

To Study the Effect of the Concentration of Carbon on Ultraviolet and Visible Light Photo Catalytic Activity and Characterization of Carbon Doped TiO₂

Rajkumar R^{1*} and Nisha Singh²

¹Department of Chemical Engineering, Bipin Tripathi Kumaon Institute of Technology, Dwarahat, Almora, Uttarakhand-263653, India

²Department of Chemical Engineering, R.N. College of Engineering and Technology, Panipat, Haryana-132103, India

Abstract

Photo catalytic degradation of pollutants in water or air using titanium dioxide has been considered one of the efficient methods but it shows poor absorption of visible light and requires ultraviolet light for its activation. Which increase the cost of system, So that we moved toward the doping of non-metal in TiO₂ which gave good result in visible and UV light, carbon doped TiO₂ is prepared using air heating method at lowest temperature and minimum time by taking glucose and ethanol as carbon source. The experimental results showed that carbon was successfully doped into TiO₂. The physical properties of carbon doped TiO₂ were studied by XRD, TG-TGA and UV spectroscopy which showed that the photo catalytic efficiency increase in UV and visible lights by creation of oxygen vacancies and Ti³⁺ in C-TiO₂ catalyst. UV spectroscopy results showed the optical response of TiO₂ was shifted from UV to the visible light region.

Keywords: C-doped TiO₂ nano particles; Photocatalysis; TiO₂; Doping with non-metals; Preparation; Low temperature

Introduction

Semiconductor titanium dioxide (TiO₂) is a promising photocatalyst for air purification, water disinfection, hazardous waste remediation and water purification [1]. It exists as three different polymorphs; anatase, rutile and brookite [2]. It is typically an n-type semiconductor due to oxygen deficiency [3]. The band gap is 3.2 eV for anatase and 3.0 eV for rutile [4,5]. Unfortunately, because of its large band gap of 3.2 eV, it can be activated only under UV light irradiation of wavelength (<387 nm). However, UV light constitutes only a small fraction (about 3-5%) of the solar spectrum; it will have a positive effect for improving the photo catalytic efficiency of TiO₂ by shifting its optical response to the visible range. Hence scientists are exploring methods to modify TiO₂ to absorb visible light. For example, carbon-doped TiO₂ was found to be effective for water splitting under visible light. Most of these investigations had been made to convert the TiO₂ so that its absorption power shift from the UV to the visible region by doping of TiO₂ with transition metals such as Cr, Fe, Mn, V [6-11], etc. However the photo catalytic activity of transition metals doping is poor because of their thermal instability [10]. The non-metal doping has been considered for about ten years [11] as a best way to change the photo-absorption properties of TiO₂ for using of solar light with applications in photocatalysis and photo electrochemistry [12-15]. Due to doping, the dopants of non-metals in the lattice might affect the band edges or introduce impurity states in the band gaps of the system [16,17]. Carbon-doped titania with high surface area (204 m²/g) was prepared by temperature programmed carbonization of K-contained anatase titania under a flow of cyclohexane at temperatures between 450 and 500°C. This carbon-doped titania has much better photo catalytic activity for gas-phase photo-oxidation of benzene under irradiation of artificial solar light than pure titania. Obviously, these non-metals doping in TiO₂ were all synthesized at high temperature. So it is still a challenge to prepare non-metal doped TiO₂ at a low temperature, especially for the energy-saving production of visible-light driven photo catalyst in a large scale for pollutants removal. They prepared carbon doped TiO₂ by hydrothermal treatment at 160°C which displayed stronger absorption

in both UV and visible range. These papers gave me the knowledge to develop a low-temperature method to prepare carbon-doped TiO₂, by using ethanol and titanium oxide Degussa (P25) as the carbon and TiO₂ sources, respectively. The carbon doping could take place at the same time under a new method by using as heating medium except water vapor treatment at 180°C for 4 h at constant heating in hot air oven. To the best of our knowledge, this is the lowest temperature to prepare carbon-doped TiO₂ using air as heating medium. It is found that the resulting carbon-doped TiO₂ by this new method exhibits much higher photo catalytic activity than the undoped counterpart and Degussa P25 on the degradation of phenol under visible and UV light. The focus of this work is on the determination of the true concentration of raw, exfoliated HiPCO SWNTs in the supernatant phase. A UV-visible absorption-based approach is suggested for a direct measurement of the SWNT and the surfactant concentration in the supernatant. UV-visible absorbance spectra of SWNTs-surfactant dispersions and surfactants alone reveal that the intensity of a certain peak, attributed to the π -plasmon resonance absorption, is unaffected by the presence of most surfactants. A calibration plot is then made by monitoring the intensity of the peak as a function of the true concentration of the exfoliated SWNTs. Thus, we are able to determine the unknown concentration of surfactant-dispersed HiPCO SWNTs in the supernatant solution, simply by measuring its optical absorbance. Moreover, we can now calculate the surfactant efficiency in dispersing SWNTs. Cryogenic-transmission electron microscopy and thermo

***Corresponding author:** Rajkumar R, Department of Chemical Engineering, Bipin Tripathi Kumaon Institute of Technology, Dwarahat, Almora, Uttarakhand-263653, India, Tel: 91-7830131877; E-mail: ranvir523@gmail.com

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gravimetric analysis techniques are used for the characterization of these dispersions and to complement the UV-visible measurements.

