

Analysis of Pure and Ag-Doped TiO₂ Thin Films Deposited by Field Assisted Spray Pyrolysis.

ABSTRACT

This paper reports the structural and optical properties of Undoped TiO₂ and 5% Ag-doped TiO₂ nanoparticles under visible- light irradiation. These films were synthesized by Electrohydrodynamic Spray Pyrolysis Technique, deposited at 250°C and later annealed at 400°C few minutes. The films were characterized by Surface Profilometry, Ultraviolet – Visible light Spectroscopy (UV-Vis Spectroscopy) and X-ray diffraction (XRD). The result from surface profilometry showed that the thickness of all the samples is thin film. XRD results showed that all the films have crystalline nature of TiO₂ and annealed films result in an increase of crystallinity. There was phase transition from hexagonal to monoclinic crystal class as we doped to 5% of Ag .The unannealed Undoped TiO₂ exhibited low absorbance within the visible spectrum but increases as we dope with 5% Ag-doped TiO₂ and effect of annealing increases the absorbance. Extinction coefficient increases within the visible region as we doped and thermal annealing also increases its effect within the visible region. The direct band-gap for unannealed films range from 4.70eV- 3.10eV while annealed films was between 3.20eV and 2.80eV. Doped Annealed films showed reduced band-gap.

Keywords: Ag doped TiO₂, Field Assisted Spray Pyrolysis, Structural Properties, Optical Properties and Wide band gap Semiconductor.

INTRODUCTION

Titanium dioxide (TiO₂) also known as titania is the most promising electron acceptor and a very useful wide band-gap semiconducting transition metal oxide which has attracted much interest among researchers due to its unique characteristics such as non-toxicity, affordability, easy handling, resistance to photochemical and chemical erosion (Hoffmann, *et al.*, 1995). It is a wide band-gap semiconductor with energy of 3.0–3.4 eV and is widely used in applications such as hydrogen production (Zaleska, 2008), gas sensor (Sayilkan, *et al.*, 2005), (Gomez & Meghraoui, 2003), photo catalytic activities (Yogeswaran & Chen, 2008), dye-sensitized solar cells and photo electrochemical cells because of its relative high efficiency and high stability. TiO₂ exists in both crystalline and amorphous forms. In Its existence in

three crystalline polymorphs, namely, anatase , rutile and brookite, anatase and rutile have a tetragonal structure, whereas brookite has an orthorhombic structure (Mahshid, *et al.*, 2007).

There are different routes that can be used to synthesize titanium dioxide. These include a conventional solid state route (Dong, 2004), (Guimarães *et al.*, 2003) , precipitation (Joo, *et al.*, 2005), (Lee & Yang, 2005), Sonochemical (Guimarães *et al.*, 2003), hydrothermal (Hidalgo, *et al.*, 2007), (Deshpande, 2011), microwave hydrothermal (Murugan, *et al.*, 2006) and sol-gel methods (Pookmanee & Phanichphant, 2009) , (Tiberiu, *et al.*, 2014) . Titanium dioxide (TiO₂) also exhibits useful electrical, optical, and photocatalytic behaviour due to the powerful oxidation and reduction properties that arise in the absorption of photon energy (Kim & Kwak, 2007).

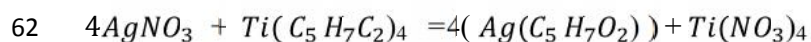
Due to TiO₂ wide band-gap which ranges from 3.0eV- 3.4eV, between the valence and conduction bands, there is significant limitation with regard to the photocatalytic applications. Hence several attempts have been made by researchers to improve its absorbance within the visible region thus enhancing its photocatalytic activities through the process of doping (Ambrus, *et al.*, 2008).

In this work we carried out a comparative analysis of the different deposited samples to identify the effect of concentration of dopant and the effect of thermal annealing on the samples using Electrohydrodynamic Spray Pyrolysis Technique. The films deposited were characterized by Surface Profilometry, Ultraviolet – Visible light Spectroscopy (UV-Vis Spectroscopy), Light Microscopy and X-ray diffraction (XRD).

