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Effect Of Doping On The Optical Properties Of Pure And Ag-Doped Tio_2 Thin Films Deposited By Field Assisted Spray Pyrolysis.

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ABSTRACT
We investigated the influence of Ag doping on TiO_2 thin films. The Undoped TiO_2 and 0.05 M Ag-doped TiO_2 Films were synthesized by Field Assisted Spray Pyrolysis Technique, deposited at 250ºC. The films were characterized by Ultraviolet – Visible light Spectroscopy (UV-Vis Spectroscopy). The results from.The Undoped TiO_2 exhibited low absorbance within the visible spectrum but increases when doped with 0.05 M Ag ion concentration. Within the visible region, the result showed transmittance around 36-87 while the result of refractive index showed that the films have sharp increase in the wavelength of 390 nm to 400 nm and then the curve decreased slowly with further increase in the wavelength. Absorption coefficient increased as TiO_2 was doped with Ag Also, Extinction coefficient increased within the visible region as we doped. The direct band-gap for films ranged from 4.70eV- 3.00eV while the indirect band-gap for films ranged between 4.60eV and 2.30eV. Doped film showed narrowed band-gap.

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

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I. INTRODUCTION

Titanium IV Oxide (TiO_2) is a polymorphous compound with a broad range of applications in catalysis and photocatalysis, gas sensors, energy storage, self cleaning devices etc. These applications are dependent on the crystallographic structure, morphology and physical properties of different phases of TiO_2 [1]. Among the numerous oxide materials, it has received unprecedented interest due to its superior physical, chemical properties, high stability and ability to be easily doped with active ions. Due to a combination of its unique properties such as high refractive index, high transmittance, chemical stability and photo-catalytic behavior, titanium dioxide constitutes a very valuable material for optical applications [2].

In recent years, many efforts have been directed toward 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 [3]. 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 [4]. 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 [5].

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 [6]. 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 [7].

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 [8]. 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 [9].

The aim of this research is to investigate the comparative photocatalytic activities of TiO_2 and Ag-doped TiO_2 (visible region active) films synthesized by Electro-hydrodynamic), spray pyrolysis technique and the heterogeneous photocatalysis in the presence of TiO_2 was also studied. The films deposited were characterized by, Ultraviolet – Visible light Spectroscopy (UV-Vis Spectroscopy).

II. EXPERIMENTAL

A Clear solution of TiO_2 was prepared from the dissolution of titanium acetyl acetonate $[Ti(C_5H_7O_2)_4]$ and propanol $[C_3H_8O]$, mixed in a conical flask and stirred for an hour with a magnetic stirrer. The clear solution was used to prepare colloidal solution of TiO_2 deposited using Field Assisted Spray Pyrolysis Technique on a pro-cleaned glass at a temperature of 250^{o}C in 10minutes.

A solution of silver nitrate $[AgNO_3]$ and propanol was also mixed and stirred for one hour with a magnetic stirrer. 0.05 M of $AgNO_3$ was added to TiO_2 and was also deposited using the same technique at the temperature of 250^{0}C within 10 minutes. Hence we produced an undoped TiO_2 film and Ag-doped TiO_2 film.

In this work, the method adopted is similar to method used by [10]. But here, we investigated specifically the optical properties of these two films (undoped TiO_2 and 0.05 M Ag-doped TiO_2) in order to ascertain the effect of the photocatalytic activities of Ag in TiO_2.

Using UV-Vis spectroscopy, the absorption spectra, transmittance, refractive index, absorption coefficient and extinction coefficient of the deposited undoped TiO_2 and Ag-doped TiO_2 thin films were recorded within the wavelength range of (UV) region of (230 nm to 390 nm), visible light (VIS) region of (400 nm to 700 nm) and near infrared (NIR) region of (714 nm to 1080 nm).

