

Influence of Ag-doping on Optical and Structural properties of TiO₂ Thin Films Deposited by Electrohydrodynamic Spray Pyrolysis.

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ABSTRACT

Aims: To study structural and optical properties of undoped titanium (IV) oxide (TiO₂) and doped with 1.0 and 1.5M of silver.

Study Design: Electro- hydrodynamic spray pyrolysis technique was used.

Place and Duration of Study: titanium acetyl acetonate [Ti(C₅H₇O₂)₄], propanol [C₃H₈O] and silver nitrate [AgNO₃] was obtained from Sheda Science and Technology Complex (SHESTCO) Abuja (Nigeria). The study was carried out between March 2017 and November 2017 at Sheda Science and Technology Complex (SHESTCO) Abuja (Nigeria).

Methodology: TiO₂ was synthesized using 0.2mol of titanium acetyl acetonate [Ti(C₅H₇O₂)₄] and 20mol of propanol [C₃H₈O] as the precursor. The silver (Ag) was obtained using 0.68 g of silver nitrate [AgNO₃], mixed with 20 mol of propanol in a conical flask and placed on a magnetic stirrer. The flow rate by volume was set at 4200 microlitres/hour and the time of deposition was set at 10 min. The Electrohydrodynamic Spray Pyrolysis Technique was set at voltage of 3.5 KV and the distance between the nozzle and the substrate (pre-cleaned glass) was 5.95 mm. Undoped TiO₂ and doped with 1.0 and 1.5M of silver was deposited at 250°C.

Results: The films were characterized by Surface Profilometry, Ultraviolet – Visible light Spectroscopy (UV-Vis Spectroscopy) and X-ray diffraction (XRD). The results from surface profilometry showed that all the samples were thin films in the range of 300 to 700 nm. XRD results reviewed crystalline structure of TiO₂. Crystal phase observed for both TiO₂ and silver-doped TiO₂ are anatase structure. These results of (UV-Vis Spectroscopy) show that the undoped TiO₂ exhibited low absorbance within the visible spectrum but increased as we doped with 1.0 M and 1.5 M of silver. The results also showed that all the films have high transmittance around 50- 95% in the visible region and NIR of the spectrum such that we can use them as optical windows in solar cell. The undoped TiO₂ has the highest transmittance and is observed that the optical transmittance decreases with increasing Ag. Extinction coefficient increases within the visible region as we doped and the results also showed that the absorption coefficient, the direct transition and indirect transition can be controlled. The study of the microstructural properties using Optical Microscopy showed increase in the number of orderly stacked grains as we doped with Ag and

average particle sizes are between 6 μm and 8 μm . The direct band-gap for the films range from 3.81 eV- 3.00 eV while the indirect band-gap for the films range from 3.80 eV – 2.60 eV. The energy gap is decreased gradually as doping increases.

Keywords: Ag doped TiO_2 , Spray Pyrolysis, Structural Properties, Optical Properties, Heterogeneous Photocatalysis

INTRODUCTION

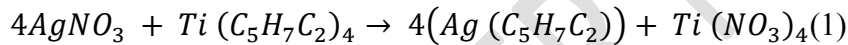
Transparent metal oxides (TMOs) in most cases have served as the inorganic semiconducting component. Among the materials reviewed titanium (IV) oxide, TiO_2 is the most promising electron acceptor because it offers good electron transport [1], excellent physical and chemical stability [2]. It is one of the most important nanomaterials which have attracted a great attention due to its unique characteristics such as low cost, easy handling, non-toxicity, and resistance to photochemical and chemical erosion [3]. Due to a combination of such unique properties as high refractive index, high transmittance, chemical stability and photo-catalytic behaviour, titanium dioxide constitutes a very valuable material for optical applications [4]. Recently, scientific efforts have been drifted towards shifting the optical sensitivity of the TiO_2 from UV to the visible-light spectrum for the efficient use of solar radiation or artificial visible light [5]. It is generally accepted that the presence of metal or non – metal dopants into TiO_2 lattice increases the photocatalytic activity of the material under visible light irradiation [6]. However, producing porous TiO_2 samples with large surface area can improve its photocatalytic properties by means of reducing the recombination rate of photo induced electron-hole pairs. This is due to their faster arrival to the reaction site of the surface and efficient charge separation which increases the lifetime of the charge carriers and enhances the photocatalytic efficiency [7]. There are different routes that can be used to synthesize titanium dioxide. These include a Solvothermal method, Sol-Gel method, Direct Oxidation method, Vapour Deposition, Electro – deposition,

