



Characterizations of Galena as Potential Photosensitizer in a Natural Dye-Sensitized Solar Cell

Akinsola Samson Ibukun^{a,b,*}, Alabi Aderemi Babatunde^a, Adedayo Kayode Seun^c, Nicola Coppede^d

^aDepartment of Physics, University of Ilorin, Ilorin, Nigeria.

^bCrown-Hill University, Eiyenkorin, Kwara State, Nigeria.

^cDepartment of Physics, University of Maiduguri, Nigeria.

^dInstitute of Materials for Electronics and Magnetism, Parma, Italy.

Abstract

Dye is one of the principal parts for high power conversion efficiency in a Dye-Sensitized Solar Cell. Conspicuous developments have taken place via the work of several researchers in engineering of novel dye structures so as to enhance the performance of the system. The properties of a natural mineral dye were studied in this work. The structure of the dye was determined and discovered to have contains constituents which could enhance better absorption of solar radiation for use in a Dye-Sensitized Solar Cell (DSSC). The Lead Sulphide and iron content of the mineral dye studied as revealed by the X-Ray diffraction analysis done suggest this. The X-Ray Fluorescence (XRF) done revealed that the concentration of Lead and Iron (Fe) is high as compared to other elements present in the material, probably as a result of the fact that it is a geological sample (of the earth) and which may even suggest its colour and hence makes it absorbs solar radiation of visible region at its wavelength (around 380 nm – 800 nm). The functional groups present in the dye as obtained from the Fourier transform infrared spectroscopy are the Amine, Carbonyl and the hydroxyl groups, all which confirms the suitability of the dye material in photosensitizing a semiconductor in a DSSC. The absorption spectra of the dye within the visible region of electromagnetic radiation shows that the material has high, increased and stable absorption of visible light which is suggesting a more durable natural dye for a DSSC than the easily degraded natural dyes of plants source.

DOI:10.46481/jnsps.2021.184

Keywords: Galena, Mineral, Dyes, Photosensitizers.

Article History :

Received: 26 March 2021

Received in revised form: 07 May 2021

Accepted for publication: 08 May 2021

Published: 29 May 2021

©2021 Journal of the Nigerian Society of Physical Sciences. All rights reserved.

Communicated by: B. J. Falaye

* Corresponding author tel. no: +2348166602544

Email addresses: siakinsola711@gmail.com (Akinsola Samson Ibukun), remi050970@gmail.com (Alabi Aderemi Babatunde), kphysicsq@gmail.com (Adedayo Kayode Seun), nicola.coppede@gmail.com (Nicola Coppede)

1. Introduction

As at the end of 2017, roughly 1.8% of the globe electrical energy came from solar photovoltaics (PV), which has a vital prospect to have a key role in all major future energy matters with an installed capacity of about 5 Terawatts by 2050 [1]. Dye-Sensitized Solar Cell (DSSC) has its genesis from the