The values of the absorption coefficient were obtained using the equation below according to [11],

$$\alpha = \frac{\ln\left[\frac{1}{T}\right]}{d} eVm^{-1} \qquad 1$$

Where T is the transmittance, d is the thickness and α is the absorption coefficient. The values of extinction coefficient of were calculated using the equation of extinction coefficient according to [12].

$$k = \frac{\alpha\lambda}{4\pi} \qquad 2$$

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

III. RESULTS AND DISCUSSION

OPTICAL PROPERTIES OF THE DEPOSITED FILMS

The absorbance spectra of the deposited films were shown in figure 1. It is found that absorbance spectra of 0.05 M Ag doped TiO_2 has high absorbance within the visible region than the undoped TiO_2. The result is in agreement with result obtained by [6]

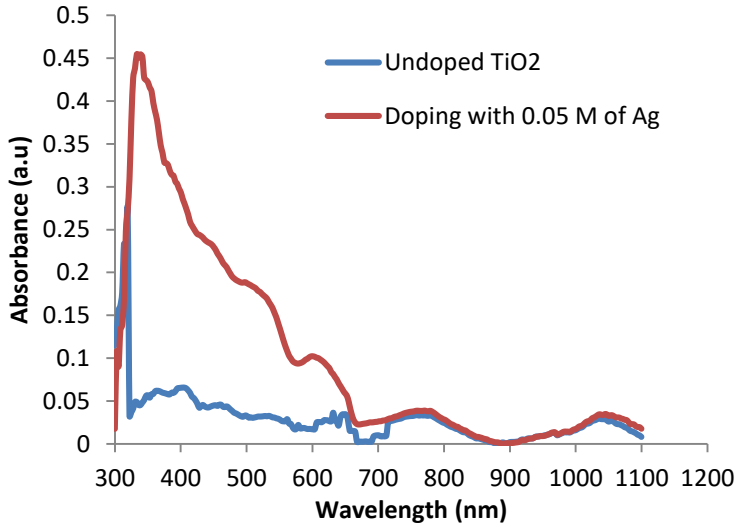

Figure 1: Absorbance Spectra for the Undoped TiO_2 and 0.05 M of Ag/TiO_2 Films.

The Figure 2 showed the transmittance of both undoped and 0.05 M of Ag/TiO_2 films. From the result obtained, we observed that the average transmittance of all the deposited films is above 70% in the visible region which is in agreement with the result obtained by [11]. There was also slight decrease in the transmittance within the visible region which is as a result of doping and is also in agreement with results obtained from [13].

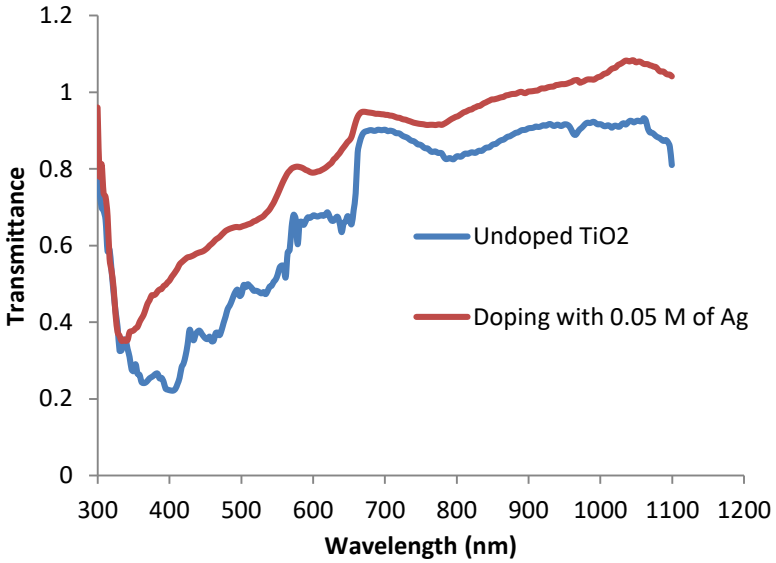

Figure 2: Transmittance for the Undoped TiO_2 and 0.05 M of Ag/TiO_2 Films.