50

51 **EXPERIMENTAL**

TiO₂ was synthesized using 0.2mol of titanium acetyl acetonate [Ti(C₅H₇O₂)₄] and 20mol of propanol [C₃H₈O] as the precursor while 0.68g of silver nitrate [AgNO₃] , mixed with 20mol of propanol in a conical flask, placed on a magnetic stirrer and was stirred with the magnetic stirring bar, until the AgNO₃ was properly dissolved served as the precursor for Silver(Ag). The precursor delivery system containing string pump was formatted using a laptop to get accurate atomization or deposition. The flow rate was set at 4200microlitres/hour, the volume was set at 400microlitres/hour and the time was set at 10mins. The Electrohydrodynamic Spray Pyrolysis Techique was set at the voltage of 3.5KV and the distance between the nozzle and the substrate (pro cleaned glass) was 5.95mm. From the precursors we obtained



63

64 5% Ag doped TiO₂ was deposited at 250°C and was duplicated to get two samples. Undoped
65 TiO₂ was also deposited at 250°C and also duplicated to two samples. Hence we have a total
66 of four(4) samples. One 5% Ag doped TiO₂ and one undoped TiO₂ were later annealed at
67 400°C in few minutes using master chef annealing machine with Model No: P70BI7L-
68 Ds(7014336), in order to expel the water of crystallization from the samples.

69 The thickness of the synthesized samples (both doped and undoped) was measured using
70 surface profilometry with a VeecoDektak 150 profiler machine. Using UV-Vis
71 spectroscopy, the absorption spectra of the deposited undoped TiO₂ and Ag- doped TiO₂
72 thin films were recorded within the wavelength range of (UV) region of (230 nm to 390 nm),
73 visible light (VIS) region of (400 nm to 700 nm) and near infrared (NIR) region of (714 nm
74 to 1080 nm). The reflectance values of the work were obtained using a relation between the
75 absorbance (A), transmittance (T) and reflectance (R), according to the law of conservation
76 of energy given by

$$A + T + R = 1 \quad 1.0$$

78 From equation 3.3, reflectance (R) was given as

$$R = 1 - T - A \quad 1.2$$

80 The values of refractive index of were obtained using the equation of refractive index
81 according to (Ali *et al.*, 2015),

$$\eta = \frac{(1+\sqrt{R})}{(1-\sqrt{R})} \quad 1.3$$

83 Where R is the reflectance and η is the refractive index.

84 The values of extinction coefficient of this work were calculated using the equation of
85 extinction coefficient according to (Mahrov, *et al.*, 2004)

$$k = \frac{\alpha \lambda}{4\pi} \quad 1.4$$

87 Where k is called the extinction coefficient (k), α is the absorption coefficient, λ is the
88 wavelength, π is equal to 3.142.

89 The microstructural properties of both doped and undoped TiO_2 were determined using Light
90 Microscope; Celestron LCD digital microscope. (Model no: 44348), under the magnification
91 of 800. The XRD pattern was recorded on a Rigaku Ultima IV X-ray diffractometer equipped
92 with a graphite- monochromated $\text{Cu K}\alpha$ radiation source (40kv, 30mA) and wave length
93 $1.54\text{\AA}$. A diffractogram was collected in the 2θ range between 3° and 90° with a step size of
94 0.01° and a scan speed of $1^\circ/\text{min}$. the XRD Pattern was processed using JCPDS card
95 numbers. We used Debye Scherer equation to calculate for the crystallite size.

$$96 \quad D = \frac{K\lambda}{\beta \cos \theta} \quad 1.5$$

97 Where D is the crystallite size, K = shape factor, which is constant (0.89), λ = wavelength
98 ($1.54\text{\AA}$), β = Full Width Half Maximum (FWHM), θ = 2 Theta, which to obtain θ , we divided
99 by 2.

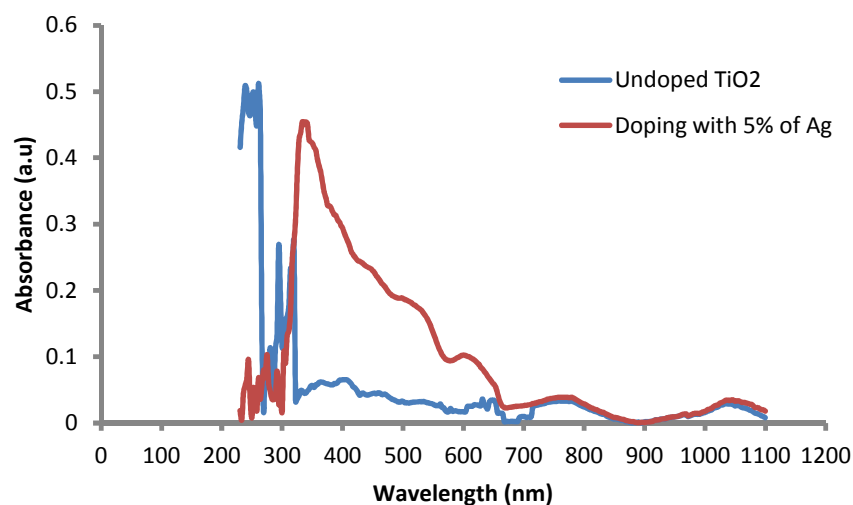
100 **RESULTS AND DISCUSSION**

101 The thickness of the synthesized samples (both doped and undoped) was measured using
102 surface profilometry with a VeecoDektak 150 profiler machine, the result showed that all
103 the samples are thin films.