suggestion of O'Regan and Gratzel and was classified as the third generation of photovoltaic devices for the conversion of visible light into electrical energy [2]. Since the advent of dye-sensitized solar cells (DSSCs) in 1991, extensive researches are seriously ongoing on it as an alternative to silicon-based solar cells, and even the thin film solar cells; owing to their simple structure, transparency, flexibility and low production cost. Regardless of these advantages, the low efficiency of DSSC when compared to the long-ranged silicon-based cells is a limitation to their commercial implementation [3]. Currently, DSSC has the potential of converting photons from sunlight to electrical energy at an efficiency of 13%, according to [4]. A concerted and intensive effort is being put towards the optimization of various components of DSSC with the aim of fabricating more efficient and stable cells. Dye-Sensitized Solar Cells which are liquid-based consist of a fluorine doped Tin Oxide frontcontact (FTO) on glass, nanoparticle photoanode covered in a monolayer of sensitizing dye, a hole conducting electrolyte, and finally graphite or platinum coated FTO counter electrode (back contact). In Dye-Sensitized Solar Cells, the dye is one of the key components for high conversion efficiencies of power. In recent time, obvious progress has been achieved in the engineering of novel dye structures in order to enhance the performance of the system. For a while, Ruthenium based organic complexes have been the most stable and effective dyes used for DSSCs. As a result, that these dyes are characterized by its toxicity, relatively expensive, and difficult method of synthesis, increasing activities for using natural dyes have been reported [5]. In particular, the amphiphilic homologues of the pioneering ruthenium-based N-3 dye have been developed. These dyes show several merits when put side by side with the N-3 dye such as: a higher ground state pKa of the binding moiety which increases electrostatic binding onto the Titanium dioxide surface at lower pH values, the decreased charge on the dye reducing the electrostatic repulsion between adsorbed dye units and hence increasing the dye loading, the oxidation potential of these dyes is shifted cathodically compared to that of the N-3 sensitizer, which increases the reversibility of the ruthenium III/II couple, and finally lead to enhanced stability. [4] stated that the sensitizers which are currently used in production of solar cells are transition metal coordination complexes like Ruthenium (II) carboxylated polypyridyl complexes, because of their high charge-transfer absorption within the entire visible range of electromagnetic radiation and highly efficient metal-ligand charge transfer transition (MLCT). However, Natural dyes are better desired than these synthetic dyes because of being more economical, easily attainable, abundant in supply and environmentally friendly. Also, they invariably have large absorption coefficient due to allowed π to π^* transitions. These pigments are derived from various

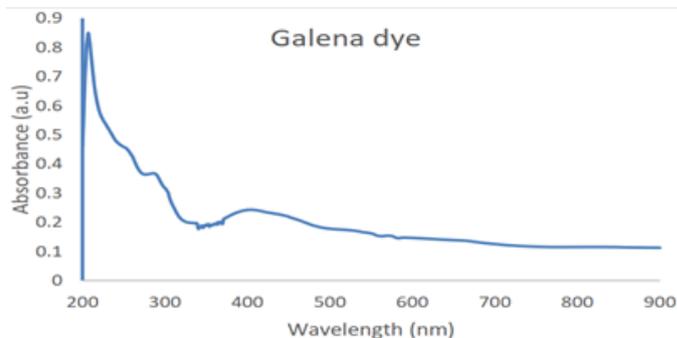


Figure 1: Absorption Spectra of Galena Dye

plant parts such as flower petals, leaves, roots and fruits pulp/bark. Therelatively quick degradation of even the natural dyes obtained from plants as compared with the metal coordination complexes calls for considering of an alternative natural dye with cost effectiveness and good stability. Natural dye can be categorized into biological and mineral dyes. The biological are the ones obtained from plants while mineral dyes are from natural minerals of the earth. In this study, dye obtained from natural mineral; Galena was characterized and the suitability in absorbing solar radiation for excitation of electrons in generating electricity via a DSSC is considered.

2. Materials and Method

rock-like mineral; Galena, was obtained from a community market around the location of study, Ilorin, Nigeria (LAT. 8.4928⁰ N, LONG. 4.5962⁰ E). The natural substance was grinded with an electric industrial grinder into a powder. The dye was separately extracted from the powder using an organic solvent (isopropyl alcohol). The structural property of the dye was studied by carrying out X-Ray Diffraction (XRD). The quantitative analyses of the dyes were done using the X-Ray Fluorescence (XRF) technique, to obtain the elemental composition of the dyes. The functional groups present in the dyes were determined using the Fourier Transform Infrared (FTIR) Spectroscopy. The Absorption spectra of the dye was studied within the visible region of the electromagnetic radiation and it was done using the UV-VISIBLE Spectrophotometer.

3. Results and Discussion

3.1. Optical Properties

Absorption of electromagnetic radiation is the process by which certain energy is being taken up with photon by matter. The absorption spectra of Galena dye is given in figure 1.