Experimental

Sample preparation

Carbon doped TiO₂ nanoparticles were prepared by air heating method by taking 4 g of TiO₂ and 40 ml ethanol. The mixture of ethanol and TiO₂ was constantly stirred by magnetic stirrer for 10 min and then heated for 4h at 180°C in hot air oven. The catalyst was kept in desiccator for cooling to obtain white powder of carbon doped TiO₂. For calcinations half of catalyst was kept in muffle furnace for 1 hour at 350°C. Similarly this method is used for making of different concentration of ethanol C-TiO₂ at are 92.20% ethanol TiO₂ at 94.04%, ethanol TiO₂, 95.17% ethanol TiO₂, 95.94% ethanol TiO₂ etc.

Characterization of C-doped TiO₂ nano particles

X-ray powder diffraction (XRD) analysis was performed using Goniometer=PW3050/60 X-ray diffract meter (CuKα k = 0.154 nm). The working voltage and current of the X-ray tube were 45 kV and 40 mA, AVarian Cary 100 Scan UV-visible system equipped with a lab sphere diffused reflectance accessory was used to obtain the absorbance spectra of the catalysts over a range of 200-600 nm. Lab sphere USRS-99-010 was employed as a absorbance standard.

Photocatalytic degradation experiments

The photocatalytic degradation experiments of methyl orange by the TiO₂ photocatalysts were performed under visible light irradiation. The photocatalytic degradation was monitored by use of a UV-Vis spectrometer at λ max = 468 nm. In all experiments a 100 mg of catalyst was suspended in 100 ml of 5 ppm methyl orange solution in a conical flask. The flask was wrapped with aluminum foil then placed in the dark for an hour for adsorption to take place. The system was then irradiated with visible light from a lamp that was fixed in the middle of the system and 12 cm above the surface of the solution. To detect changes in concentration, aliquots of methyl orange (5 mL) were taken after every 30 minutes and centrifuged. The absorbance of the clean solution was measured by a UV-Vis spectrometer.

Results and Discussion

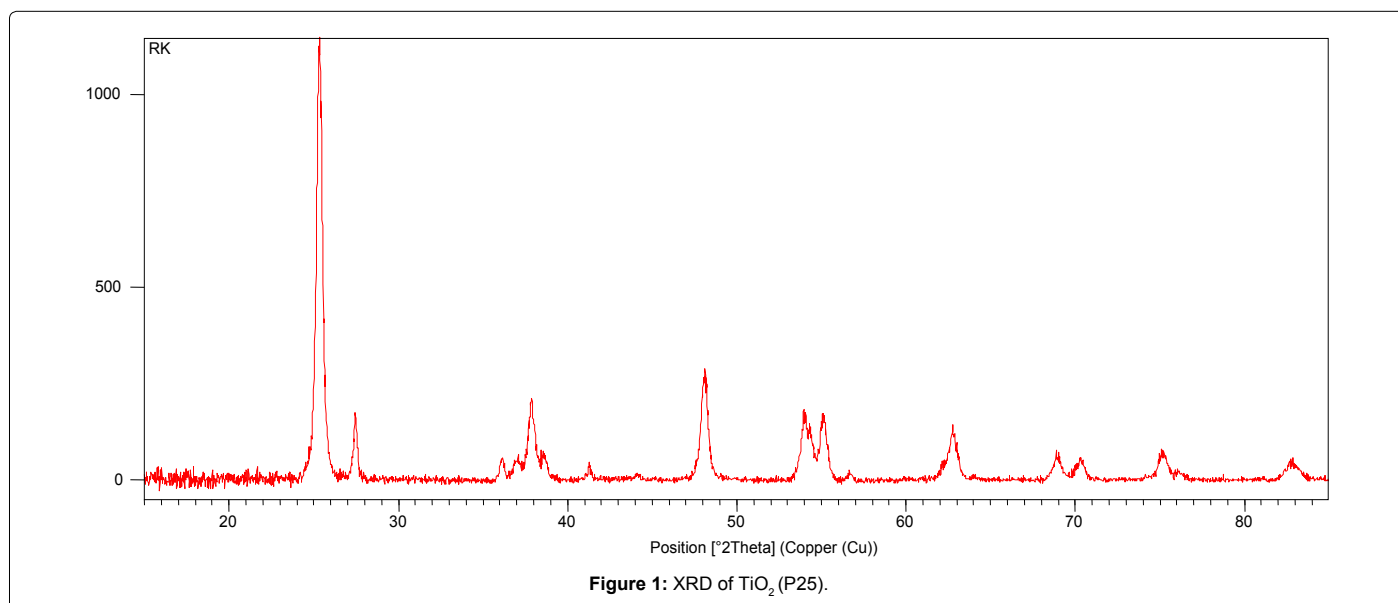
Crystal characterization

To characterize the crystalline structure of the carbon doped and undoped TiO₂ samples, for that XRD patterns in Figures 1 and 2 were obtained. The pattern of undoped TiO₂ showed the presence of anatase and brookite. However, only anatase is present in the XRD pattern of C-doped TiO₂ indicate the doping of carbon prohibit the formation of brookite. It can be also found that the crystal size of anatase decrease with the carbon doping by comparing the (101) peak of anatase in Figures 1 and 2. This decrease on crystal size can be attributed to dissimilar boundaries created by carbon doping. Meanwhile, the significant decrease on the intensity of XRD pattern of TiO₂. The crystal size decrease can be attributed to dissimilar boundaries created by carbon doping, because of the significant decrease on the intensity of XRD pattern of TiO₂. The diffraction peaks of XRD of carbon doped TiO₂ were not observed which showed that carbon was highly dispersed on TiO₂ or XRD was not sensitive enough to detect such minor changes to TiO₂.

