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The Effect of Silver Doping on Optical Properties of TiO_2

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Abstract
The Optical Properties of two groups of samples were studied.
Group one samples made of titanium dioxide (TiO_2); while group two samples were doped by (Ag); $AgTiO_2$.The optical characteristics of the prepared samples have been investigated by UV/Vis spectrophotometer in the wavelength range (240 – 700nm). The maximum value absorbance for TiO_2 sample equal (3.27 a.u) at wavelength (306 nm) but Ag TiO_2 was decreases to (3.17 a.u) at same wavelength. The value of absorption coefficient (α) for TiO_2 was greater than $AgTiO_2$ sample ($1.5X10^5$ cm^{-1} at the same wavelength). The value of energy band gab (E_g) was decreased from (3.152eV) for the TiO_2 sample to (3.123eV) at ($AgTiO_2$) sample, the decreases of (E_g) may be related to decrease in grain boundaries and their density due to the doping effect of the TiO_2 samples. The magnitude of optical conductivity ($1.35X\ 10^{12}$ Sec^{-1}) for all samples confirms the presence of very high photo-response of the samples; this can be useful in optoelectronic applications.

Keywords: *Titanium Dioxide, optical characteristics, doping, optical conductivity, optoelectronic applications.*

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I. Introduction

Titanium dioxide (TiO_2), a metal oxide semiconductor, has been found to be one of the most effective photo catalysts due to its high efficiency and stability [1] the strong oxidation and reduction power of photo excited titanium dioxide was realized from the discovery of the Honda-Fujishima effect. In 1972, Fujishima and Honda reported photo induced decomposition of water on TiO_2 electrodes. Since Frank and Bard first examined the possibilities of using $TiO_2$to decompose cyanide in water, there has been an increasing interest in environmental applications. TiO_2 photo catalysts are widely used for air purification, deodorization, sterilization, anti-fouling, and mist removal [2,3]. Although TiO_2 has the advantage of good chemical stability, high activity, absence of toxicity and relative low price [4] however, its band gap is so large (Eg = 3.20 eV) that it can only be excited by ultraviolet light with a Wavelength no longer than 387.5 nm,[8] which accounts for only 5% of the incoming solar energy. Thus, it is significant to develop a visible-light driven photo catalyst with high photo catalytic activity or this purpose, an initial approach of doping TiO_2 with transition metals was extensively investigated[5,6]However, the photo catalytic activity of metal doping is impaired by thermal instability and an increase in carrier recombination facilities. Therefore, many researchers have started to use anionic nonmetal dopants to extend the photo catalytic activity into the visible-light region because the related impurity states are near the valence band edge and do not act as charge carriers. TiO_2 is white, inexpensive, and nontoxic [7]. It is one of the most widely used photo catalysts for disinfection [6, 8]. Since the discovery of the photo catalytic splitting of water on aTiO_2 electrode under ultraviolet (UV) light [9], a great deal of research efforts have been made on semiconductor-based photo catalysts on both energy conversion and environmental applications.

II. Materials & Method

Distilled water was used as solvent in the process. The water employed in all preparations was purified by a distilled, Titanium tetrachloride, Silver.

Synthesis of TiO_2: 50 ml of $TiCl_4$ solution were slowly added to 200 ml of distilled water in an ice bath. After the addition completed, the mixture then was stirred for 30 minutes at room temperature. The solution was heated in water bath for 90 minutes under refluxing. Then, it was filtered using vacuum pump and calcined at 600^oC in the muffle furnace for two hours [10].

Synthesis of Ag-TiO_2 Nanoparticles: Liquid Impregnation Method. In the liquid impregnation method [11] silver ion (Ag+) doped on TiO_2 was prepared according to the following steps. We prepare 80 g of TiO_2Ag nanoparticles; 79.2 g of TiO_2 was added to 500mLof deionizer water. Preparation of silver-doped TiO_2

nanoparticles, 1.7 g of$AgNO_3$ for doping was added to TiO_2 suspension; the silver concentration was of 1% (mole ratio) versus TiO_2.The slurry was stirred well for 6 hours and allowed to rest for 24 h and then dried in an air oven at 100◦C for 12 h. The dried solids were crushed to fine powder in an agate mortar and calcined at 400◦C for 6h in a muffle furnace. In this method the metal gets deposited on the surface of the photo catalyst [12].

III. Results

The optical characteristics of the prepared samples have been investigated by UV/Vis spectrophotometer in the wavelength range (240 – 700nm) as shown below.

