result in thermal instability, there is need to investigate materials which are non -toxic and at the same time stable in operation. The use of algal mediated nanoparticles as co-photoanode material to enhance the performance of DSSCs has been rarely documented. In this work, silver nanoparticles synthesized using microalgae were used as co photoanode material with TiO_2.

2.0 Materials and Methods

2.1 Harvesting and preparing microalga powder

Coelastrella sp MG257917 previously isolated in our lab was cultured in BG 11 medium (Adenigba *et al*., 2020). The culture flask was incubated under natural light and the flasks were shaken twice daily to allow uniform penetration of light. The alga biomass was harvested on the 21st day using a centrifuge at 5000 rpm for 20 min. The biomass of the alga was washed with sterile distilled water to remove the culture medium that was present in the cell (Aziz *et al*. 2014). The algae powder was obtained by drying the filtrate obtained at 80^oC.

2.2 Synthesis of silver nanoparticles from microalgae

Silver nanoparticles were synthesized from the microalgae following the work of Aziz *et al*. (2014). One gram of algal powder was hydrolyzed by adding 100 ml of distilled water to the powder and boiled at 100^oC for 20 minutes. The cell-free extract of the microalga was removed from the mixture in a centrifuge at 5000 rpm for ten minutes. To synthesis silver nanoparticles from the extract, 90 ml of 1 mM $AgNO_3$ was added to 1 ml of the extract. The mixture was observed for colour change.

2.3 Characterization of silver nanoparticles synthesized from microalgae

Bioreduction of silver nanoparticles was first observed with the change in colour and the spectra of the reaction mixture were measured using a Double beam spectrophotometer using a quartz cuvette of 1 cm optical path length with spectra range from 300 and 800 nm. The silver nanoparticle of the microalga was prepared for scanning electron microscopy (SEM) to determine the size and morphology of the nanoparticles. The elemental composition of the silver nanoparticles was measured with the same equipment. FT-IR measurement was carried out using Fourier-transform infrared spectroscopy (FTIR, Nicolet Avatar, Thermo, US) in the range of 4000-400 cm^{-1} was used to determine the presence of the different functional groups present in the silver nanoparticle.

2.4 Extraction of dye from the macroalga

Organic dye was prepared from a macroalga, *Eichhornia crassipes*. *Eichornia crassipes* were washed with distilled water, dried, and ground to powder. One gram of the powder was immersed in 100 ml of absolute ethanol; the mixture was left for 48 hrs. The solution was filtered using Whatman filter paper (125 mm), the biomass was discarded while the dye- ethanol solution was obtained. The solution was placed in a rotary evaporator to remove the solvent from the dye. The UV absorption spectrum of the dye was measured and the dye was used as a sensitizer in DSSCs.

2.5 Determination of optimum conditions for the efficiency of dye-sensitized solar cells.

2.5.1 Determination of the optimum quantity of titanium dioxide and nanoparticles as photoanode

Three gram (3g) of TiO_2 nanopowder was poured into 25 ml of ethanol, the mixture was sonicated for 45 minutes at 90 °C on a hot plate with a magnetic stirrer until a homogenous paste was obtained. Suspension of silver nanoparticles of *Coelastrella* sp (CO-AgNPs) and TiO_2 were prepared using different mixing ratio to determine the best quantity of each material which will give the highest absorbance. The volume of the nanoparticles suspension ranged from 1 ml to 6 ml with one step while the quantity of TiO_2 added to the nanoparticles was 1 ml and this was made constant. Optical characterization was carried out to determine the best concentration.

2.5.2 Determination of the best dye loading time

The best algal silver nanoparticle -TiO_2 mixing ratio from the previous experiment was selected. Six different substrates were prepared for this experiment. The substrates were placed in the dye and were withdrawn from the dye every 3 hours (i.e 3, 6, 9, 12, 15, and 18 hrs). The substrates were characterized after 18 hours and the absorbance of each dye loading time was calculated and compared.

2.6 Fabrication of dye-sensitized solar cell

2.6.1 Assemblage of dye-sensitized solar cell

The optimum conditions obtained above were adopted in the fabrication of algal dye-sensitized solar cells. The Doctor Blade technique was used in the deposition of the CO-AgNPs +TiO_2 on the conductive glass while a control photoanode with the only TiO_2 without any nanoparticles was also prepared. The photoanodes were placed on a hot plate to be heated at 150 °C for 10 min. Each photoanode was dipped into a dye solution for the optimum dye loading time obtained in the earlier experiment. The counter electrode was prepared by using a graphite pencil to deposit graphite on the conductive side of the glass. The anode was removed from the dye solution, rinsed with ethanol, and combined with the cathode, Lugol's iodine which was used as the electrolyte was placed in between the two electrodes. A binder clip was used to hold the electrodes together.

2.6.2 Current-Voltage (IV) characterization of the fabricated algal-based DSSC

The fabricated DSSC of each microalga was characterized to obtain both the photocurrent and voltage using a solar simulator (Newport model No. 9600) with incident light power of 100 mW/cm^2 (AM 1.5). The cell surface area exposed to the light was 1 cm^2. The cell was exposed to light and dark to investigate the behaviour of the bio-synthesized AgNPs cells under different conditions.