The recently started R&D activity of growth and characterization of NLO single crystals has been continued in view of (i) growing good quality crystals (ii) growing big size crystals suitable for device applications related to photonics, (iii) to enhance the efficiency of second harmonic generation (SHG) by using different dopants and functional groups, (iv) to search new NLO materials and grow their single crystals, (v) to evaluate their crystalline perfection by high-resolution XRD and (vi) other studies like powder XRD, FTIR, UV-Vis. etc. In this endeavor and with the help of various collaborators working in this upcoming area we have achieved several important R&D results leading to twenty one articles in leading SCI journals and one article in non SCI journal. Some of these important results are briefly described in Figures 1 and 2.

If a sample contains anatase and rutile, the mass fraction of anatase (W_A) and rutile (W_R) can be calculated from the equations 1 and 2:

$$W_A = \frac{K_A A_A}{K_A A_A + A_R} \quad (1)$$



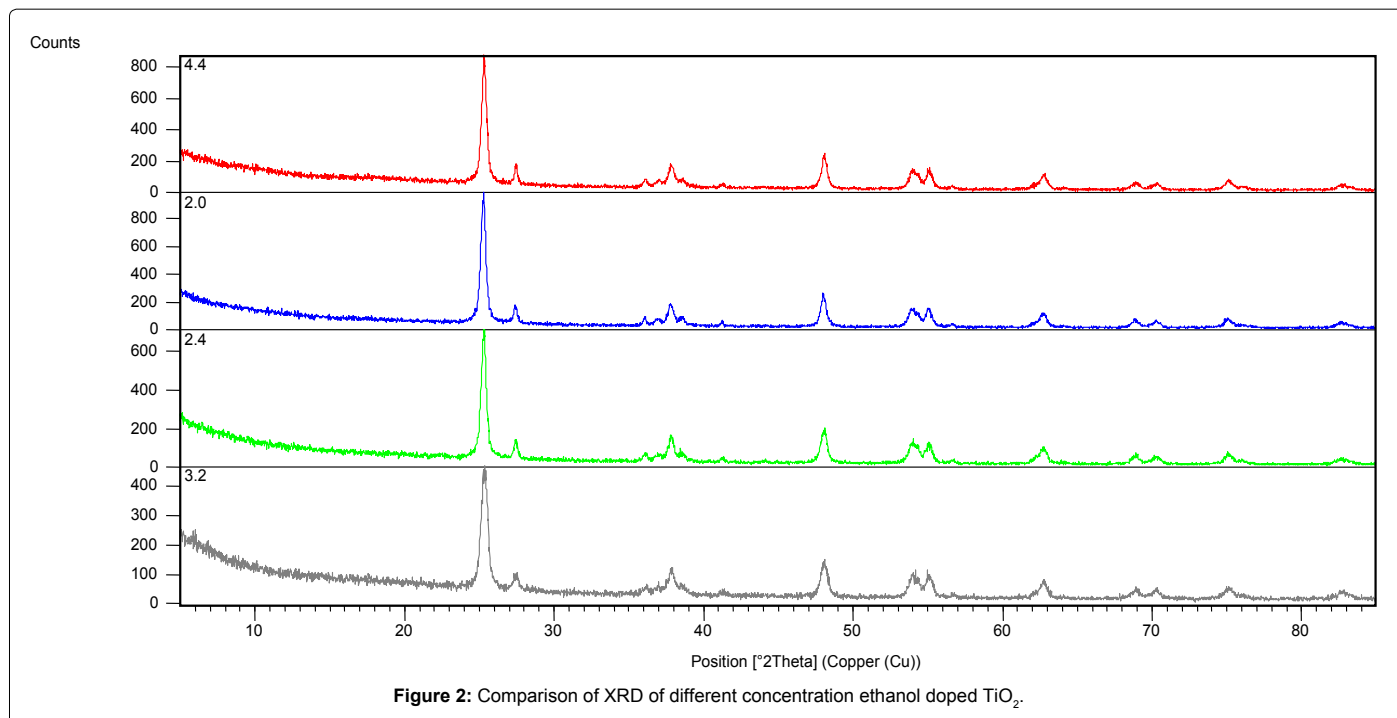


Figure 2: Comparison of XRD of different concentration ethanol doped TiO₂.