Sonochemical method, Microwave method [8]. One example of vapour deposition is the Chemical vapour deposition (CVD). It is a chemical process used to produce high quality, high-performance, solid materials. It's a very versatile and widely used manufacturing process and a very general process that can be tailored to many different applications. The majority of its applications involve applying solid thin-film coatings to surfaces, but it is also used to produce high-purity bulk materials and powders, as well as fabricating composite materials via infiltration techniques [9]. This process is often used in the semiconductor industry to produce thin films. It has been used to deposit a very wide range of materials. One great advantage of CVD processing is that it can create coatings of uniform thickness even over complex shapes. It is also a technique subject to constant refining and expansion, pushing materials research in new directions such as the production of large-scale sheets of graphene, or the development of solar cells that could be "printed" onto a sheet of paper or plastic [10]. For the liquid-phase chemical vapour deposition method, it comprises of mechanical techniques and electro processes. Mechanical techniques include spray pyrolysis (eg. Electro-hydrodynamic), spray-on techniques, spin-on techniques, liquid phase epitaxy [11]. These techniques are used for depositing coatings from liquid media that are subsequently reacted chemically to form the inorganic thin film product by spraying, spinning, dipping and draining, flow coating, roller coating, pressure-curtain coating, brushing, and offset printing of reagent solutions. Liquid spray coating is probably the most versatile mechanical coating technique of the deposition techniques noted, and it is particularly well-suited for high-speed automated mass production [12]. The aim of this work is to produce high-quality silver (Ag)-doped TiO_2 thin films for optical application by using Electro-hydrodynamic Spray Pyrolysis Method. Distinctive attention was paid to the influence of

the processing factors, such as dopant concentration into the targets on the optical properties of the films during the deposition.

EXPERIMENTAL

TiO₂ was synthesized using 0.2mol of titanium acetyl acetonate [Ti(C₅H₇O₂)₄] and 20mol of propanol [C₃H₈O] as the precursor. Silver (Ag) was obtained using 0.68g of silver nitrate [AgNO₃], mixed with 20mol of propanol in a conical flask and placed on a magnetic stirrer. The flow rate by volume was set at 4200 microlitres/hour and the time of deposition was set at 10min. The Electro-hydrodynamic Spray Pyrolysis Technique was set at voltage of 3.5 kV and the distance between the nozzle and the substrate (pre cleaned glass) was 5.95mm. From the precursors we obtained



Undoped TiO₂ and doped 1.0 and 1.5M of silver (Ag) were deposited at 250°C. The thicknesses of the synthesized samples (both doped and undoped) were measured using surface profilometry with a Veeco Dektak 150 profiler machine. Using UV-Vis spectroscopy, the absorption spectra, extinction coefficient, absorption coefficient, refractive index of the deposited undoped TiO₂ and Ag-doped TiO₂ thin films were also recorded. Using the law of conservation of energy [13] the reflectance values of the samples were obtained. Where (A) absorbance, (T) transmittance and (R) reflectance respectively.

$$A + T + R = 1 \quad (2)$$

From equation 2, reflectance (R) was given as

$$R = 1 - T - A \quad (3)$$

The optical constants are the index of refraction (η) and the extinction coefficient (k). The optical constants of a thin film material are most commonly and reliably determined from the simultaneous measurement of transmittance and reflectance of the film. The values of the refractive index of the samples were obtained using (equation 4) [13].

$$\eta = \frac{(1 + \sqrt{R})}{(1 - \sqrt{R})} \quad (4)$$

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

Absorption Coefficient measures the rate of decrease in the intensity of electromagnetic radiation (beams of photons or particles). The absorption coefficient determines how far into a material light of a particular wavelength can penetrate before it is absorbed. The results of the absorption coefficient of the samples were obtained using (equation 5)[13].

$$\alpha = \frac{\ln\left[\frac{1}{T}\right]}{d} \text{ eVm}^{-1} \quad (5)$$

Where, T is the transmittance, d is the thickness and α is the absorption coefficient.