3.0 Results and Discussion

The addition of 1 mM $AgNO_3$ to the cell-free extract of *Coelastrella* sp resulted in a colour change of the mixture from pale green to brown within 25 minutes of incubation (Figure 1). The rapid colour change was compared with existing reports on the biosynthesis of nanoparticles using algae. The colour change from light green to brown observed in the synthesis of silver nanoparticles in this work is in line with the report of Dubey *et al*., 2009; Ahmad *et al*., 2003; Aziz *et al*., 2014; Karthikeyan *et al*., 2015. A similar change in colour was observed in the silver nanoparticles synthesized from microalgae. The colour change was reported to be a result of excited electrons which are the outcome of plasmon vibrations.

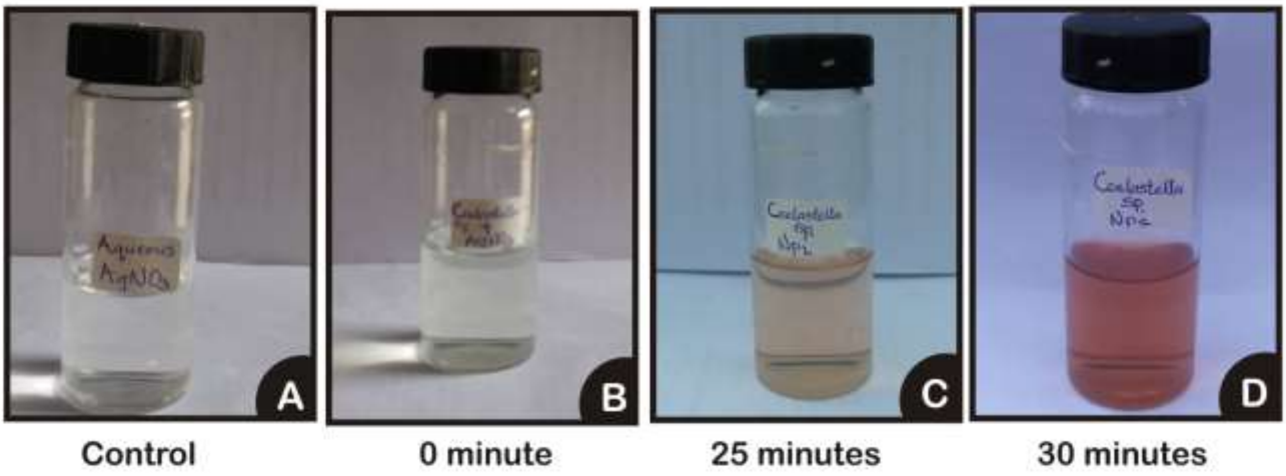

Figure 1: Progressive colour change in the bio-synthesized AgNPs (A= 1 mM AgNO3; B= mixture of *Coelastrella* sp and $AgNO_3$ at 0 hr; C= synthesis at 25 minutes; E= synthesis at 30 minutes).

3..2 UV-visible absorption spectrophotometry

The bioreduction process was further monitored using UV-vis spectrophotometer, the surface plasmon resonance of the nanoparticles of *Coelastrella* sp was at 430 nm (Figure 2). This absorption spectrum was similar to those reported for silver nanoparticles of *Turbinaria conoides*, a brown marine alga which had a broad spectrum at 420 nm (Rajeshkumar *et al*. 2012). Karthikeyan et al. (2015) also reported synthesis of AgNPs from both *C.vulgaris* and *C. calcitrans* with a strong Plasmon vibration at 436 nm and 420 nm respectively. Aziz *et al*. (2014) reported a broad peak of 420 nm from AgNPs synthesized from *Scenedesmus abu.*