Sample	Size(nm)
TiO ₂	48.22
88.75% ethanol and 4 g TiO ₂	41.74
92.20% ethanol and 4 g TiO ₂	43.68
94.04% ethanol and 4 g TiO ₂	60.20
95.17% ethanol and 4 g TiO ₂	61.01
95.94% ethanol and 4 g TiO ₂	62.50

Table 1: Size comparisons between TiO₂ and its carbon TiO₂.

$$W_R = \frac{A_A}{K_A A_A + A_R} \quad (2)$$

Where A_A and A_R are the integrated intensity of the anatase (101) and rutile (110) peaks, respectively, W_A and W_R represents the mass fraction of anatase and rutile, respectively, and K_A is a coefficient and its value is 0.886. The average crystallite sizes of anatase were determined as follows:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where λ is the wavelength of characteristics X-ray applied and β is the half-value width of anatase (101) peak obtained by XRD and is X-ray diffraction angle. According to the Scherrer equation using the data of each different phase after correcting the instrumental broadening in Table 1.

UV-vis diffuse reflectance spectra

UV vis absorption of undoped TiO₂, 88.75%, 92.20%, 95.94% ethanol doped TiO₂ are shown in Figures 3 and 4 respectively. Carbon-doped TiO₂ sample absorbs more light in the range of 400-450. Obviously, the optical absorption edges of these non-metal doped samples shift to the lower energy region compare to the undoped TiO₂. This showed that our method is effective to extend the absorption to visible light range. A plot of the $(ah\nu)^{1/2}$ versus the energy of absorbed light affords the band

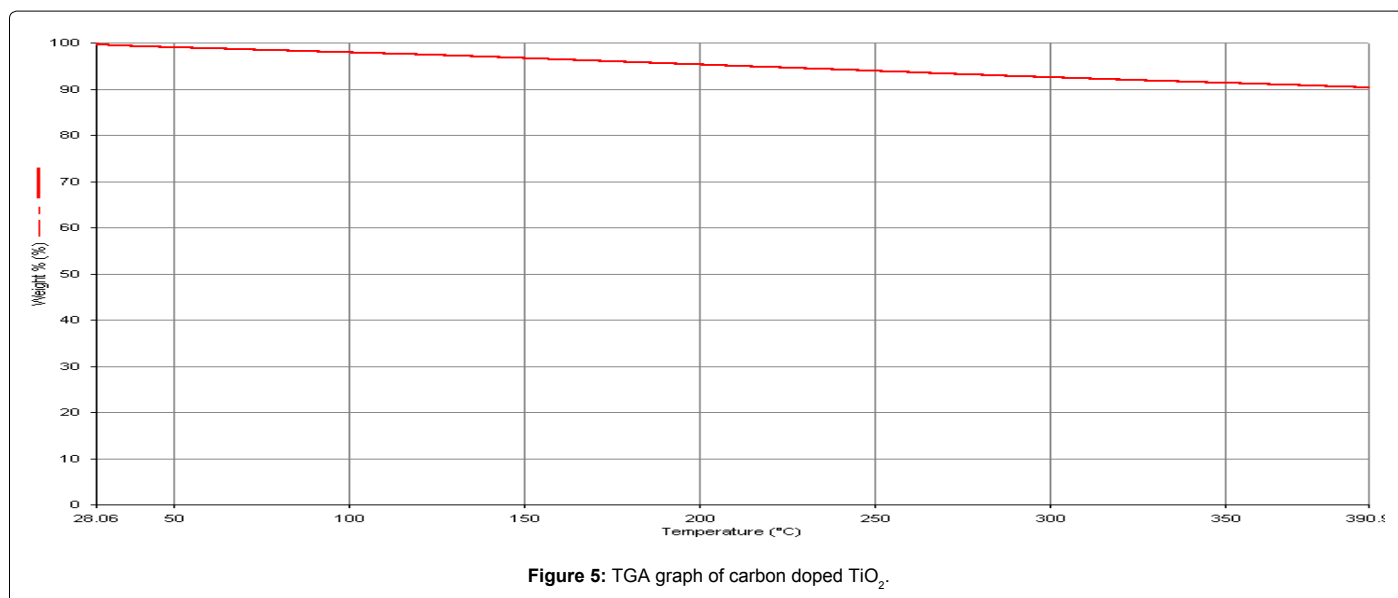
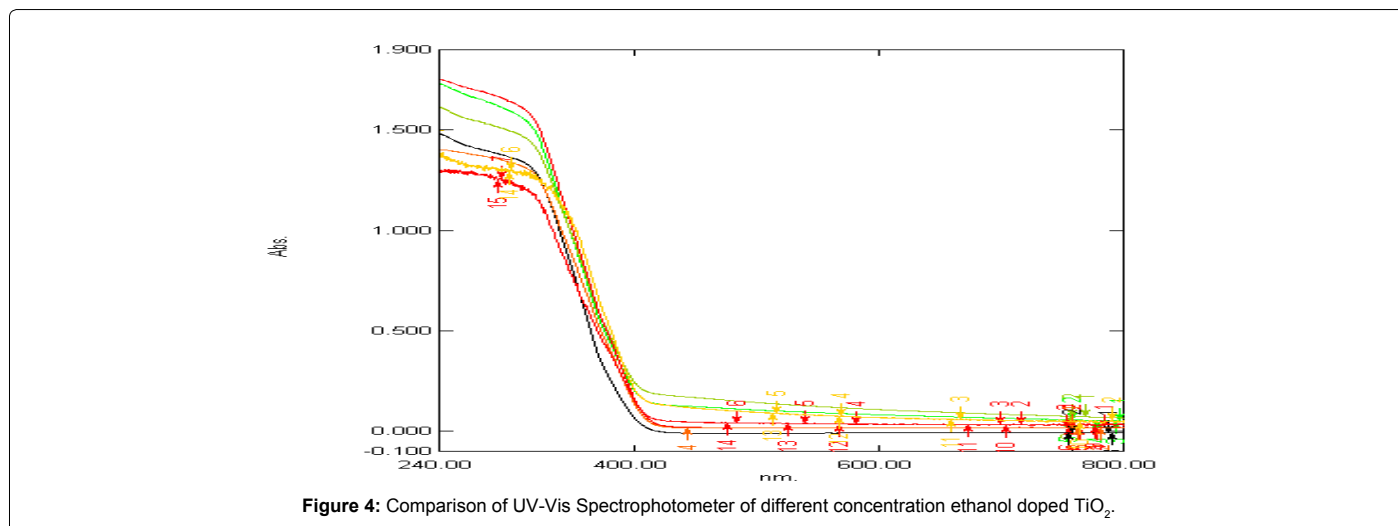
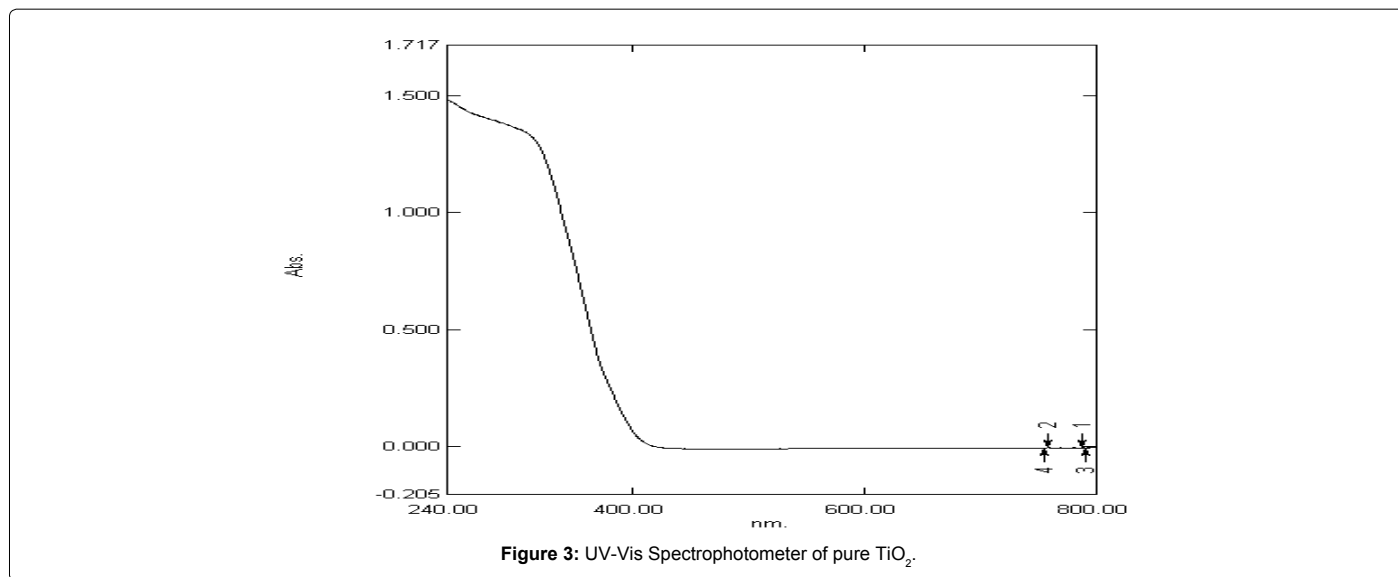
gap energy approximately 2.90 and 3.1 eV for the carbon-doped TiO₂ and pure TiO₂, respectively. This result obviously reveals the band gap of the carbon-doped TiO₂ is narrower than that of the pure TiO₂.