Figure 3 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 decreased slowly with further increase in the wavelength.

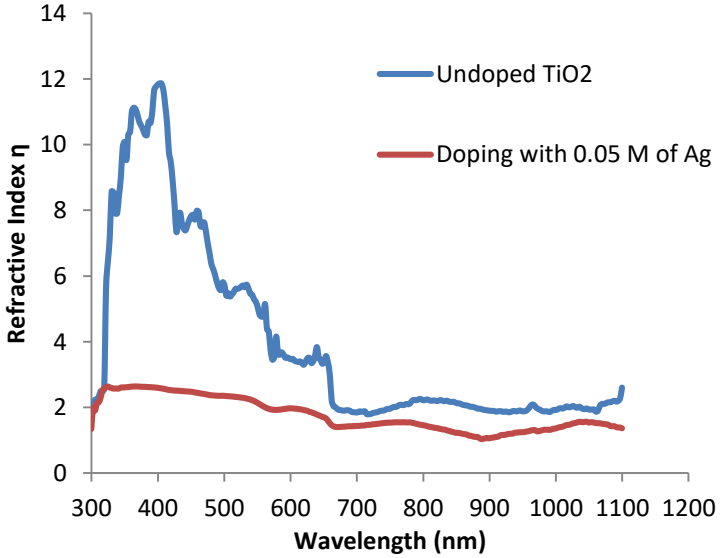

Figure 3: Refractive index against the Wavelength for Undoped and 0.05 M Ag/TiO_2 doped Films

Figure 4 below showed the Absorption coefficient of undoped and Ag/doped TiO_2 films. Its result Showed that doping with Ag brings about increase in the absorption coefficient of the film within the visible region. This result is in accordance with result obtained by [14].

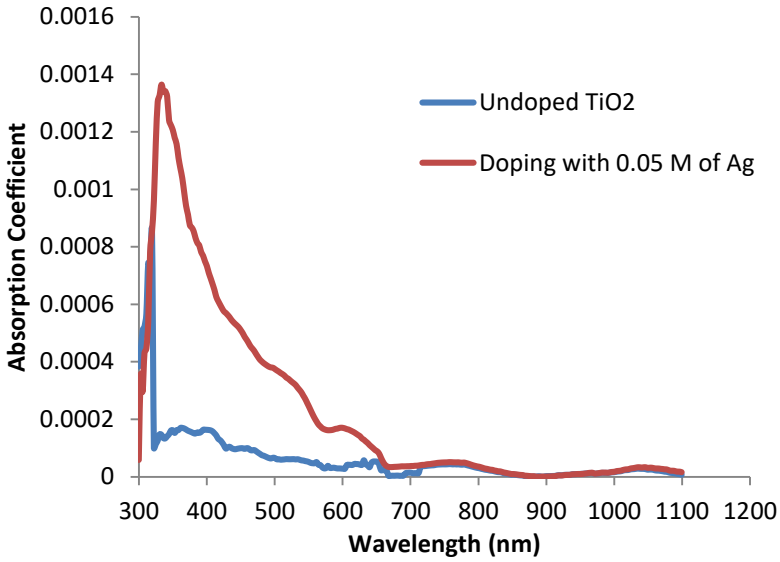

Figure 4: Absorption Coefficient against the Wavelength for undoped and 0.05 M Ag/TiO_2 doped Films

Figure 5 below showed the extinction coefficient of undoped and Ag/doped TiO_2 films. It showed that doping increases the extinction coefficient of the film within the visible region. 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 0.05 M of Ag brings about increase in the Extinction coefficient due to increase in the absorption. This result is in agreement with the result obtained by [15].