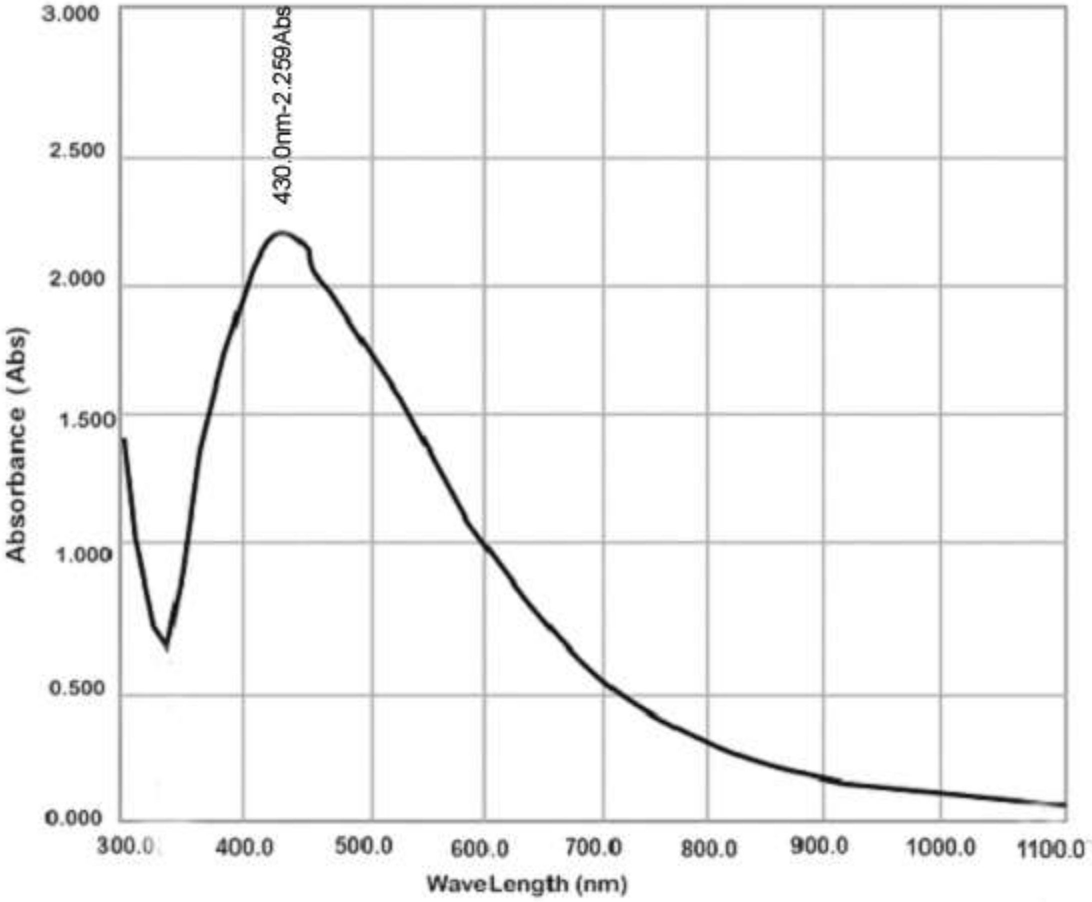

Figure 2: UV-vis spectrum of silver nanoparticles synthesized from *Coelastrella* sp.

3.1.3 Scanning Electron Microscopy

The determination of both morphology and size of the nanoparticles was carried out using SEM. The polydispersed nanoparticles have a spherical shape with size ranging from 21 -105 nm (Figure 3). The spherical shape could be as a result of the presence of some capping agents which have adhered to the surface of the AgNPs (Vivek *et al*. 2011). Spherical shaped silver nanoparticles from *Caulerpa racemosa* ranged in sizes from 5 to 25 nm, this was lower than the nanoparticles synthesized in this work. Sudha *et al*. (2013) synthesized nanoparticles from some cyanobacteria isolated from the mangrove forest. The nanoparticles were polydispersed and spherical with sizes ranging from 44 to 79 nm.

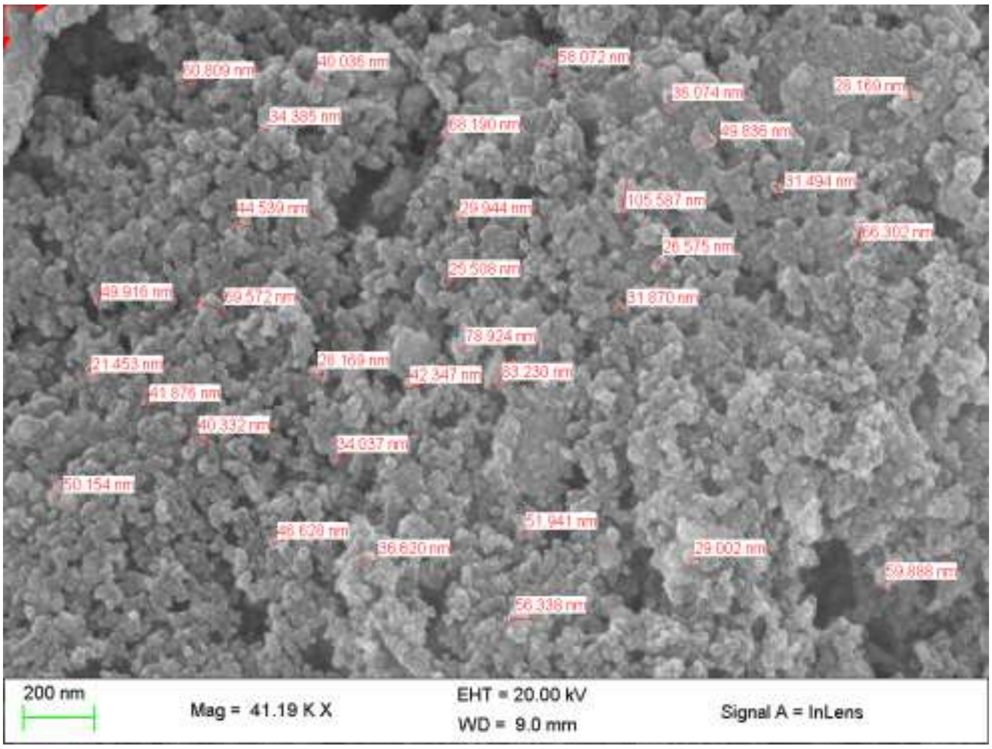

Figure 3: SEM image of silver nanoparticles synthesized from *Coelastrella sp*

3.1.4 Energy- dispersive x-ray

The EDX carried out on CO-AgNPs showed that silver was the most prevalent element and the weight composition of 97.96 % and a strong energy signal at 3 keV (Figure 4).