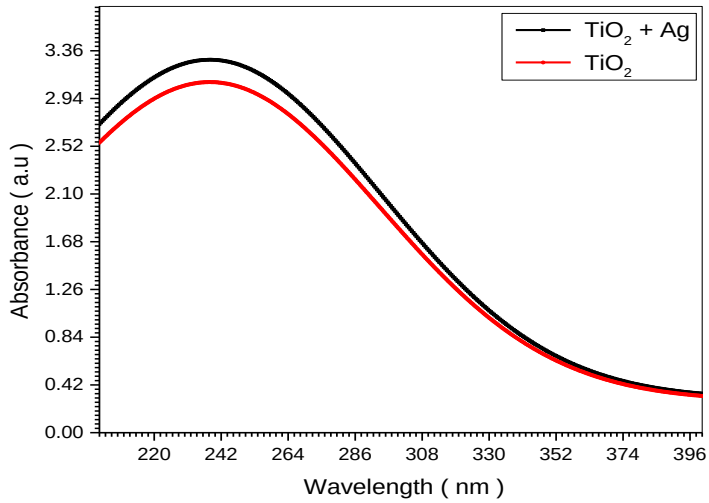

Fig (1): Optical absorbance spectra of TiO_2 and ($AgTiO_2$) samples

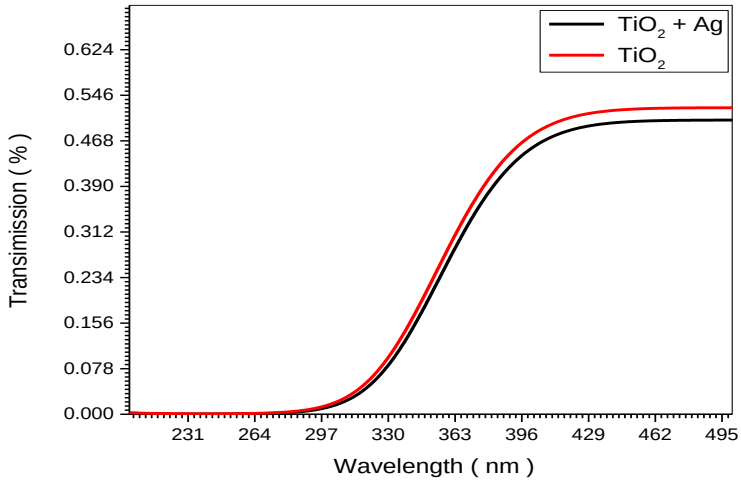

Fig (2): Optical transmittance (T) spectra of TiO_2 and ($AgTiO_2$) samples

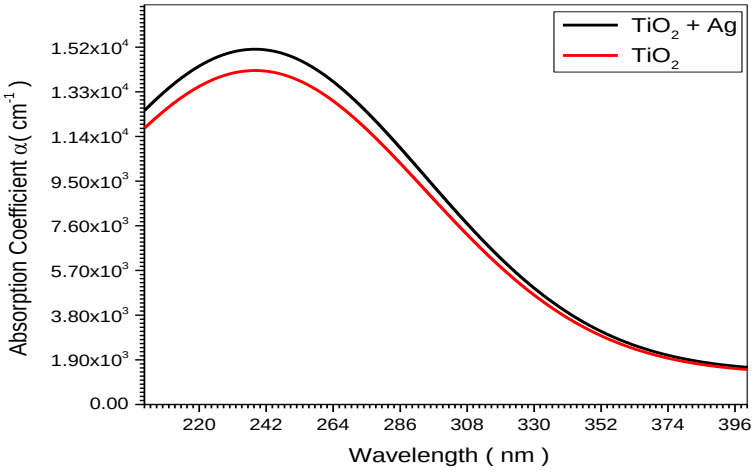

Fig (3): Variation of absorption coefficient (α) with (λ) for TiO_2 and (Ag TiO_2) samples