TGA analysis

To see the variation in weight of C-TiO₂, TGA measurements were carried out. The results are shown in Figure 5. As expected, the C-TiO₂ powders can be oxidized by oxygen in the air at an elevated temperature of From 300°C the total weight increase is about 10%. If some amount of carbon were oxidized, the weight increase would be 31.25% as calculated from the reaction: C-TiO₂ + 4O₂ - TiO₂ + CO₂. The amounts of residual carbon and are dependent on the hot air oven temperature.

Photocatalytic activity

The effect of catalyst concentration on photo catalytic degradation efficiency of TiO₂ was investigated by keeping all other experimental parameter constant. It is observed that there is steady increase in the degradation efficiency up to 5 g/l of the catalyst beyond which the degradation efficiency decrease. Within the range of catalyst dose from 2.5 to 5.0 g/l, observed phenomena enhancement in degradation may be due to an increase in available absorption and catalyst sites on the surface of carbon doped TiO₂. A further increase in concentration of catalyst however, may cause light scattering, blocking of UV light and particles of agglomeration which decrease the number of active sites.



The result indicates that an optimized catalyst concentration 5 g/l is necessary for enhancing the degradation efficiency, as shown in Figures 6 and 7.

Figures 8 and 9 shows the photocatalytic degradation curves of 100ppm over the P25, 88.75%, 92.20%, 95.94% ethanol doped

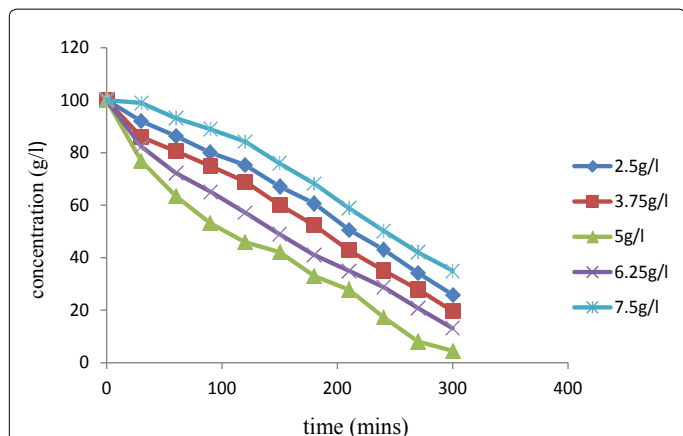


Figure 6: Comparison of degradation of phenol with loading concentration of TiO₂ photo catalyst in UV light.

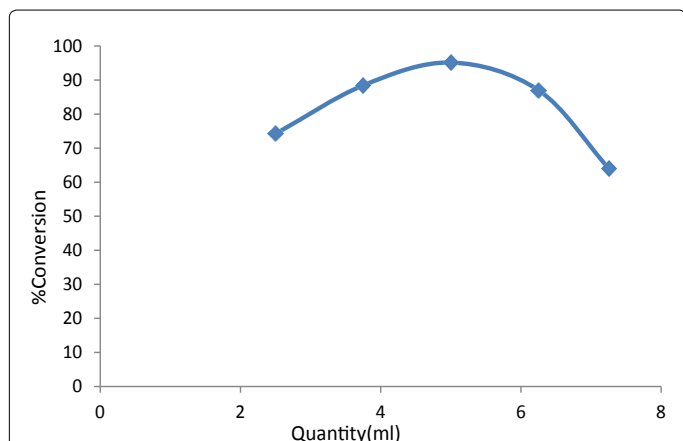


Figure 7: Comparison of % conversion between different quantities of catalyst loading of TiO₂.

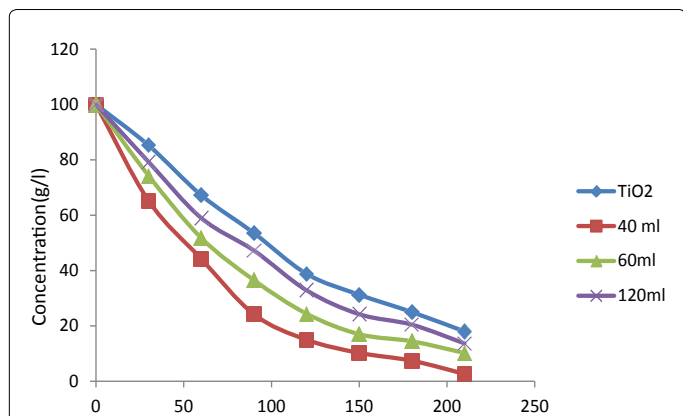


Figure 8: Comparison of degradation of phenol with different concentration ethanol doped TiO₂ and undoped TiO₂ of photo catalyst in UV light.

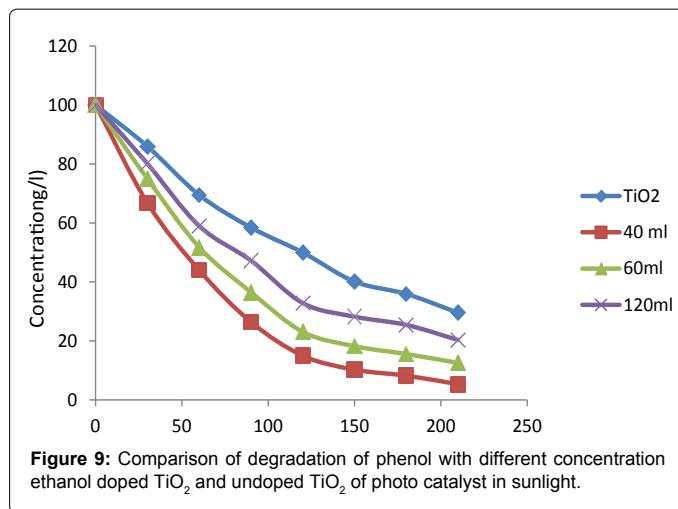


Figure 9: Comparison of degradation of phenol with different concentration ethanol doped TiO₂ and undoped TiO₂ of photo catalyst in sunlight.