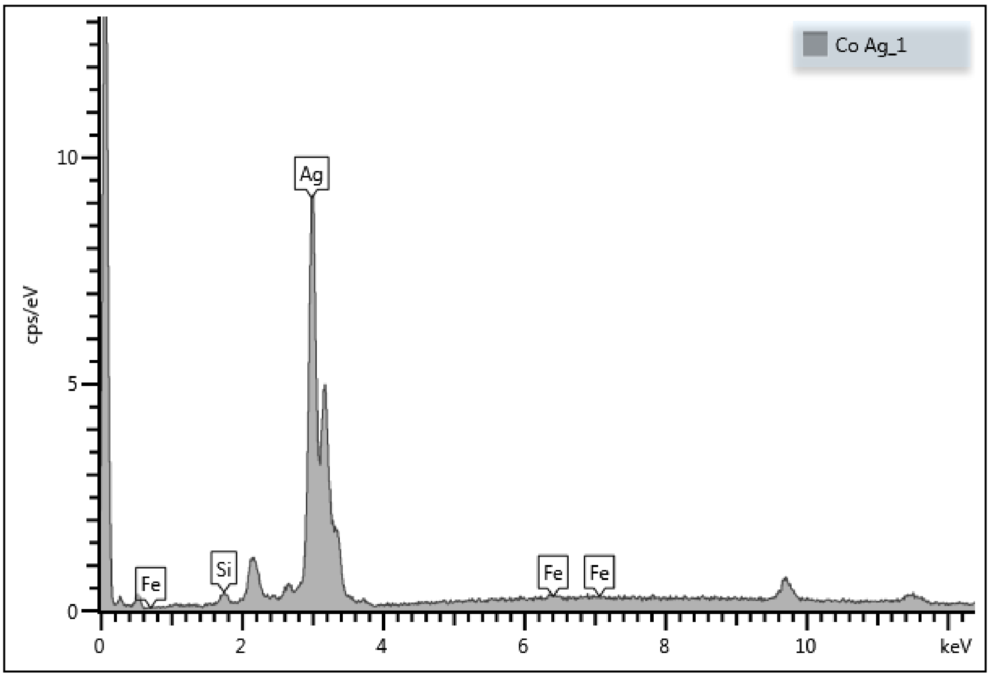

Figure 4: EDX of silver nanoparticles from *Coelastrella sp*

3.1.5 Fourier transform infrared spectroscopy

The FT-IR spectroscopy reveals the presence of different functional groups with peaks at 3287 cm^{-1}, 2103 cm$^{-1,}$ and 1637 cm^{-1} (Figure 5). These are typically broad peak H - bond of alcohol, C≡C and C≡N stretching vibrations, and olefinic C=C stretch of alkenes. The functional groups which took part in the synthesis of the nanoparticles were H-bond of alcohol, C≡C and C≡N stretching vibrations, and olefinic C=C stretch of alkenes (Devi and Bhimba 2012). These functional groups were responsible for the capping and stabilization of nanoparticles (Castro *et al*. 2013). Similar to the FTIR analysis in this study, Zheng *et al*. (2015) reported the participation of aromatic compounds, alkane, or amine as capping agents for silver nanoparticles in seawater.

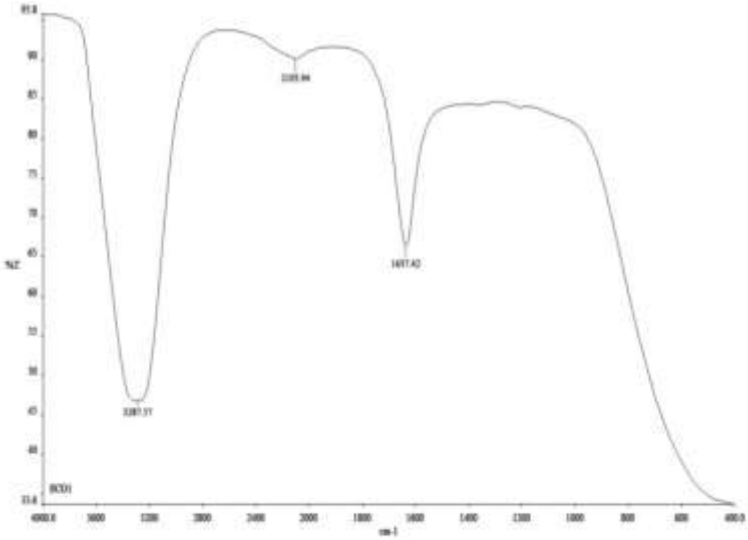

Figure 5: FTIR spectra of silver nanoparticles synthesized from cell-free extract of *Coelastrella. sp.*