The values of extinction coefficient of the samples were calculated using (equation 6) [14].

$$K = \frac{\alpha\lambda}{4\pi} \quad (6)$$

Where k is called the extinction coefficient (k), α is the absorption coefficient, λ is the wavelength.

The X- ray diffraction pattern was recorded on a Rigaku Ultima IV X-ray diffractometer equipped with a graphite- monochromated Cu $K\alpha$ radiation source (40kV, 30mA) and wave length 1.54Å. Diffractograms were collected in the 2θ range between 3° and 90° with a step size

125 of 0.01° and a scan speed of $1^\circ/\text{min}$. the XRD Pattern was processed using JCPDS card numbers.
126 We used Debye Scherer Equation to determine the crystallite size.

$$127 \quad D = \frac{k\lambda}{\beta \cos \theta} \quad (7)$$

128 Where D is the crystallite size, K= shape factor, which is constant (0.89), λ = wavelength
129 ($1.54\text{\AA}$), β = Full Width Half Maximum (FWHM), $\theta = 2$ Theta.

130 The Tauc's relation (Equation 8) was used to estimate the optical band gap

$$131 \quad \alpha h\nu = A(h\nu - E_g)^n \quad (8)$$

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

$$134 \quad E_g = h\nu = \frac{hc}{\lambda} \quad (9)$$

135 Where C is the velocity of light, λ is the wavelength in meters (m), ν is the transition frequency
136 and h is the Planck's constant. Since $1\text{J} = 1.602 \times 10^{-19} \text{ eV}$
137 We substituted these variables into equation 9 and obtained

$$138 \quad h\nu \text{ (eV)} = \frac{1.241}{\lambda(\mu\text{m})} \quad (10)$$

139 From equation 10 we calculated the photon energies in (eV) for various wavelengths λ in(μm).
140 A graph of $(\alpha h\nu)^2$ versus $h\nu$ for both undoped and doped samples were plotted and the direct
141 band gap was determined by extrapolating the straight portion of the graph on $h\nu$ axis at
142 $(\alpha h\nu)^2 = 0$ which gives the band gap of both doped and undoped films. Figure 6 shows the plot

of $(\alpha h\nu)^2$ against photon energy. The direct band gap energy was extrapolated at the axis of the photon energy $(h\nu)$ where $(\alpha h\nu)^2 = 0$. The Figure gives the direct band gap of 3.81 eV for undoped or pure TiO_2 , 3.20 eV for 1.0 M of Ag/TiO_2 and 3.00 eV for 1.5 M of Ag/TiO_2 . The direct band gap of undoped or pure TiO_2 3.81 eV is in agreement with the result obtained by [15].

RESULTS AND DISCUSSION

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

The absorbance spectra of the deposited films were shown in Figure 1. It is obvious that the absorption edge was shifted to visible region due to Ag doping. Hence, silver (Ag) doping caused decrease in the energy band-gap of the films. The more we dope with Ag, the higher the absorbance within the visible region. This result is agreement with results obtained by [17] and [15].