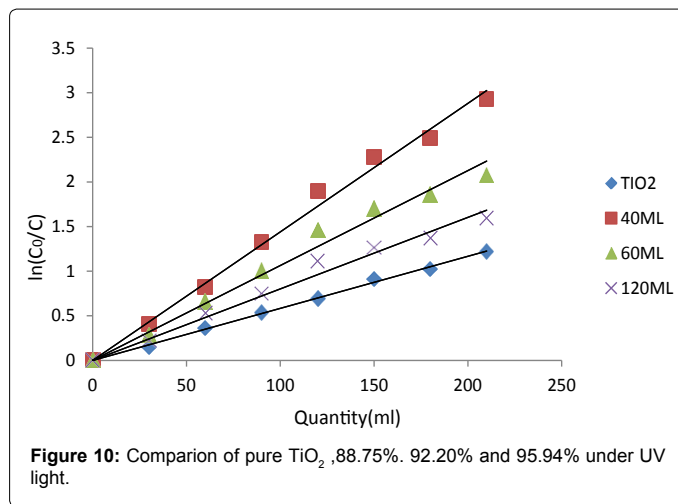
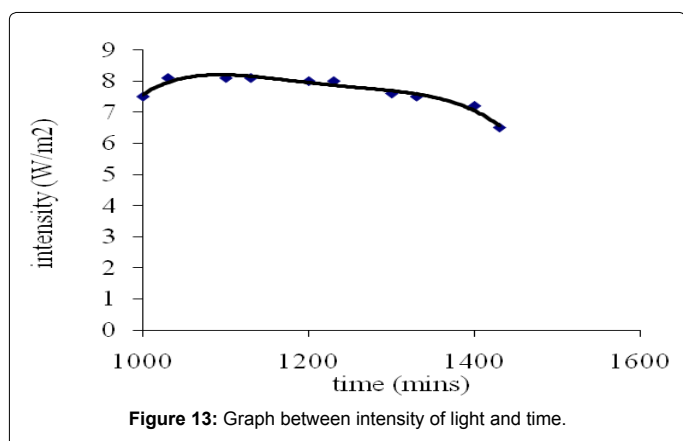
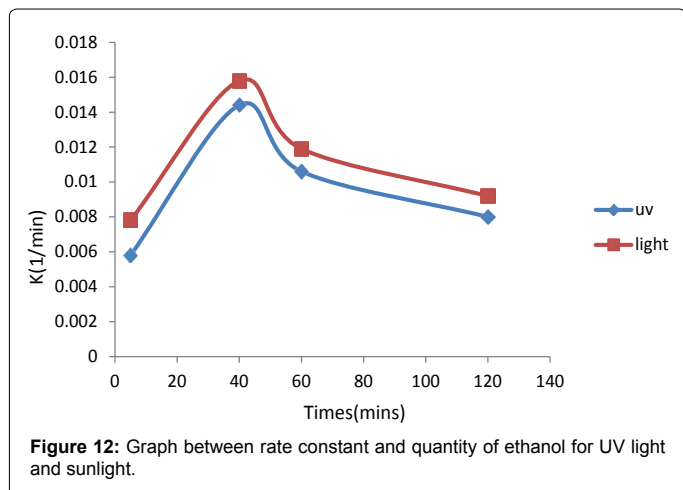
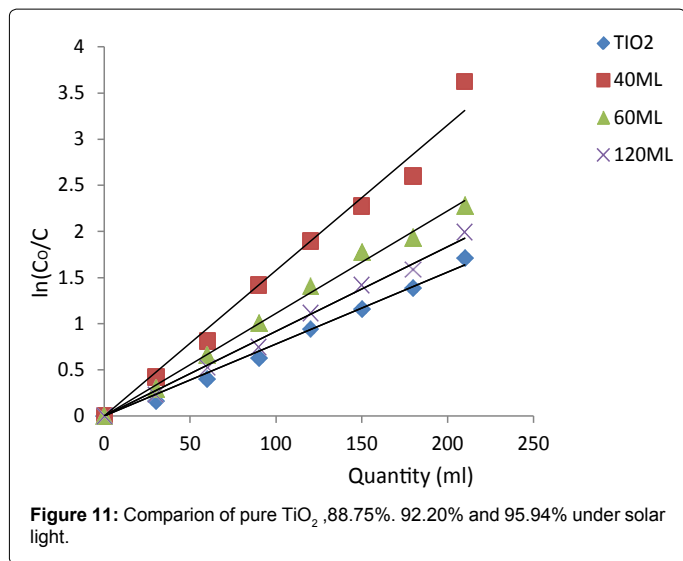


Figure 10: Comparison of pure TiO₂, 88.75%, 92.20% and 95.94% under UV light.

TiO₂ photocatalysts with different carbon concentration and got maximum degradation near about 97% of 100 ppm phenol solution at 88.75% ethanol doped TiO₂ under UV/Vis light. The photocatalytic degradation of 100 ppm phenol solution reaction times is first order with K from 0.0144 to 0.0058 min⁻¹ in concentration range of 88.75% -95.94% ethanol in TiO₂ as confirmed by the linear transformation of ln (C₀/C)~t shown in Figures 10 and 11. Apparent rate constants in UV light were obtained with various catalyst samples with different ethanol concentration from Figure 12 and graph shows that K decrease with increase in the initial concentration of ethanol and maximum K is 0.0144 for 88.75% ethanol doped in TiO₂ because XRD and UV result shows that 88.75% C-TiO₂ have minimum partial size (41.74 nm) and maximum shift in visible region (450 nm). When ethanol concentration added greater than 88.75% that decrease photocatalytically active sites on the surface of catalyst particles and reducing the interaction of photons with these sites, which can reduce the photocatalytic activity.