104 **OPTICAL PROPERTIES OF THE DEPOSITED FILMS**

105 The absorbance spectra of the deposited films were shown in Fig. 1a and 1b. It is found that
106 absorbance spectra of 5% Ag doped TiO_2 has high absorbance within the visible region than
107 the undoped TiO_2 . Comparing the annealed and unannealed films, it also showed that
108 annealed films have the best absorbance within the visible region than unannealed films.

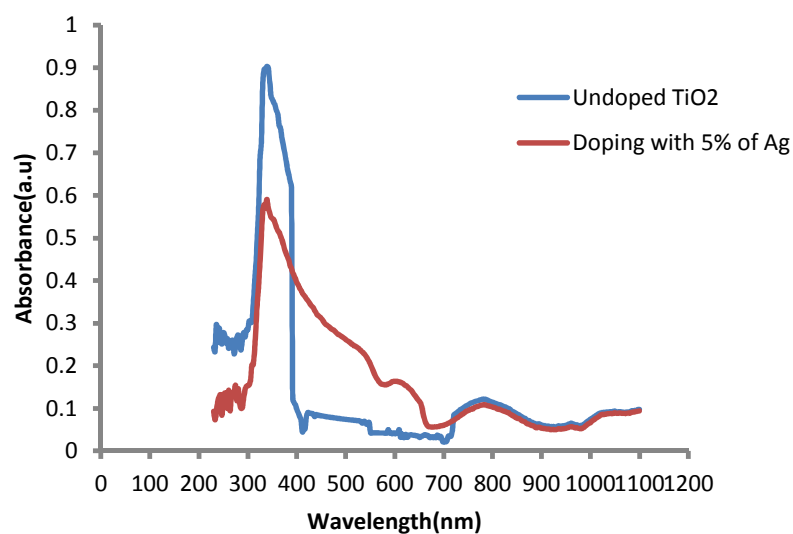
109



110

111 **Figure 1a: Absorbance Spectra for the Doped Unannealed Samples.**

112



113

114 **Figure 1b: Absorbance Spectra for the Doped Annealed Samples.**

115 Figures 2a and 2b below showed the extinction coefficient of unannealed samples and
 116 annealed samples. It showed that doping increases the extinction coefficient of the film
 117 within the visible region.

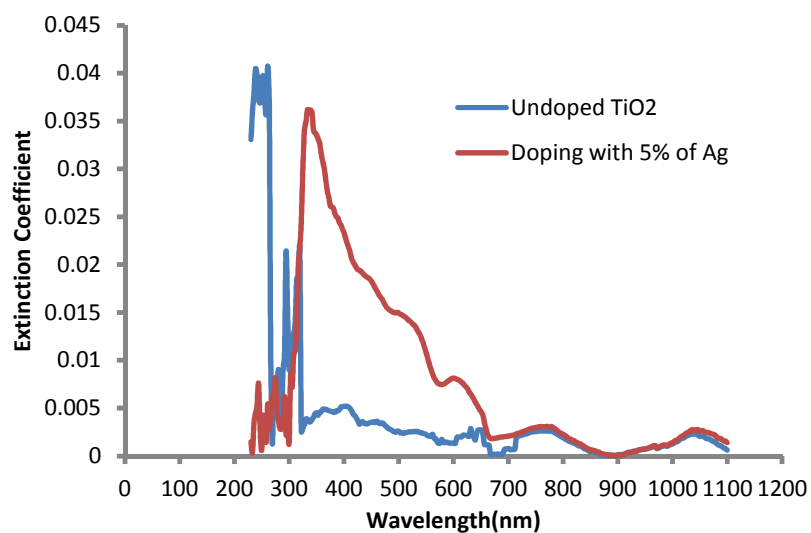


Figure 2a: Dependence of Extinction Coefficient on the Wavelength for undoped and doped unannealed Sample