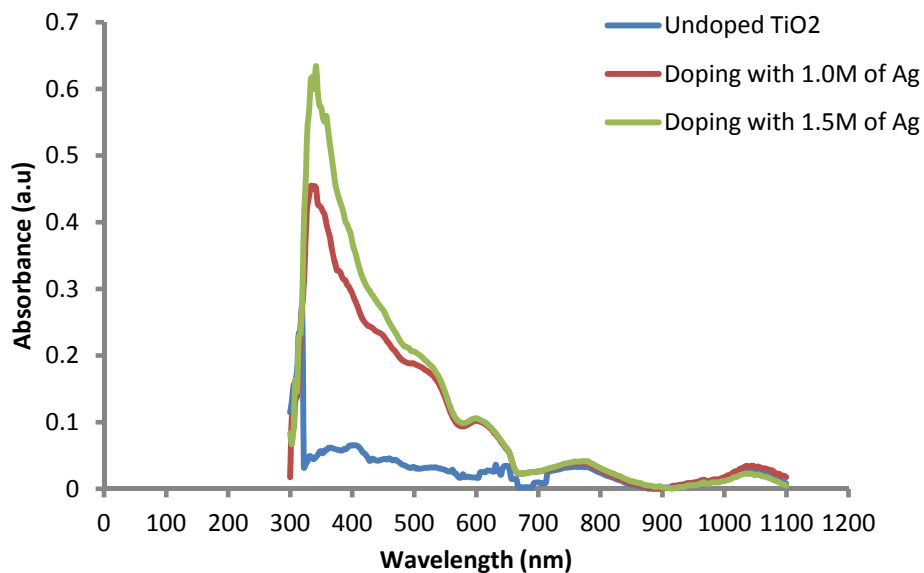


Figure 1: Absorbance Spectra for the Undoped and Doped Samples.

From the result obtained in Figure 2, we observed that the average transmittance of all the deposited films is above 75% in the visible region which is in agreement with the result obtained by Hassan *et al.*, [18]. We also observed that the effect of doping with different concentrations of silver brought about slight decrease in the transmittance within the visible region which is also in agreement with results obtained from [20].

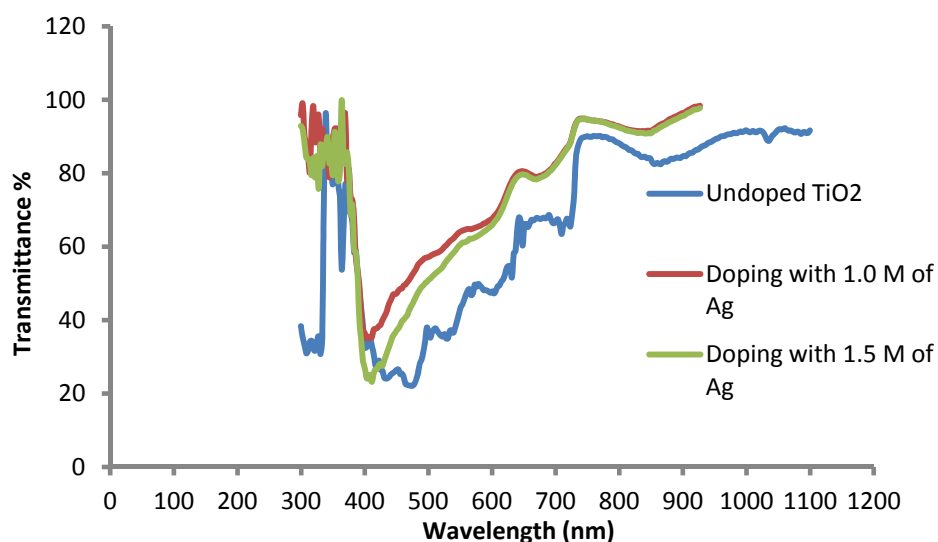


Figure 2: Dependence of Transmittance on Wavelength for Undoped and Doped Samples.

The result obtained in Figure 3 shows that absorption coefficient is inversely proportional to the transmittance. Increase in Ag content increased the absorption coefficient of the films within the visible region. The result is accordance with result obtained by [20].