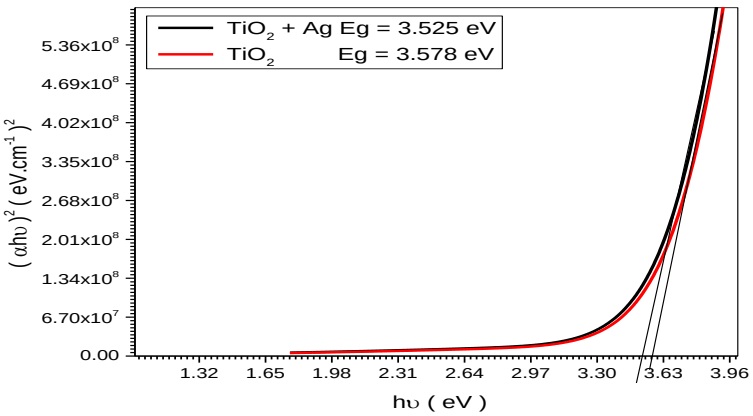

Fig (4): The optical energy gap (E_g) value) of TiO2and ($AgTiO_2$) samples

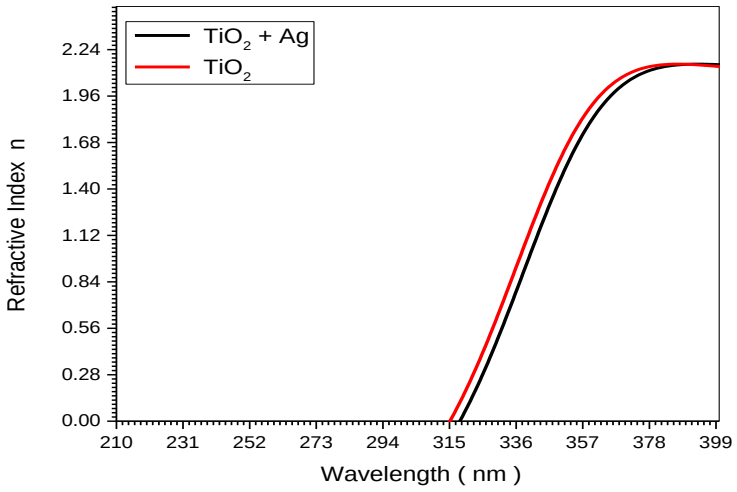

Fig (5): Variation of refractive index (n) with wavelength (λ) for TiO_2 and (Ag TiO_2) samples

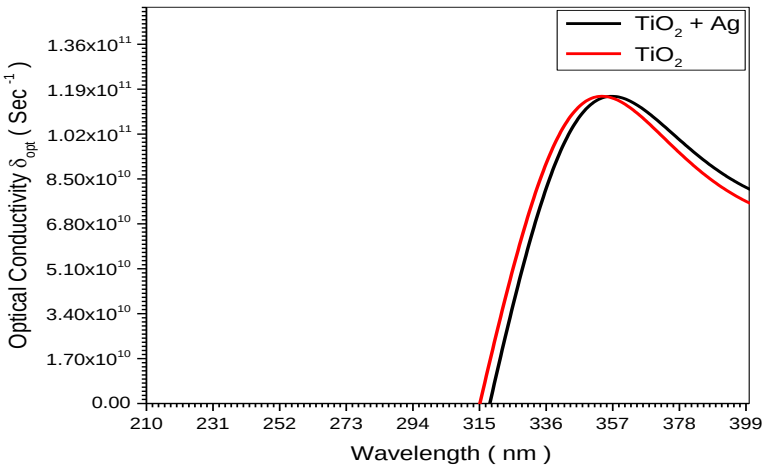

Fig (6): Plot of optical conductivity as a function of wavelength for TiO_2 and ($AgTiO_2$) samples

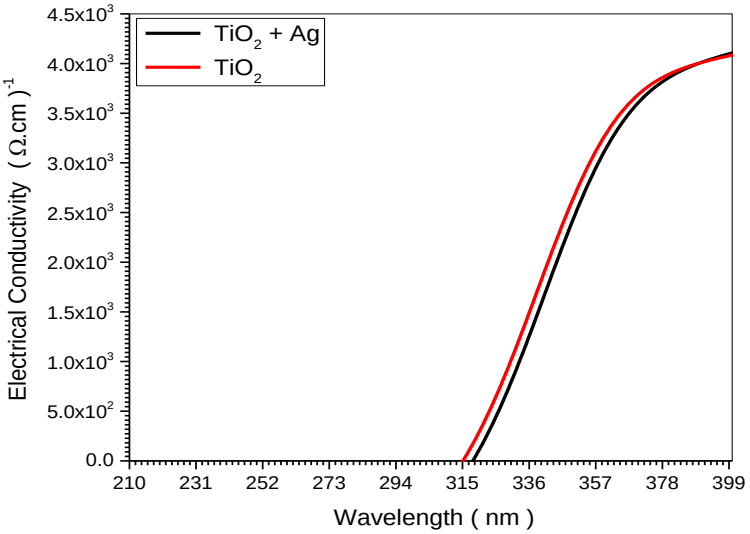

Fig (7): Plot of electrical conductivity as a function of wavelength for TiO_2 and (Ag TiO_2) samples