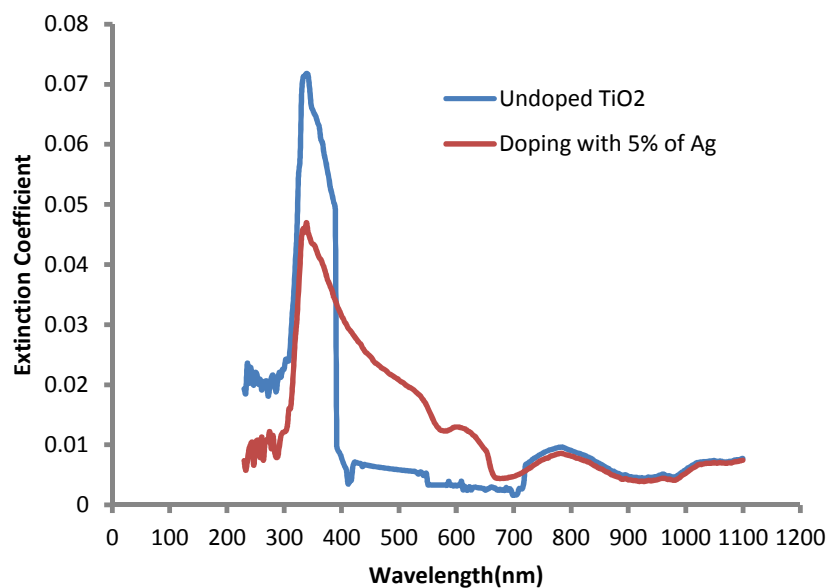


Figure 2b: Dependence of Extinction Coefficient on the Wavelength for undoped and doped annealed Samples.

using Tauc's relation

$$\alpha h\nu = A [h\nu - E_g]^n$$

126 where $h\nu$ is the photon energy, h is Planck's constant, α is the absorption Coefficient, A is the
127 constant, for direct transitions $n=2$, and E_g is the optical band gap, which is given as

$$128 \quad E_g = h\nu = \frac{hc}{\lambda} \quad 1.8$$

129 c is the velocity of light $= 3 \times 10^8 \text{ms}^{-1}$, λ is the wavelength in meters (m). ν is the transition
130 frequency, h is the Planck's constant $= 6.62 \times 10^{-34} \text{Js}$. Since $1 \text{J} = 1.602 \times 10^{-19} \text{eV}$

131 We substituted these variables into equation 3.14 and obtained

$$h\nu(\text{eV}) = \frac{hc}{\lambda_o} = \left(\frac{6.63 \times 10^{-34} \text{Js} \times 3 \times 10^8 \text{ms}^{-1}}{\lambda \times 1.602 \times 10^{-19} \text{c}} \right) = \left(\frac{6.63 \times 10^{-34} \text{Js}^{-1} \times 3 \times 10^8 \text{ms}^{-1}}{\lambda(\text{nm}) \times 10^{-9} \times 1.602 \times 10^{-19} \text{c}} \right)$$

$$132 \quad h\nu(\text{eV}) = \frac{1.241}{\lambda(\mu\text{m})} \quad 1.9$$

133 From equation 1.9 we calculated the photon energies in (eV) for various wavelengths λ
134 in(μm). A graph of $(\alpha h\nu)^2$ versus $h\nu$ for both unannealed and annealed samples were plotted
135 and the direct band gap was extracted by extrapolating the straight portion of the graph on $h\nu$
136 axis at $(\alpha h\nu)^2 = 0$ which gives the band gap of both unannealed and annealed films. For
137 unannealed, the undoped TiO_2 has the band gap of 4.70eV while 5% -doped Ag has band gap
138 of 3.10eV which shows that doping brings about reduction of the energy band gap from the
139 graph below