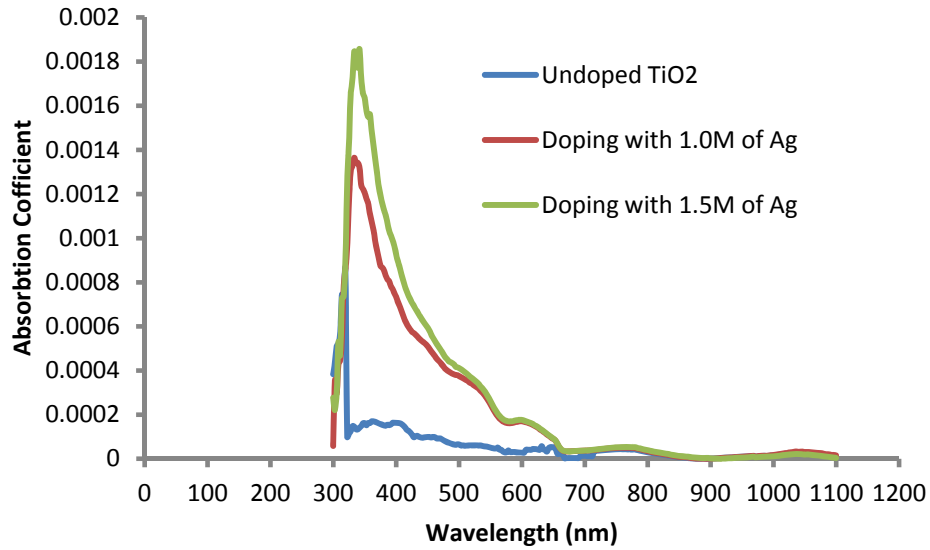


Figure 3: Absorption Coefficient against Wavelength for Undoped and Doped Samples

Figure 4 shows the variation in refractive index films with wavelength. It is observed that the refractive index for the films have sharp increase in the wavelength of 390 nm to 400 nm and then the curve increased slowly with further increase in the wavelength.

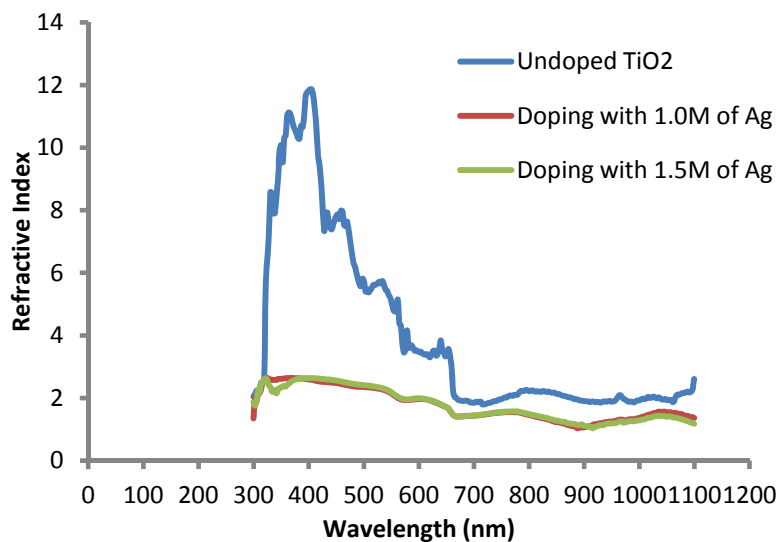


Figure 4: Variation of Refractive index for Undoped and doped Samples.

Fig. 5 shows the variation in extinction coefficient of the films deposited. It is clear that the graph of the extinction coefficient has the same behaviour with that of the absorption (absorbance). The influence of doping TiO_2 with different concentration of Ag brought about increase in the Extinction coefficient due to increase in the absorption. Hence as the concentration of Ag increased, the Extinction Coefficient increased. This result is in agreement with the result obtained by [15].

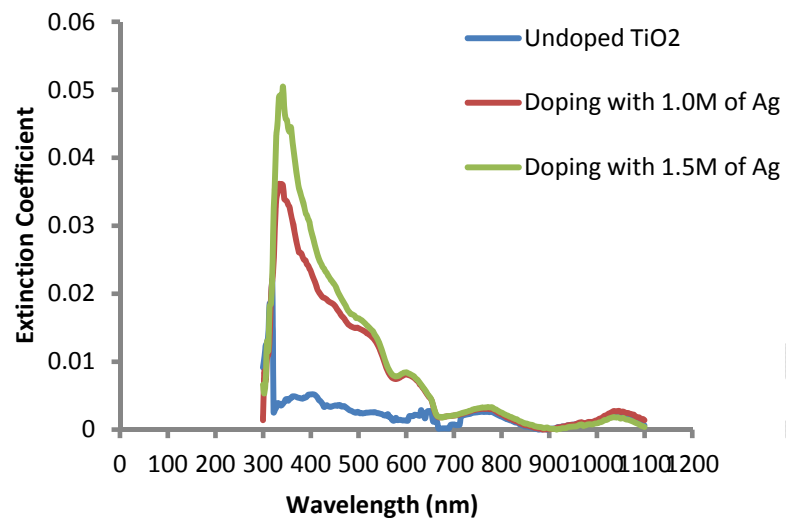


Figure 5: Dependence of Extinction Coefficient on the Wavelength for Undoped and Doped Samples.