3.2 Uv-Vis absorption Studies of Extracted Dye from E. crasspies

The dye extracted from *Eichornia crassipies* had five different absorbance peaks at 414.0 nm, 504 nm, 536 nm, 608 nm, and 666 nm (Figure 6). It was able to absorb light at both ultraviolet and visible region. Absorbance at 666 nm suggests the presence of chlorophyll while the other spectra confirm the presence of other pigments apart from chlorophyll. This agrees with a report by Adedokun *et al*. (2016) that carotenoids absorb spectra with wavelength ranging from 400 -550 nm. Also, Dumbrava *et al*. (2016) extracted dye from *Enteromorpha intestinalis* and had absorbance spectra with two broad bands and two peaks on 413 nm and 663 nm which confirm the presence of both carotenoids and chlorophyll. Chlorophyll is important for energy harvesting, energy conversion from solar to chemical energy, and transfer of electrons to the photoanode (Adedokun *et al*. 2017). However, carotenoids are also important pigments in photosynthetic organisms like algae. They aid in solar energy absorption for photosynthesis and also prevent the destruction of chlorophyll from the effect of excessive light (Armstrong and Hearst, 1996).

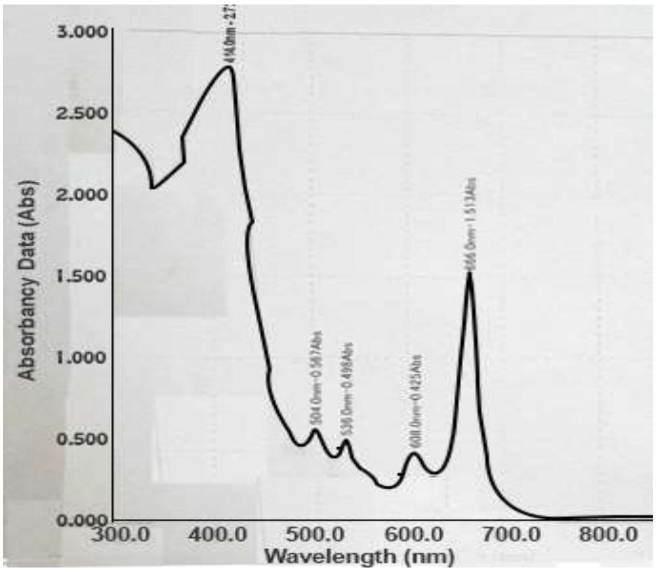

Figure 5: UV -vis absorption spectra of dye extracted from *Eichornia crassipies*

3.3 Optimum conditions for the efficiency of dye-sensitized solar cells.

3.3.1 Optical properties of nanoparticles at different TiO_2 and nanoparticles concentration

Different quantity of *Coelastrella* sp based silver nanoparticles were embedded in TiO_2 nanopowder, the optical properties of each suspension in terms of absorbance and reflectance were measured. The optimum quantity with the highest absorbance of 3.14 a.u at 252 nm for CO-AgNPs was 1:1 (1 ml of AgNPs in 1 ml of TiO_2). Much has not been reported on the use of AgNPs from microalgae as co photoanode material with TiO_2. The cells had maximum absorbance mostly at the ultraviolet region with reflectance at the visible region for all the CO-AgNPs while the maximum reflectance of 34.33 % at 484.75 nm was obtained at 1:2 (Figure 6). The maximum absorbance was obtained at 1:1 and the lowest reflectance was obtained at the same combination. The higher the absorbance of the cell, the lower the reflectance.