140

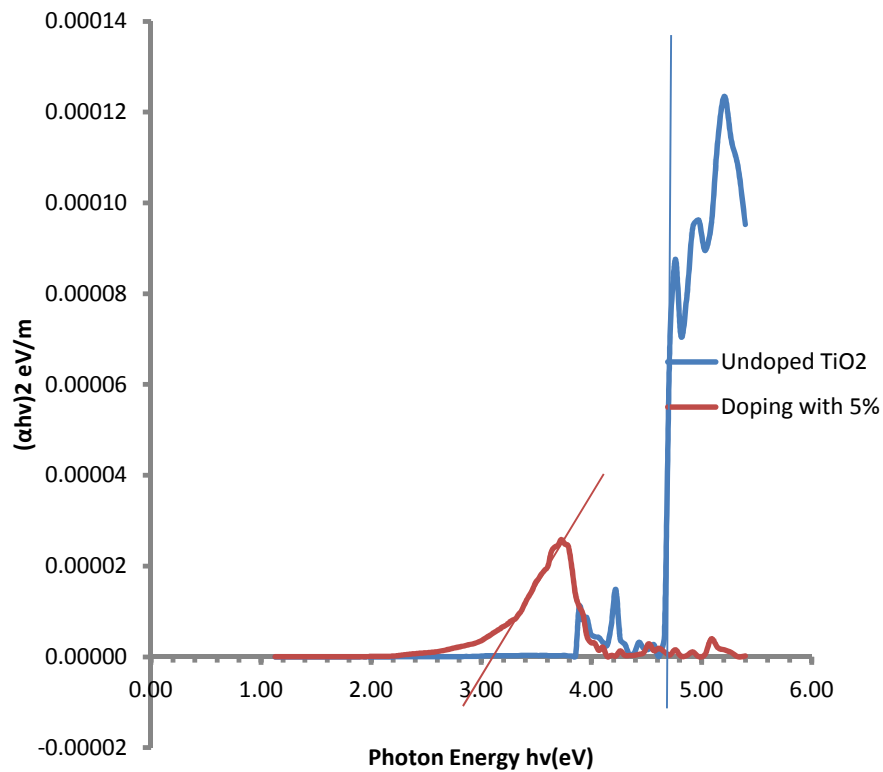


Fig 3a: Direct Band gap for Unannealed Undoped TiO₂ and 5%-doped Ag Films.

For the annealed films, the undoped TiO₂ has the band gap of 3.20eV which is in agreement with undoped TiO₂ result obtained by (Hassan *et al.*, 2008) while the 5%-doped Ag has 2.80eV similar to result obtained by (Ayieko *et al.*, 2012). The annealed films have narrowed energy band gap than the unannealed films.

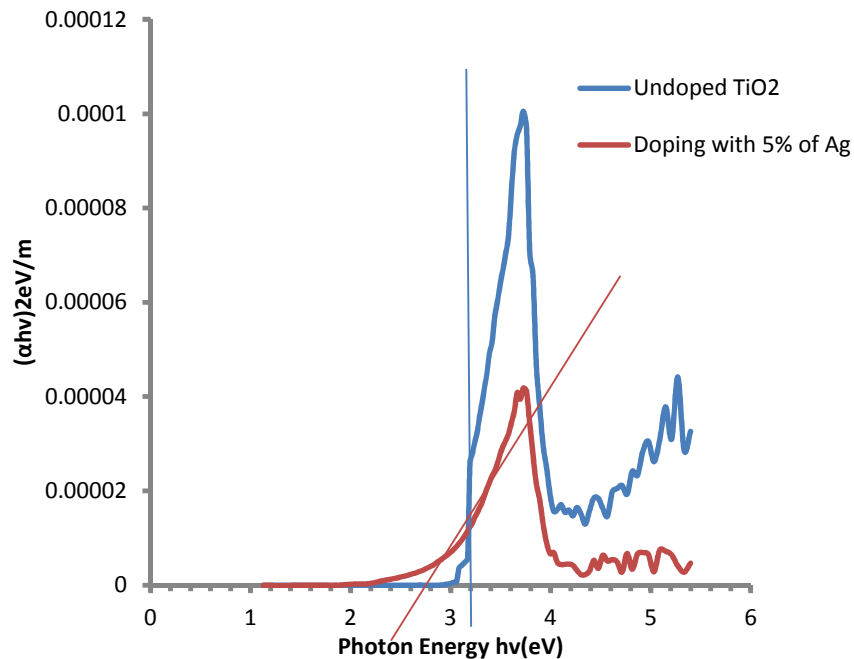


Fig 3b: Direct Band gap for Annealed Undoped TiO₂ and 5%-doped Ag Films.

The X-ray Diffraction

The X-ray diffraction patterns for both Annealed and Unannealed undoped TiO₂ samples with peaks at $2\theta = 25.30^\circ, 27.56^\circ, 37.99^\circ, 48.25^\circ, 54.22^\circ, 62.65^\circ$ and 74.80° which correspond to miller indices [101], [110], [103], [200], [105], [213] and [107] respectively. These results correspond to crystalline phase of TiO₂ and falls under the hexagonal crystal class. There average crystallite size was found to be 8.78nm and 8.76nm respectively. Comparing the two, the annealed TiO₂ pattern had well defined or high intensity of peaks than the undoped unannealed TiO₂ sample.