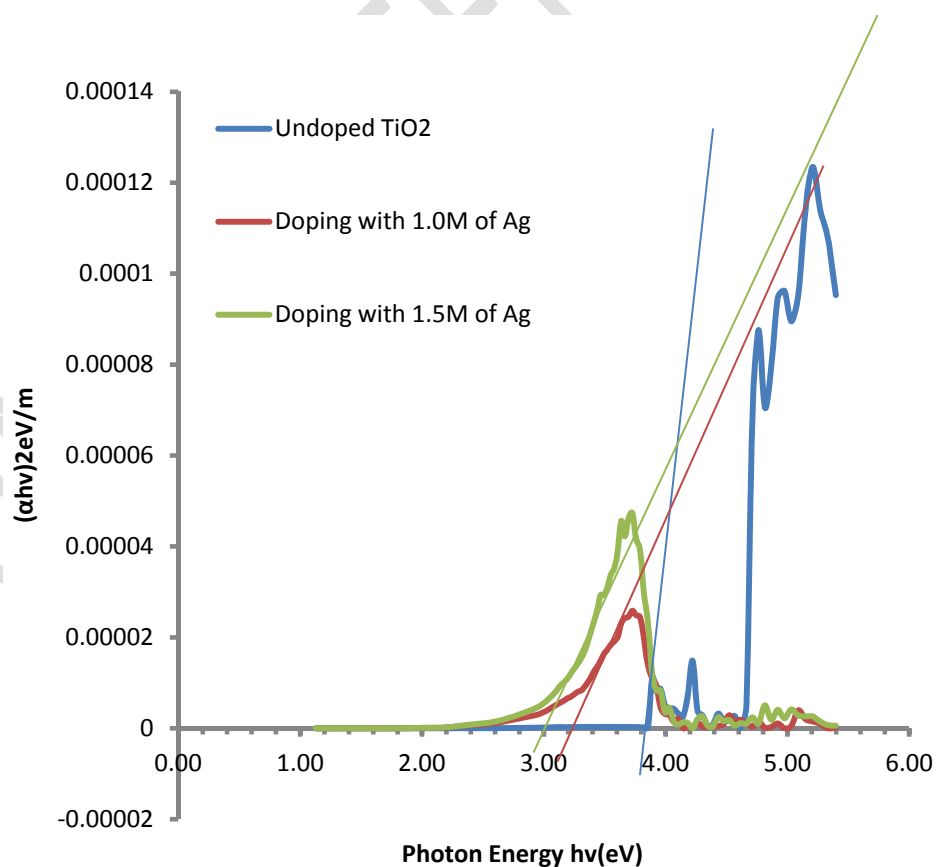


Fig 6: Direct Band gap for Undoped and Ag doped TiO₂ Samples.

Figure 7 shows the plot of $(\alpha h\nu)^{1/2}$ against photon energy. The indirect band gap energy was also extrapolated at the axis of the photon energy ($h\nu$) where $(\alpha h\nu)^{1/2} = 0$. Figure 6 gives the indirect band gap of 3.80 eV for undoped TiO₂, 2.80 eV for 1.0 M of Ag/TiO₂ and 2.60 eV for 1.5 M of Ag/TiO₂. From the results, these band gap values shows that optical band gap energies of pure or undoped TiO₂ decreases with doping of silver ions, which allow the delay in the recombination rate and enhances the photocatalytic activities of TiO₂ [16].