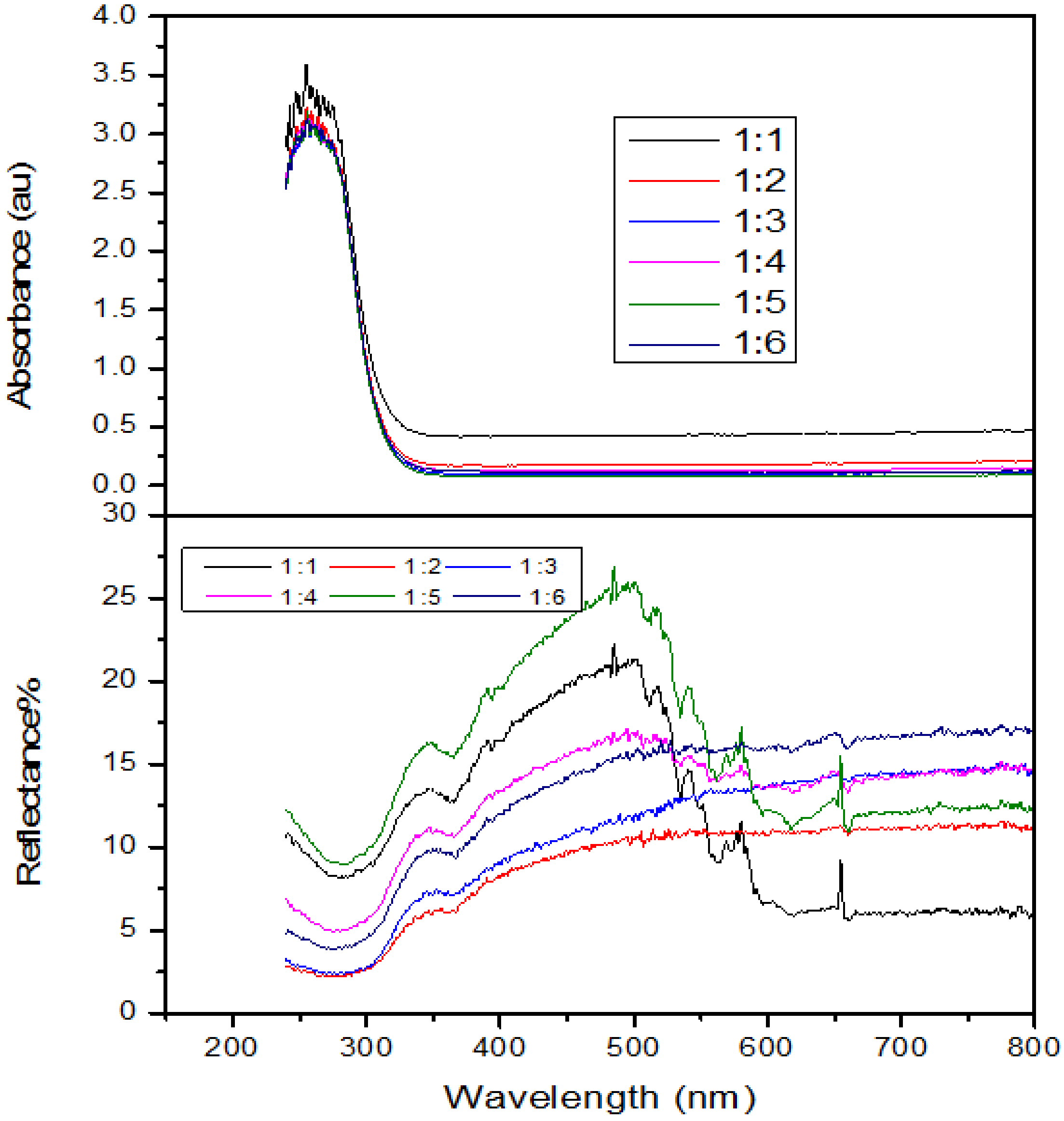

Figure 6: Optical properties of TiO_2 and silver nanoparticles from *Coelastrella* sp at different concentrations.

3.6 Effect of different dye loading time on the optical properties of microalgal mediated cells

The TiO_2 and silver nanoparticles coated substrate of each micro-alga with the highest absorbance from the previous experiment were immersed in the dye. They were removed at different dye loading hours (3 hours, 6 hours, 9 hours, 12 hours, 15 hours, and 18 hours). The substrate was characterized to determine the absorbance and reflectance at each dye loading time. The dye loading time for AgNPs substrate of

Coelastrella sp with the maximum absorbance of 4.32 a.u at 248 nm was 15 hours, while the reflectance of 34.83 % at 998.94 nm was at 18 hours (Figure 7). The optical measurement in terms of absorbance and reflectance showed that the longer the cells stayed in the dye, the better the performance of the cell. Taya *et al*. (2013) reported the extraction of natural dyes from both fresh and dried materials, the optimum dye loading time for the cell in spinach extract was 12 hours.