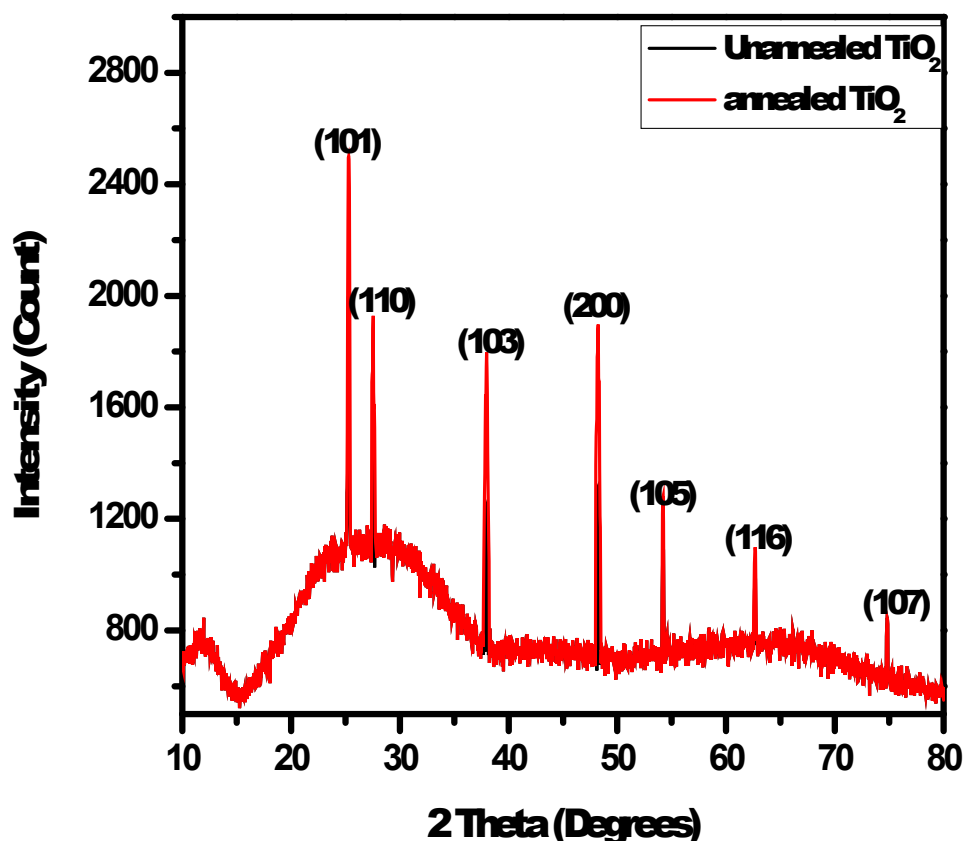
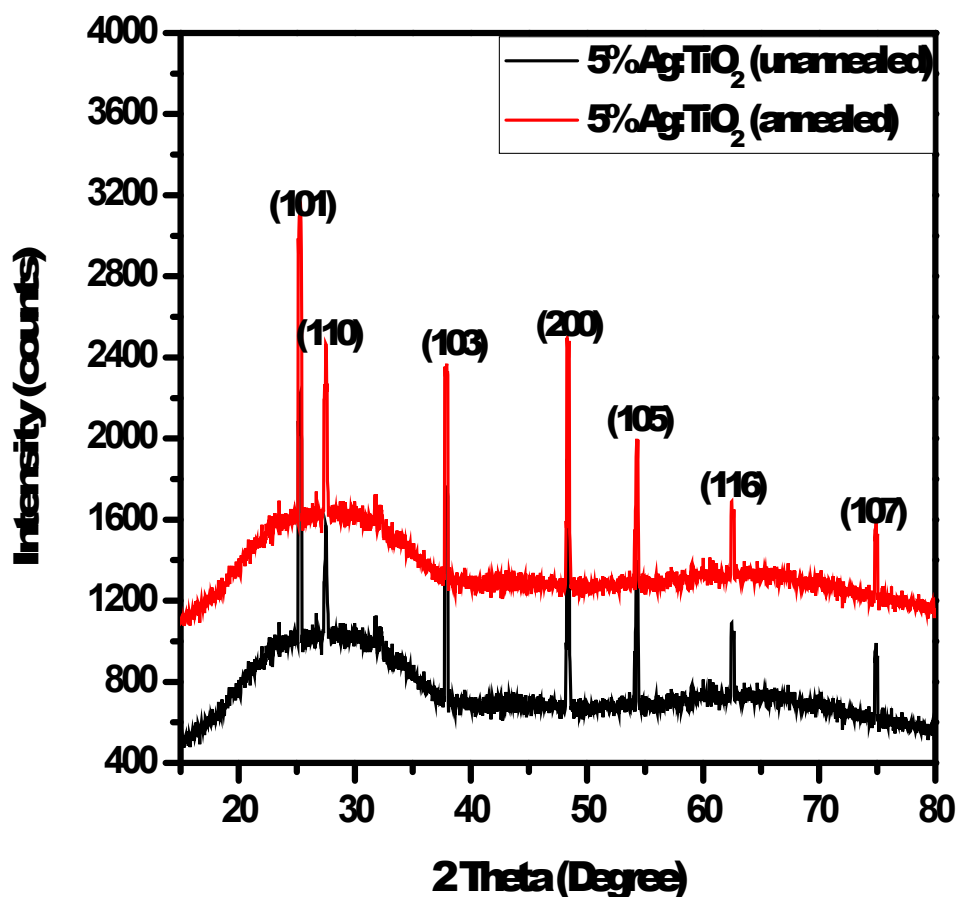