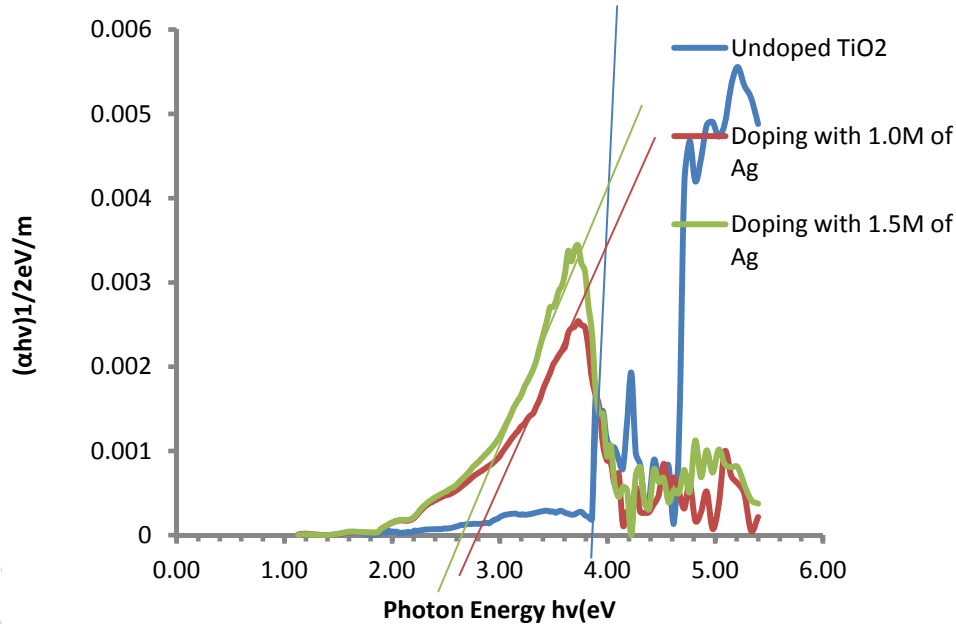


Fig 7: Indirect Band gap for Undoped and Doped Samples.

The Micrograph Analysis

Fig 8a- 8c, show the micrograph of samples of undoped TiO₂, 1.0 M and 1.5 M of Ag using Celestron LCD digital microscope, model #44348 with magnification of 800. Fig. 8a shows the micrograph of undoped TiO₂ sample which revealed rough surface morphologies and larger pores on the film, which may be due to the aggregation of tiny crystals. Using imageJ software,

we obtained an average particle size of $6.00\mu m$. Fig 8b showed an increase in the number of orderly stacked particles. There was reduction in the size of pores compared to undoped TiO_2 sample. The average particle size of $7.00\mu m$ was obtained using imageJ software. While in Fig 8c, observations revealed that micro grains are packed closely compared to both undoped TiO_2 and 1.0 M. Average particle size of $8.00\mu m$ was obtained for the sample.