The photocatalytic degradation of 100ppm phenol solution reaction times is pseudo first order with K from 0.0154 to 0.0078 min⁻¹ in concentration range of 88.75% - 95.94% ethanol in TiO₂ as confirmed by the linear transformation of ln (C₀/C)~t shown in Figure 11. We analyze that when we increase concentration of ethanol in TiO₂ degradation of phenol under solar light increases because rate constant increase and varies in between 0.0158 to 0.0078 min⁻¹. As shown in Figure 13 the rate constant in solar light is higher than that of



UV light so degradation of phenol solution in solar light is higher than UV light. The increased photoactivity of carbon-doped TiO₂ may be associated with more-complex phenomena than the simple presence of the impurity atoms, such as, for instance, concomitant changes in the stoichiometry of the sample. According to laser flash photolysis experiments, 15 the holes formed upon visible light excitation are less

reactive than those formed upon UV excitation in pure TiO₂, because they are trapped at midgap levels induced by carbon doping. Lesser mobility is expected only for the holes but not for the electrons, which are excited into the conduction band. This means that carbon-doped systems exhibit decreased direct oxidation ability. On the other hand, reduction properties or indirect oxidation properties (via reactions with surface intermediates of water oxidation or oxygen reduction) are much improved upon irradiation with visible light, also because the holes trapped at the carbon doping site do not serve as effective charge recombination centers [15] and carbon doping favors the formation of oxygen vacancies. This feature makes nonmetal doping of TiO₂ much more appealing than transition-metal doping. Analysis of the computed electronic structure shows that carbon doping in anatase results in a series of localized occupied states in the band gap whose density and nature are dependent on the interaction with the oxide matrix, the dopant concentration, and the presence of oxygen vacancies. It was observed that rate constant of 40 ml ethanol doped have higher in UV light than visible. Under UV irradiation, the best degradation of phenol was achieved in the presence of 88.75% ethanol in TiO₂ and, it was observed that at relatively high ethanol concentrations, nanoparticles agglomerated which resulted in decreased surface area and the corresponding decrease photocatalytic activity in sun light. Therefore, increasing the dopant concentration has two opposite effects on the photocatalytic activity of the carbon doped TiO₂ catalysts; increasing light absorption capacity and decreasing surface area. The photocatalytic activity depends on which one of these is the dominant factor. A lesser amount of surface hydroxyl groups was observed in the case of undoped TiO₂ compared with the ethanol doped TiO₂. This could be one of the reasons for the lower activity of the undoped TiO₂ catalysts. Most of the non metal doped TiO₂ samples absorb in the visible region was no direct correlation between the light absorption capacity of the carbon doped TiO₂ catalysts and the rate of phenol solution degradation. It should be noted that the degradation rates in the presence of carbon doped TiO₂ catalysts under UV were in general less than that of the undoped TiO₂. Recombination of photo generated electrons and holes are one of the most significant factors that deteriorate the catalytic properties.

Intensity of sunlight

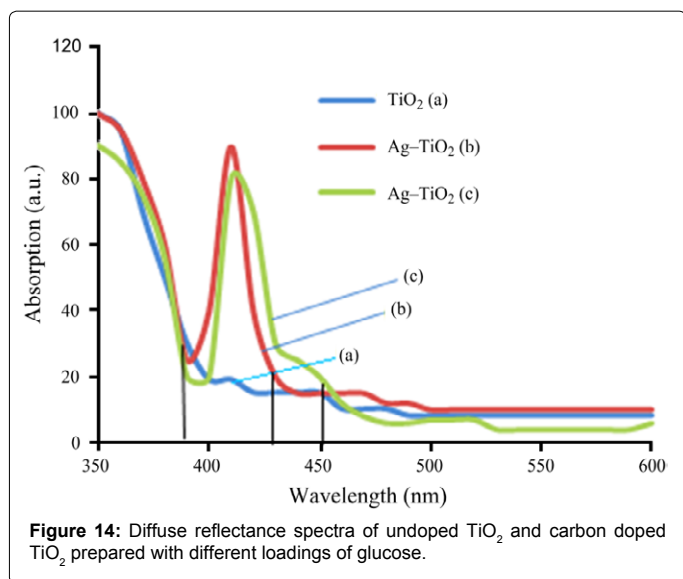
This was clearly explained in Figure 13.

UV-Vis absorption of the TiO₂ nanoparticles

The UV-visible absorption spectra of the C-doped TiO₂ were shifted by between 7 nm to 36 nm depending on the doping level as shown in Figure 14. The highest shift of 36 nm was due to TiO₂ doped with the lowest concentration of dopant (0.093 M glucose) while the lowest shift of about 7 nm was recorded for the sample doped with the highest concentration of dopant (0.278 M glucose). The absorbance increased with a decrease in the loading of the glucose, indicating that a higher concentration of the glucose led to a smaller particle size. The band gap was therefore increased as particle size decreased.

Conclusions

A visible-light-active carbon TiO₂ nano particles acts as a photocatalyst was prepared by a new approach through carbon doping by using ethanol as carbon source at a lowest temperature by heating with air. Carbon-doped TiO₂ possessed a high surface area and exhibited obvious absorption in the visible light range than P25 and undoped counterpart. It was found that carbon-doped TiO₂ showed significantly higher absorbance in visible than P25 and undoped TiO₂ under visible



light irradiation. Our method is potential for industrial production of visible-light driven photocatalyst because of its convenience and energy-saving.

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