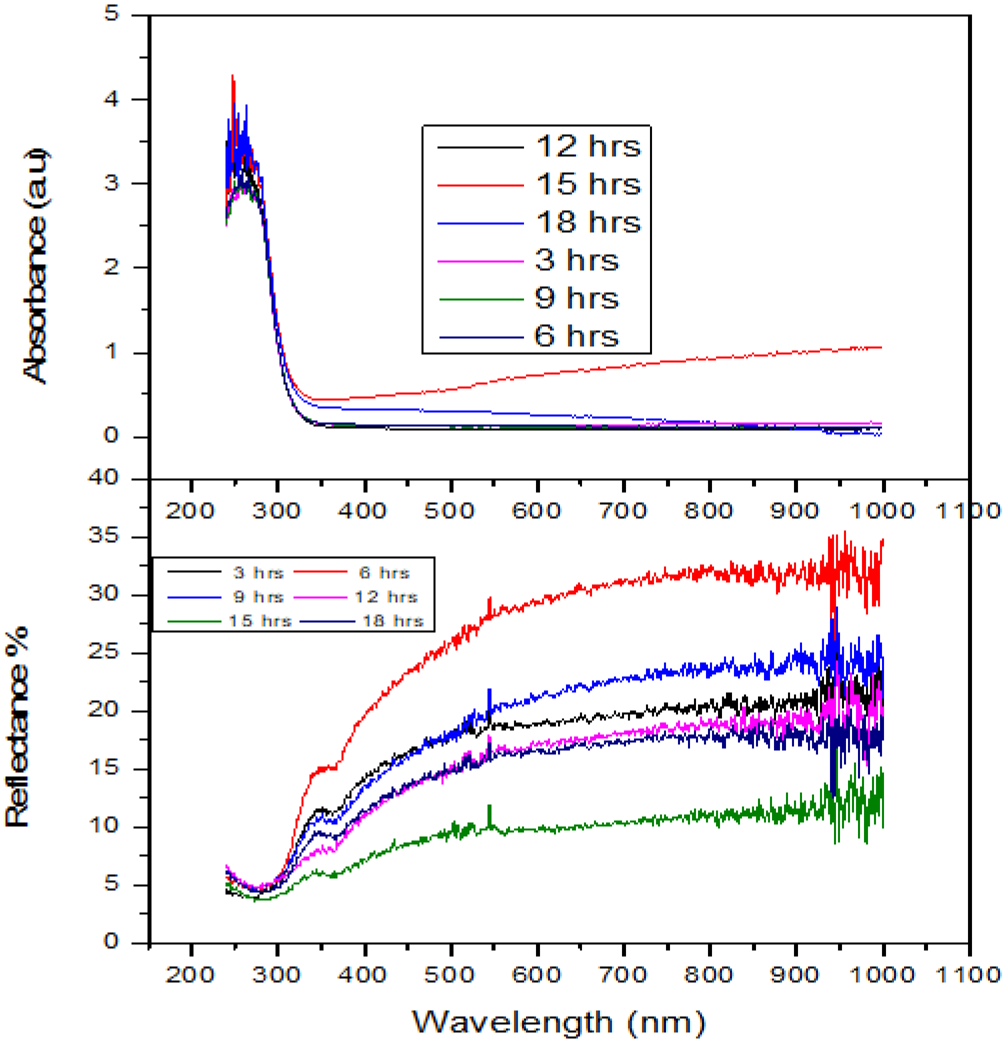

Figure 7: Optical properties of *Coelastrella* sp AgNPs substrate at different dye loading time

3.7 Power conversion efficiency of algal-based dye-sensitized solar cells

The behaviour of the algal nanoparticles and TiO_2 based DSSCs were examined under simulated solar light of 100 mW/cm^2. The graph of the photocurrent produced against voltage was plotted for the cell under both light and dark conditions. The DSSC fabricated using AgNPs of *Coelastrella* sp embedded in TiO_2 as photoanode had a maximum current density of 3.6 mA/ cm^2 under illumination while 3.7 mA/ cm^2 was obtained without illumination (Figure 8). The cell which contained only TiO_2 as photoanode had a photocurrent density of 0.05 mA/ cm^2 under the light while 0.019 mA/ cm^2 was the dark current density in the absence of light (Figure 9).

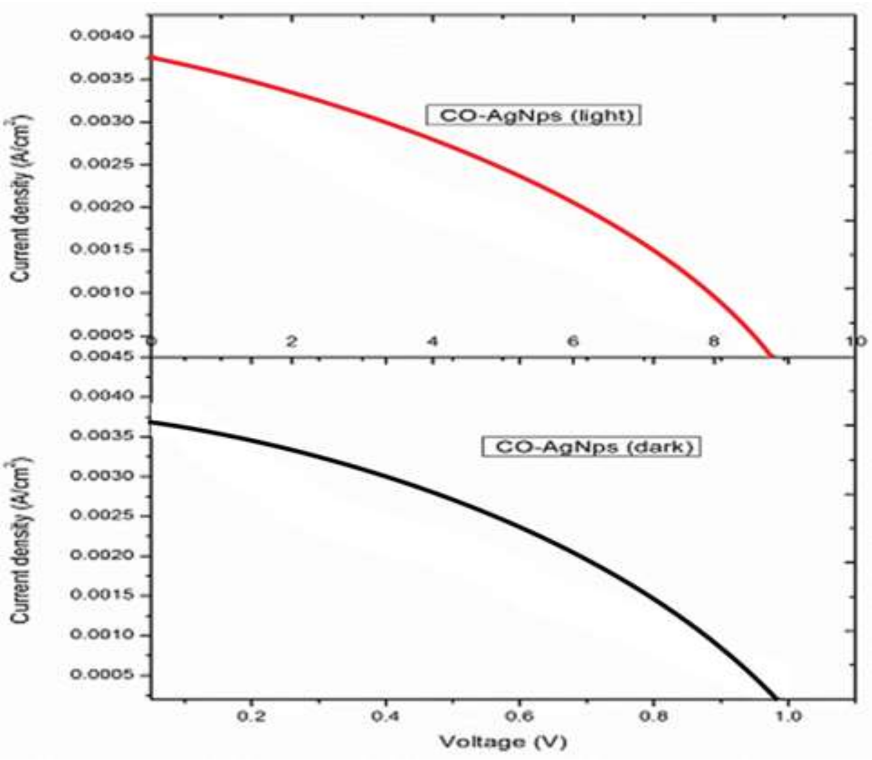

Figure 8: Photocurrent and voltage plots obtained under light and dark by *Coelastrella* sp AgNPs -TiO_2 based DSSC.