Figure 5: X- ray Diffraction Pattern for Undoped Unannealed TiO₂ and Undoped Annealed TiO₂

The X-ray diffraction patterns for 5% Ag of both annealed and unannealed samples has diffraction peaks at $2\theta = 25.33^\circ, 27.49^\circ, 37.98^\circ, 48.31^\circ, 54.28^\circ, 62.47^\circ$ and 74.89° which correspond to miller indices [101], [110], [103], [200], [105], [213] and [107] respectively. The results show the crystalline nature of TiO₂. There was phase transition, from hexagonal to monoclinic but there was no significant shift in the peak position of diffraction patterns of both annealed and unannealed 5% doped with Ag, except the changes in the intensity of these peaks. Annealed sample had well defined or high intensity of peaks than the unannealed sample due to annealing of the sample. The average crystallite size was found to be 8.8nm and 8.76nm respectively.



169

170 **Figure 6: X- ray Diffraction Pattern for both 5% of Ag/TiO₂ Annealed and Unannealed Samples**171 **CONCLUSION**

172 In this paper we have reported the structural, optical properties of TiO₂ and Ag-doped TiO₂
 173 synthesized using Electrohydrodynamic spray pyrolysis equipment. The XRD pattern
 174 showed crystalline nature of TiO₂. There was phase transition as a result of doping and there
 175 was increase in the crystallinity of the films in the case of annealed. UV- vis spectroscopy
 176 revealed the shifting of absorption edge of silver-doped TiO₂ to the visible region compared
 177 to that of Undoped TiO₂ and the annealed films showed higher absorbance than unannealed
 178 films. The Extinction coefficient showed that as the dopants are been added to the parent
 179 material, the extinction coefficient values of the films increases within the visible region. The

direct band gap for annealed showed more decrease in energy band gap than the unannealed doped samples. For the unannealed, the direct band gap ranges from 4.70eV – 3.10eV and the annealed the direct band gap ranges from 3.20eV – 2.80eV. The undoped TiO₂ nanoparticles showed poor photocatalytic activity, while doping of silver ions improves the efficiency under the visible –light irradiation.

REFERENCES

- Ambrus, Z., Bala'zs, N., Alapi, T., Wittmann, G., Sipos, P., Dombi, A., & Mogyoro, K. (2008). Synthesis, Structure and Photocatalytic properties of Fe (III)-doped TiO₂ prepared from TiCl₃. *Journal of Applied Catalysis*, 81, 27–37.
- Ayieko, C.O., Musembi, R.J., Waita, S.M., Aduda, B.O., & Jain, P. K. (2012). Structural and Optical Characterization of Nitrogen-doped TiO₂ Thin Films Deposited by Spray Pyrolysis on Fluorine Doped Tin Oxide (FTO) Coated Glass Slides. *International Journal of Energy Engineering*, 2, 67-72 <http://dx.doi.org/10.5923/j.ijee.0203.02>.
- Deshpande, A.G. M. (2011). Role of Lattice Defects and Crystallite Morphology in the UV and Visible-light-induced Photo-catalytic properties of Combustion-prepared TiO₂. *Journal of Materials Chemistry and Physics*, 126, 546–554.
- Dong Hyun Kima, H. S. (2004). Photocatalytic Behaviours and Structural Characterization of nanocrystalline Fe-doped TiO₂ Synthesized by Mechanical alloying. *Journal of Alloys and Compounds*, 375, 259–264.
- Gomez, A., & Meghraoui, M. (2003). Holocene Faulting and Earth Quake Recurrence along the Serghaya Branch of the Dead Sea Fault System in Syria and Lebanon. *Geophysical Journal International*, 21, 658-674.
- Guimarães, J., Abbate, M., Betim, S., & Alves, M. (2003). Preparation and Characterization of TiO₂ and V₂O₅ nanoparticles produced by Ball-milling. *Journal of Alloys and Compounds*, 352, 16–20.
- Gupta, K., Singh, R.P., Pandey, A., Pandey A., & Beilstein, J. (2013). Photocatalytic Antibacterial Performance of TiO₂ and Ag-doped TiO₂ against *S. aureus*, *P. aeruginosa* and *E. coli*. *Journal of Nanotechnology*, 4, 345–351. <http://dx.doi.org/10.3762/bjnano.4.40>.
- Hassan, M.M., Haseeb, A.S., Saidur, H., & Masjuki, M. (2008). Effects of Annealing Treatment on Optical properties of Anatase TiO₂ Thin films. *International Journal of Chemical and Biomolecular Engineering*, 1, 93-97.