Electromagnetic spectrum comprises of Radio wave, Infrared, Visible light, region (about 380 nm – 800nm), since

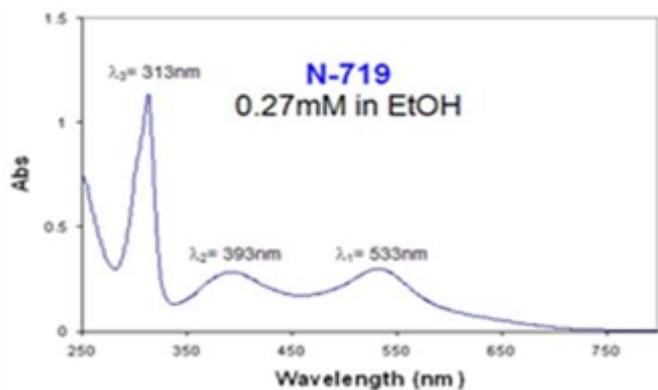


Figure 2: Absorption Spectra of Ruthenium-based dye, N-719 (Product No. 703214). Source: [6]

the dye is being studied as a potential photosensitizer in a Dye-Sensitized Solar Cell (DSSC) which absorbs solar radiation within the visible region of the electromagnetic radiation. It was observed (from figure 1) that the dye has absorption of solar radiation within the visible region.

Considering Figure 2, the absorption of solar radiation, based on the absorbance value of a typical Ruthenium-based dye (a synthetic dye) is just a little higher than that of the mineral dye; which shows a promising substitute to the relatively expensive synthetic dye. It is indeed a potential photosensitizer in a DSSC, as substitute to dyes of plants sources. In addition, galena is a natural semiconducting material with an energy gap of about 0.4eV. Indeed, it's a strong absorber of solar radiation. The dye extract exhibited a strong absorption broad band in the visible region with a peak at around 408 nm (absorbance value of 0.2424 a.u. Inferably, very little composition of the dye for absorbing the electromagnetic radiation was present. Further work can still be considered on solvents or process of making the galena powder well dissolved for a uniform analysis by the UV-VIS spectroscopy. Galena is fundamentally a Lead ore i.e.; Lead Sulphide and lead is metal. This intense absorption in the visible region has been reported for anthocyanin and is the reason for the efficient harvesting of photons in Natural DSSC. Anthocyanins are group of naturally occurring phenolic compounds responsible for the colour of many flowers and fruit. Ruthenium-based dye exhibit ligand-centered charge transfer (LCCT) transitions ($\pi - \pi^*$) as well as metal-to-ligand charge transfer (MLCT) transitions ($4d - \pi^*$) that can be observed in the absorption spectra of N-719 dye (Figure 2). The absorption bands at lower energies represent the MLCT transitions (λ_1 and λ_2) whereas the more energetically demanding transitions (λ_3 and λ_4) correspond to LCCT transitions. Promotion of an electron from π – bonding orbital to an antibonding π orbital* is denoted by $\pi - \pi^*$ transition. Section of molecules which can undergo such detectable electron transitions can be referred to as ch

Table 1: Elemental composition of Galena

Elements	Concentration
Ca	< 411.684
Sc	< 78.741
Ti	263.183 ± 50.390 ppm
V	< 203.917
Cr	< 141.133
Mn	< 38.203
Fe	965.357 ± 44.279 ppm
Ni	318.054 ± 36.217 ppm
Cu	345.412 ± 21.042 ppm
Zn	141.191 ± 11.137 ppm
Ga	490.431 ± 40.761 ppm
Pb	3690.413 ± 462.395 ppm
Se	188.198 ± 32.007 ppm
Br	< 412.070
Rb	< 26.176
Sr	< 30.008
Y	< 1220.770

-romophores since such transitions absorb electromagnetic radiation (light), which may hypothetically be perceived as colour somewhere in the electromagnetic spectrum. The absorption spectra of galena dye given in Figure 1 shows absorption bands (408 nm and around 573 nm) at more energetically demanding transitions which is close to LCCT transitions within the visible region, hence favoring a good absorption of solar radiation for the operation of a solar cell.