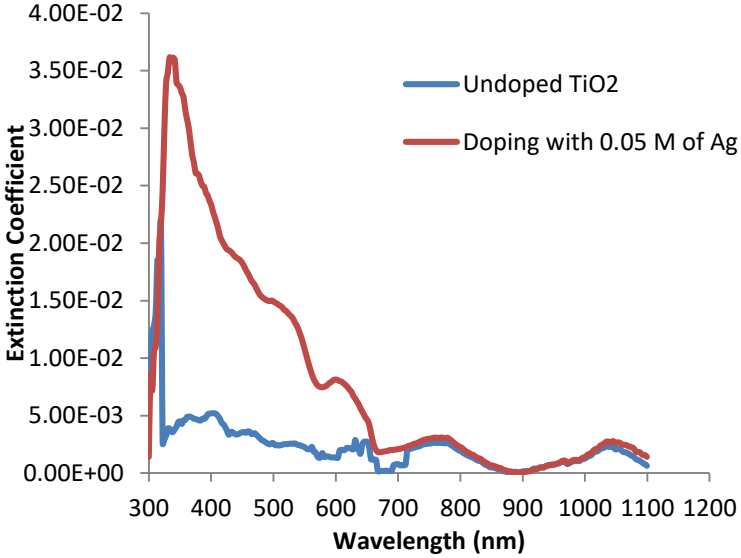

Figure 5: Extinction Coefficient against the Wavelength for undoped and doped 0.05 M of Ag/TiO_2 Films.

Using Tauc's relation

$$\alpha h\nu = A[h\nu - Eg]^n \quad (4)$$

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

$$E_g = h\upsilon = \frac{hc}{\lambda} \quad (5)$$

C is the velocity of light= $3 \times 10^8 ms^{-1}$, λ is the wavelength in meters (m). υ is the transition frequency, h is the Planck's constant = 6.62x10 $^{-34}$Js. Since 1J $= 1.602 \times 10^{-19}$ eV
We substituted these variables into equation (5) and obtained

$$h\upsilon(eV) = \frac{hc}{\lambda_o} = \left(\frac{6.63\times10^{-34}Js^{-1}\times3\times10^{8}ms^{-1}}{\lambda(nm)\times10^{-9}\times1.602\times10^{-19}c}\right) = \frac{1.241}{\lambda(\mu m)}\upsilon\ (eV) \qquad 6$$

From equation (6), we calculated the photon energies in (eV) for various wavelengths λ in(μm). A graph of $(\alpha h\nu)^2$ versus $h\nu$ for both undoped TiO_2 and 0.05 M doped Ag samples were plotted and the direct band gap was extracted by extrapolating the straight portion of the graph on $h\upsilon$axis at $(\alpha h\upsilon)^2 = 0$ which gives the band gap of both films. For the undoped TiO_2 has the band gap of 4.70 eV while 0.05 M -doped Ag has band gap of 3.00 eV which shows that doping brings about reduction of the energy band gap.

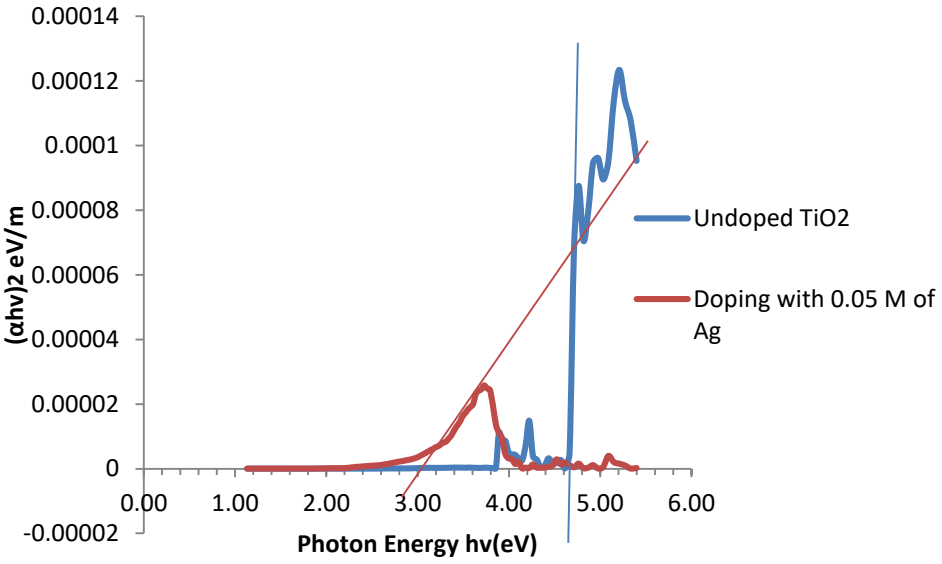

Fig 6: Direct Band gap for Undoped TiO_2 and 0.05 M-doped Ag Films.