- 213 Hidalgo, M. C., Moncayo, M. A., Maicu, M., & Colón, G. (2007). Hydrothermal Preparation of highly
214 Photoactive TiO₂ Nanoparticles. *Journal of catalysis today* , 129, 50-58.
- 215
- 216 Hoffmann, M. R., Martin, S.T., Choi, W., & Bahnemann, D. (1995). Environmental Applications of
217 Semiconductor Photocatalysis. *Journal of Chemical reviews* , 95, 69-96.
- 218 Kim, D. S., & Kwak, S.Y. (2007). The Hydrothermal Synthesis of Mesoporous TiO₂ with high
219 Crystallinity, Thermal Stability, large Surface area, and Enhanced Photocatalytic activity.
220 *Journal of Applied Catalysis*, 323, 110-118.
- 221 Joo, J., Kwon, S., Yu, J., & Hyeon, T. (2005). Synthesis of ZnO Nanocrystals with Cone, Hexagonal
222 Cone, and Rod Shapes via Non-Hydrolytic Ester Elimination Sol–Gel Reactions. *Journal of*
223 *Advance Materials* , 17, 1873–1877.
- 224 Lee, J. H., & Yang, Y. S. (2005). Effect of HCl Concentration and Reaction time on the change in the
225 Crystalline State of TiO₂ prepared from Aqueous TiCl₄ Solution by Precipitation. *Journal of*
226 *the European Ceramic Society*, 25, 3573–3578.
- 227 Mahrov, B., Boschloo G., Hyfeldt A., Siegbahn H., & Rensmo H. (2004). Photoelectron Spectroscopy
228 Studies of Ru(dcbpyH₂)₂(NCS)₂/CuI and Ru(dcbpyH₂)₂/CuSCN Interfaces for Solar Cell
229 Applications. *Journal of Physical Chemistry*, 108, 11604 –11610.
- 230 Mahshid , S., Askari, M., & Ghamsari , M.S.(2007). Effect of Brookite presence on Nanocrystalline
231 Anatase – Rutile phase Transformation. *International Journal of nanotechnology* ,8, 11365-
232 8486. <https://doi.org/10.1504/ijnt.2009.027559>.
- 233 Murugan, A.V., Samuel, V., & Ravi, V. (2006). Synthesis of Nanocrystalline Anatase TiO₂ by
234 Microwave hydrothermal method. *Journal of Materials Letters* , 60, 479-480.
- 235 Pookmanee, P., & Phanichphant, S. (2009). Titanium Dioxide Powder prepared by a Sol-gel method.
236 *Journal of Ceramic Processing Research* , 10, 167-170.
- 237 Sayilkan, F., Asilturk, M., Sayilkan, H., Onal, y., & Akarsu, M. (2005). Characterization of TiO₂
238 Synthesized in Alcohol by a Sol-Gel Process: Effects of Annealing Temperature and Acid
239 Catalyst. *Turkisk Journal of Chemistry*, 30,697-706.
- 240 Tiberiu, D., Ligia, T., Adriana, R., & Maria, Z. (2014). Nanosized Al₂O₃-TiO₂ Oxide powder with
241 Enhanced Porosity obtained by Sol-gel method. *Journal of Academia Română* , 59, 125-134.
- 242 Yogeswaran, U., & Chen, S.M. (2008). Recent Trends in the Application of Carbon Nanocubes-
243 Polymer Composite Modified Electrodes for Biosensors. *Journal of Analytical Letters* , 2, 210-
244 243.
- 245 Zaleska, A. (2008). Characteristics of Doped-TiO₂ Photocatalys. *Journal of Physiocochemical*
246 *Problems of Mineral Process* , 4, 211-222.