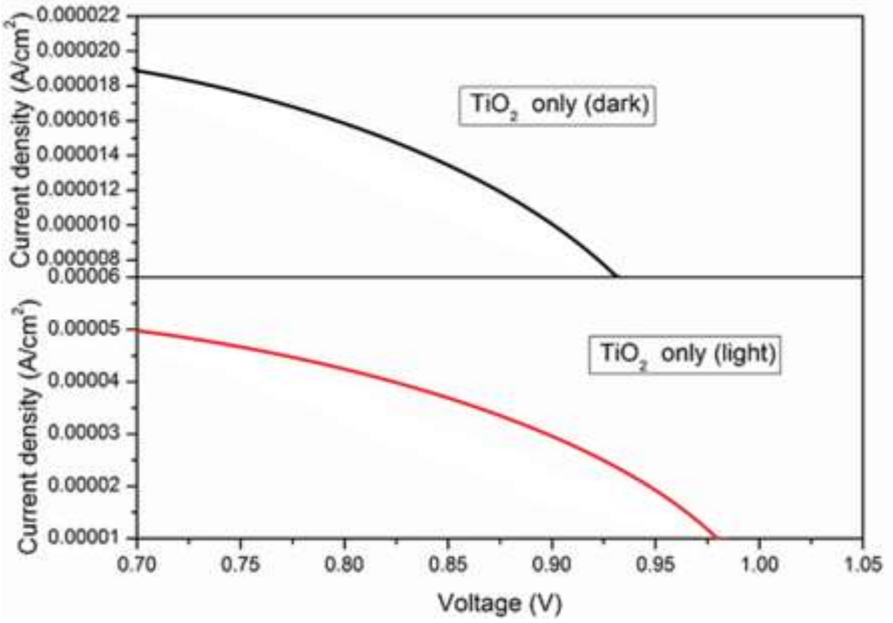

Figure 9: Photocurrent and voltage plots obtained under light and dark by TiO_2 based DSSC.

Photoelectrochemical parameters which include: short circuit current (Jsc), open-circuit voltage (Voc), maximum current (Imax), maximum voltage (Vmax), fill factor (FF) and energy conversion efficiency (Ƞ) were extracted from the current and voltage (IV) relationship of the cell (Table 1). The bio-synthesized AgNPs based cell had solar to the electrical energy conversion efficiency of 1.09 % when exposed to light while the conversion efficiency of the cell in the absence of light was 0.95 %. On the other hand, the cell with only TiO_2 as photoanode had a conversion efficiency of 0.03 % when exposed to light and 0.004 % in the absence of light. Algal based nanoparticles have found use in different areas, especially as antimicrobial and antioxidant agents. The photoelectronic properties of algal-based nanoparticles were harnessed in this work and the nanoparticles of *Coelastrella* sp was used in combination with TiO_2 as photoanode in DSSC. There are different components in DSSC that interact to determine the overall efficiency of the cell.

The highest conversion efficiency was obtained with cells exposed to light rather than when expose to dark. The bio-synthesized AgNPs based photoanode performed best under both light and dark conditions while the least efficiency was from photoanode with the only TiO_2. The performance of the bio-synthesized AgNPs based DSSCs could be as a result of the algal nanoparticles embedded in TiO_2 nanopowder photoanode. As photosynthetic organisms, they contain chlorophyll which can serve as a photosensitizer. As a result, the algal nanoparticles could have possibly acted as both photoanode and sensitizer. The efficiency of 0.95 % from the algal-based AgNPs DSSCs obtained in the dark proved that microalgae as photosynthetic organisms have both light and dark cycles. The low conversion efficiency of the TiO_2 could be attributed to the organic dye used as a sensitizer; the TiO_2 photoanode anode is dependent on the efficiency of the dye which traps photon from the sun and transfers electrons to the photoanode.

Table 1 Photoelectrochemical parameters for algal silver nanoparticles based DSSC and only TiO_2 based DSSC.

Cells	Voc (V)	Isc (A)	Imax(mA)	Vmax (V)	Fill factor	Efficiency (%)
SCO Light	0.98	0.0038	0.0025	0.6	0.40	1.09
SCO Dark	0.98	0.0036	0.0020	0.62	0.35	0.95
SC Light	0.96	0.00005	0.00035	0.86	0.062	0.03
SC Dark	0.92	0.000019	0.000014	0.84	0.007	0.004

Key; SCO= AgNPs of *Coelastrella* sp; SC=Control

3.8 Conclusion

The DSSC was fabricated using a modified photoanode (1:1 of CO-AgNPs and TiO_2), the power conversion efficiency was 1.09% and 0.95% when exposed to light and dark respectively. The enhancement of TiO_2 photoanode with silver nanoparticles synthesized from a microalga was achieved. Optimization of the other parameters apart from the two investigated in this work needs to be done to achieve better performance with the modified photoanode.

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