3.2. Quantitative Analysis

The elemental composition of the Galena dye was summarized in table 1. From the analysis it was observed that the elements with the prominent concentrations in the dye material are Lead (Pb) and Iron (Fe) with 3690.413 ppm and 965.357 ppm respectively.

The high concentration of Pb and Fe in the sample could be as a result of the fact that it has its source from the earth (being a natural mineral). Also, the iron concentration in the dye material could be responsible for its lustrous black colour (see figure 3) which could eventually favours it high absorption of electromagnetic radiation in the visible region. Although Iron (Fe), Copper (Cu), Silver (Ag) etc. are naturally parts of the common impurities of galena ore.

The results discussed under the optical properties and as seen in table 2 justify this fact and also as revealed by the result given by the XRD pattern.

Colours in the visible region of the electromagnetic spectrum are red, orange, yellow, green, blue, indigo and violet. These Colours absorb at different wavelengths of light (table 2), which in turn carry different magnitude of energy. The ma-



Figure 3: Image of Galena (source:[7])

Table 2: Corresponding wavelength of colour in the visible region

Elements	Concentration
Red	622-780
Orange	597-622
Yellow	577-597
Green	492-577
Blue	455-492
Violet	390-455

material being considered has a colour close to the ones within the wavelength range of 390 nm – 577 nm, as it is in table 2.

3.3. Fourier Transform Infrared Spectroscopic (FTIR) Analysis of the Dye

An FTIR spectrum of the Galena dye is shown in Figure 4. The functional groups present in an organic dye responsible for the absorption of solar radiation are actually the Amine, hydroxyl and the carbonyl groups.

In addition to the high absorption coefficient in the visible region of the electromagnetic spectrum, the presence of hydroxyl and carbonyl anchoring groups in the dye as revealed by the stretching vibrations at 2883.1 cm^{-1} , 2933.4 cm^{-1} , 2970.7 cm^{-1} and 1654.9 cm^{-1} respectively will enable their adsorption onto the surface of semiconductor to be used in a DSSC. The presence of the Amine group in the dye is revealed by the vibration at 3332.2 cm^{-1} . The absorption bands for bending vibrations are typically found in the fingerprint region ($1400 - 600\text{ cm}^{-1}$). These vibrations correspond to the likely metal-bonded compounds present in the region which character-

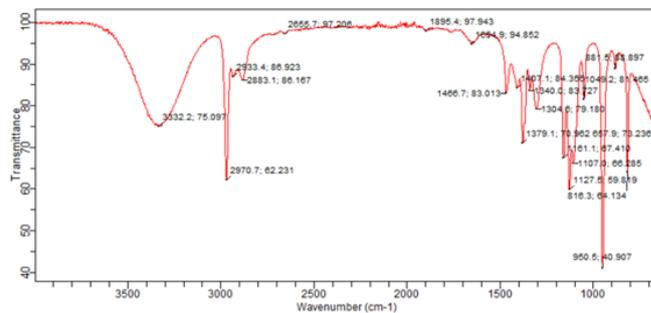


Figure 4: FT-IR spectra of Galena dye

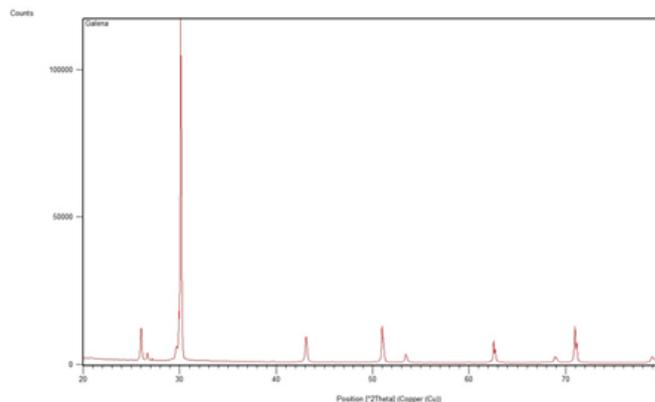


Figure 5: XRD pattern of Galena sample obtained for an organic dye

ization carried out using the X-ray Diffraction (XRD) technique revealed.