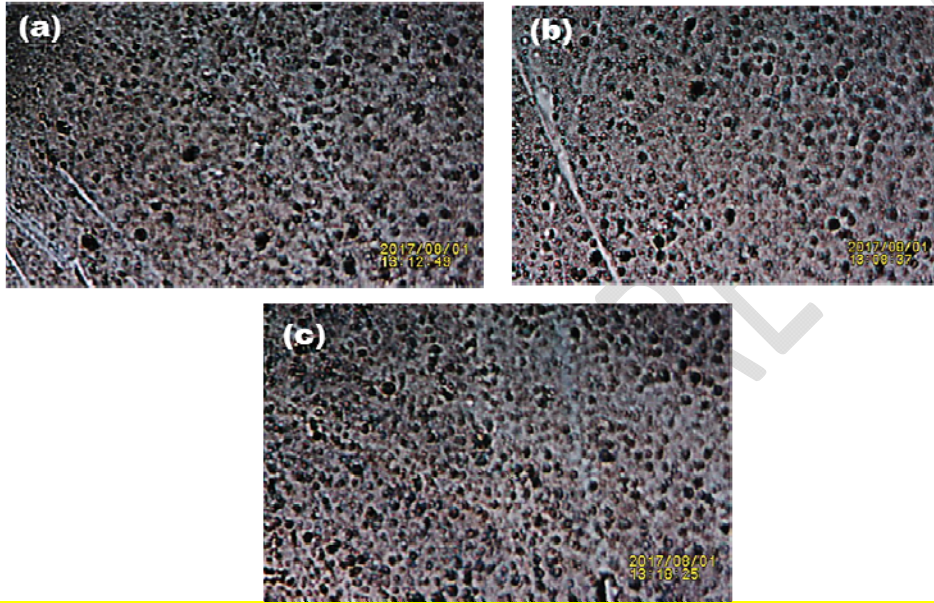


Fig 8: The Micrograph of Undoped TiO_2 and Ag doped TiO_2 : (a) undoped TiO_2 , (b) 1.0 M of Ag/ TiO_2 Sample and (c) 1.5 M of Ag/ TiO_2 Sample.

The X-ray Diffraction

The X-ray diffraction patterns for both undoped TiO_2 and doped 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 is shown in Fig. 8. The x – ray diffraction patterns of deposited samples are attributed to reflections of anatase phase with tetragonal crystal structure corresponding to the JCPDS card number (021 – 1272). There is no peak corresponding to the rutile phase of the TiO_2 . The dome shape observed in the XRD spectra between 20° and 35° is attributed to amorphous nature of deposited sample at $250^\circ C$

temperature. This shows that there is a phase transition during the formation of the samples from amorphous to anatase phase. The results correspond to those obtained by [21], [22]. These results correspond to crystalline phase of TiO_2 . Using Debye-Scherrer equation, $D = k\lambda/\beta\cos\theta$, the average crystallite was 8.76 nm, 8.90 nm and 9.00 nm respectively. Comparing the three patterns we observed that increase in the impurities (concentration of Ag) brings about increase in the intensity of the peaks.

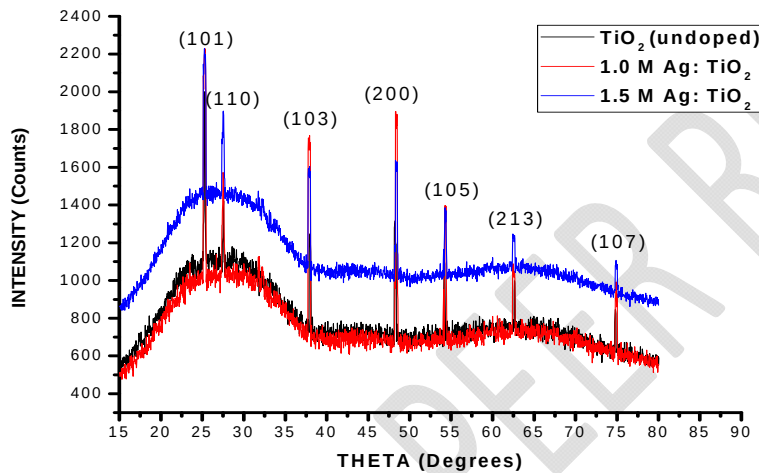


Fig 9: XRD Pattern for Undoped and Doped Samples

CONCLUSION

In this paper we have reported the structural, optical properties of TiO_2 and Ag-doped TiO_2 synthesized using Electro-hydrodynamic spray pyrolysis equipment. The X-ray diffraction pattern showed crystalline nature of TiO_2 . The UV-vis spectroscopy revealed the shifting of absorption edge of silver-doped TiO_2 to the visible region compared to that of Undoped TiO_2 . The Extinction coefficient showed that as the dopants are added to the parent material, the extinction coefficient values of the films increase within the visible region. The average

transmittance for TiO₂ films is over 72% hence we can use these samples as an optical window in solar cell. Using Optical Microscopy showed that Ag-doped TiO₂ samples have micro-grains that are closely packed compared to undoped TiO₂ sample. Also the optical properties of the thin films have allowed direct transition and allowed indirect transition. Increase of the Ag content of the films causes a decrease in the optical band gap values, hence the undoped TiO₂ film showed poor photocatalytic activity, while doping of silver ions improves the effectiveness under the visible –light radiation.

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