IV. Conclusion

The optical absorption (A) and transmittance (T) spectra in the (240–700) nm wavelength range for the TiO_2 and (Ag TiO_2) samples are depicted in Fig. (1) and (2). The peak absorption observed at 240 nm in UV region then it decreases at wavelength >240 nm. The absorption edge of the samples occurs at wavelength (240 nm) corresponding to photon energy (5.17eV) as show in fig (1).In fig (2) show that transmittance spectra of TiO_2 and (Ag TiO_2) samples, also show that the transmittance spectra of TiO_2 and (Ag TiO_2) samples as the same range of the absorption, and the transmittance value increase when to doping the sample by Ag at 240 nm. The absorption coefficient (α) of the of TiO_2 and ($AgTiO_2$) samples were found from the following relation [13, 14].

$$\alpha = \frac{2.303xA}{t}$$

Where (A) is the absorbance and (t) is the optical axes length on the sample. Fig (3) shows the plot of (α) with wavelength (λ), which obtained that the value of α equal 1.51 x10^5 cm^{-1} for $AgTiO_2$sample in (240 nm) , this means that the transition must corresponding to a direct electronic transition [15] , and the properties of

this state are important since they are responsible for electrical conduction. Also fig (3) shows that the value of (α) for the $AgTiO_2$was greater than TiO_2 sample
($1.42x10^5$ cm^{-1} at the same wavelength). The increase in absorbance after doping by Ag may be due to the increase in grain size and decrease in the number of the defects. Optical energy gap (E_g) has been calculated by the following relation [16, 13]

$$(\alpha h\upsilon)^2 = C\,(h\upsilon - Eg)$$

Where (C) is constant by plotting $(\alpha h\upsilon)^2$vs. Photon energy (hυ) as shown in fig (4) the optical energy gap (E_g) value of TiO_2 and (Ag TiO_2) samples by extrapolating the straight thin portion of the curve to intercept the energy axis, the value of the energy gab has been calculated. [16] The value of (E_g) was decreased from (3.578) eV for the TiO_2sample to (3.525) eV at ($AgTiO_2$) sample. The decreasing of (E_g) may be related to decrease in grain boundaries and their density due to the doping effect of the TiO_2 sample. It was observed that the different structures of the sample confirmed the reason for the band gap shifts.

The refractive index (n) is the relative between speeds of light in vacuum to its speed in material which does not absorb this light. The value of n was calculated from the equation [14, 13]:

$$n = \left[\left(\frac{1+R}{1-R}\right)^2 - (1+k^2) \right]^{\frac{1}{2}} + \frac{(1+R)}{(1-R)}$$

Where (R) is the reflectivity the variation of (n) vs. (λ) is shown in fig (5) which shows that the maximum value of (n) is (2.152) for all samples at wavelength (390nm). Also we can show that the value of (n) begin to decrease in the UV region of spectrum. Also (n) value decrease with doping at (371 nm), this means that the sample become more transparent in the UV region. The optical conductivity is a measure of frequency response of material when irradiated with light which is determined using the following relation,

$$\delta_{0pt} = \frac{\alpha n c}{4\pi}$$

Where (c) is the speed of the light. The electrical conductivity can be estimated using the following relation [17, 13].

$$\delta_e = \frac{2\lambda\delta_{0pt}}{\alpha}$$

The high magnitude of optical conductivity ($1.162x10^{11}$ Sec^{-1}) confirms the presence of very high photo-response of the samples. The increased optical conductivity at short wavelength is due to the high absorbance of TiO_2 and (Ag TiO_2) samples and may be due to electron excitation by wavelength as it is shown in Fig (6) and (7) .

The optical absorption (A) and transmittance (T) spectra in the (240–700) nm wavelength range for the TiO_2 and (Ag TiO_2). The absorption edge of the samples occurs at wavelength (306 nm) corresponding to photon energy (4 eV). The value of absorption coefficient (α) equal $1.48x10^5$ cm^{-1} for $AgTiO_2$ sample in the UV region(310 nm) , this means that the transition must corresponding to a direct electronic transition. The value of (E_g) was decreased from (3.152) eV for the TiO_2sample to (3.123) eV at ($AgTiO_2$) sample. The decreasing of (E_g) may be related to decrease in grain boundaries and their density due to the doping effect of the TiO_2 sample. The maximum value of (n) is (2.17) for all samples at wavelength (445 nm) . The increased of optical conductivity at low wavelength is due to the high absorbance of TiO_2 and (Ag TiO_2) samples and may be due to electron excitation by wavelength 306 nm.

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