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 ($h\upsilon$) where $(\alpha h\nu)^{1/2}= 0$. Figure 8 gives the indirect band gap of 4.60 eV for undoped TiO_2 for undoped TiO_2. This result obtained for undoped may be as a result of method of deposition, temperature or the substrate used for the atomization according to [16]. While for 0.05 M of Ag/TiO_2 has the indirect band gap of 2.30 eV which is in accordance with the result obtained by [17] .

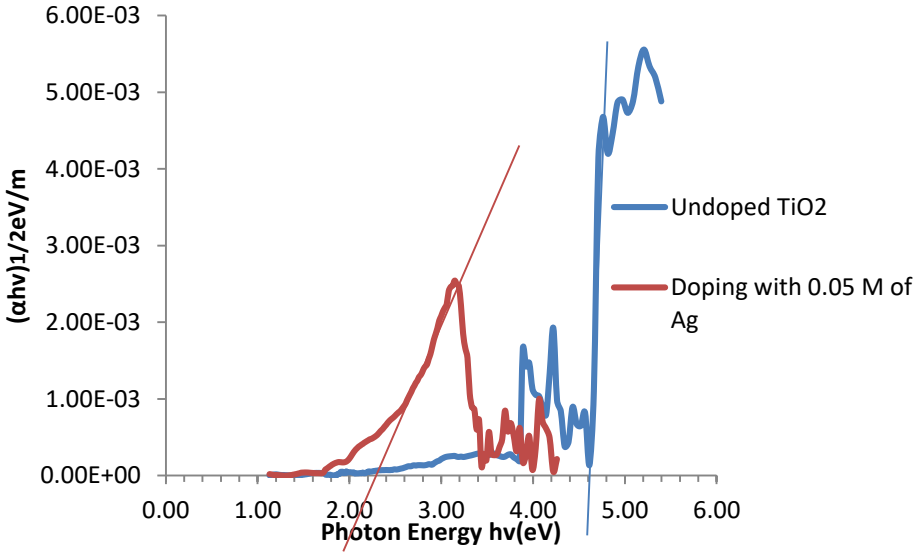

Fig 7: Indirect Band gap for Undoped TiO_2 and 0.05 M-doped Ag Films.

IV. CONCLUSION

The effect of doping 0.05 M of silver (Ag) on the the optical properties of TiO_2 using Field Assisteds Spray Pyrolysis equipment was reported. 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 transmittance of the films showed increase in the value from 36-87 within the visible region, also the refractive index result of the films showed have sharp increase in the wavelength of 390 nm to 400 nm and then the curve decreased slowly with further increase in the wavelength. The Absorption coefficient showed that doping with 0.05 M of Ag in TiO_2 brought about increase in the absorption coefficient values of the films within the visible region. The Extinction coefficient showed that as the dopant (Ag) is been added to the parent material(TiO_2), the extinction coefficient values of the films increased within the visible region within the visible region. The direct band gap for doped film showed more decrease in energy band gap than the undoped film, having more semiconducting behaviours than undoped TiO_2 film. The direct band gap ranges from 4.70 eV – 3.00 eV. Also the indirect band gap for doped film showed more decrease in energy band gap than the undoped film and the indirect band gap ranges from 4.60 eV – 2.30 eV. The undoped TiO_2 nanoparticles showed poor photocatalytic activity, while doping of silver ions improves the efficiency under the visible –light irradiation.

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