3.4. 3.4 X-Ray Diffraction Characterization

The dye material was subjected to X-ray Diffraction. The XRD pattern obtained for the dye was given in Figure 5. The 2θ peak values considered are as follows: 26.0° , 30.1° , 43.1° and 52.5° corresponding to diffraction from planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1) respectively for the galena.

The XRD patterns confirm the presence of Lead Sulphide, in the dye material, as this matches with the JCPDS Card no. [05-0592]. It is confirmed to be of face-centered cubic crystal. The multiple peaks obtained from the X-ray diffraction point to the fact that it is also polycrystalline. The crystal plane (2 0 0) is the prominently seen in the XRD pattern. This is in agreement with the report of [8]. The prominent peak in the XRD pattern corresponds to the galena, (PbS) mineral in the galena ore sample as other mineralogical content of the ore could be sphalerite (ZnS), Pyrite (FeS₂), Chalcopyrite (CuFeS₂), etc. The confirmed PbS, a semiconducting material, in the galena ore actually makes it a potential absorber / good photosensitizer in a natural DSSC.

4. Conclusion

This research focuses on the properties of a mineral dye which make it suitable as a potential photosensitizer in a Dye-sensitized solar cell (DSSC). The dye, though from a material being used for different purposes, among which is cosmetics in some part of Africa for decades, is discovered to possess, through the characterizations carried out, tendencies of being a good absorber of solar radiation in the visible region of electromagnetic radiation. This is expected to yield an improved power conversion efficiency of the cell.

References

- [1] A. Le Donne, T. Vanira & B. Simona, "New Earth-Abundant Thin film Solar cells Based on chalcogenides", *Frontiers in Chemistry*. **7** (2019) 1.
- [2] S. A. Monzir, B. A. Mahmoud, A. Naji, M. A. Amal, A. T. Sofyan, M.E Taher & S. E. Hatem, "Dye-Sensitized Solar Cells Using Fifteen Natural Dyes as Sensitizers of Nanocrystalline TiO₂", *Science Technology and Development* **34** (2015) 135. DOI: 10.3923/std.2015.135.139
- [3] H. Y. Jun, W. B. Chung, H. K. Kyung & W. C. Hyung, "Characteristics of the Dye-sensitized solar cells using TiO₂ Nanotubes Treated with TiCl₄", *Materials* **7** (2014) 3522.
- [4] G. William, K. Hyeonggon, S. Tajbik, Y. Sunil, C. Tulio, N. Fred & U. Jamal, "Fabrication, Optimization and characterization of Natural Dye sensitized solar cell", *Scientific Reports* **7** (2017) 41470.
- [5] M. A. Ahmed Hemdan, S. H. M Moataz, M. K. Y. Ghad, M. A. Ahmed, S. H. & S. G. K. Ahmed, "Dye-Sensitized Solar cells (DSSCs) Based on Extracted Natural Dyes", *Journal of Nanomaterials*. Article ID 1867271. <https://doi.org/10.1155/2019/1867271>
- [6] D. Hans & H. Yanek, *Ruthenium-based dyes for Dyesensitized Solar Cells*, Dyesol LTD, Australia, 2017.
- [7] <http://www.rocksandminerals.com/lead.htm> (accessed on 27th September, 2019).
- [8] M. P. C. Kalika, D. Kuldeep, D. Joyeeta, H. Nilakhi, D. Purbasha, D. Ronita, P. Sanchayita, S. Trinayan & B. K. Sarma, "X-ray diffraction line profile analysis of chemically synthesized lead sulphide nanocrystals", *Materials Letters* **87** (2012) 84.