

## Enhance Photocatalytic Degradation of Cobalamin by TiO<sub>2</sub> with Single Walled Carbon Nanotubes

Firas H. Abdulrazzak

Chemistry Department, College of Education for Pure Sciences, Diyala, University, Diyala, Iraq

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### Abstract

Different ratios of composites were synthesized by impregnation methods which consisted of single walled carbon nanotubes with TiO<sub>2</sub> (P25). The ratios that used in this work were 0, 0.25, 0.50, and 1.00% from the SWNTs with TiO<sub>2</sub>. These photocatalysts were characterized by Raman spectroscopy, XRD, UV-visible reflectance, and Surface area (BET) with using total organic carbon TOC to measure the mineralization process for Cobalamin. The result shows that single walled carbon nanotube was succeeding to increase the activity of TiO<sub>2</sub> when exhibits higher photocatalytic activity than pristine TiO<sub>2</sub>. The single walled carbon nanotubes can comparatively better improve the adsorption and activity of photocatalytic degradation of Cobalamin onto TiO<sub>2</sub> as compared with pristine TiO<sub>2</sub>. The results showed that, the adsorption of synthesized composites increases to 4.02% and percent of remaining TOC was 13.79% after 8h, while the synergetic effect R reach to 34% for TiO<sub>2</sub>/1%SWNTs as compare with pristine TiO<sub>2</sub>.

**Keywords:** SWNT, P25, TiO<sub>2</sub>/SWNT Composite, Cobalamin, Out Situ Activity

### 1. Introduction

TiO<sub>2</sub> one of the most common semiconductors which knowing as a photocatalyst that published in many literatures [1-2]. an inexpensive photocatalyst photostability, nontoxicity and many physiochemical properties[3-4] make TiO<sub>2</sub> ideal nanomaterial for huge applications such fuel cell [5] treatments air and water pollutants [6], hydrogen production [7]. Many attempts were done to modify TiO<sub>2</sub> by addition metals such as Pt, Au [8-9] or semiconductors such ZnO [10] coupling with secondary semiconductors [11] to increase the activity for different reactions. The new material to sciences at 1991[12] which represent by carbon nanotubes CNTs with high surface area and conductivity encouraged researchers to use it in a lot of fields [13]. Carbon nanotubes include single-walled carbon nanotubes SWNT and multi-walled carbon nanotubes MWNT [14]. The roles of CNTs with TiO<sub>2</sub> were reported in many literatures most of them [15-16] agreed with: i-withdraw the exiting electron from TiO<sub>2</sub> to CNTs, ii- prevents the recombination of e<sup>-</sup>/h<sup>+</sup>, iii- dispersion of the electrons into more regions to increase the probability of a photoreaction.

The addition CNTs to TiO<sub>2</sub> can be done using different techniques such sol-gel [17], chemical vapor deposition [18] and electro-spinning methods [19] every methods produce specific properties for the product. The addition high ratios of CNT [20] to TiO<sub>2</sub> showed in lower

photocatalytic activity that related to reduces the penetration of light to the surfaces of TiO<sub>2</sub> particles. The SWNTs [21] enhanced the TiO<sub>2</sub> to made selective photocatalytic oxidation for phenol as compare with pure anatase and Degussa P25. The behavior explains stabilizes charge separation reduces charge Recombination, And assembly provides better catalyst-support in exist of SWNTs. The addition of SWNTs to TiO<sub>2</sub> was more active than MWNTs [22] when used to degradation of Cobalamin which related homogenous distribution and reduce the agglomerates of the TiO<sub>2</sub> with SWNTs. In this work TiO<sub>2</sub> Degussa (consist of 80%, Anatase and 20% Rutile) was impregnated out-situ using SWNTs. the activity of synthesis composite was measured by making degradation for Cobalamin (C<sub>63</sub>H<sub>88</sub>CoN<sub>14</sub>P). Cobalamin, known as vitamin B12, which distinguishes by the cobalt atom in a Corrine ring [23]. The degradation of Cobalamin in aqueous solution was investigated using the prepared composite SWNT/TiO<sub>2</sub>. The effect of SWNT on the physical properties of TiO<sub>2</sub> was measured by using UV-visible reflectance, Raman spectroscopy, XRD and Surface area (BET).

### 2. Experimental

#### 2.1 Materials

The SWNTs, selected as the support material (consisted of 77% SWNTs, and a diameter of 0.7-1.1nm) were

fabricated by using a chemical vapor deposition supplied from Aldrich. The TiO<sub>2</sub> sample were purchased from Degussa, Germany (TiO<sub>2</sub>-P25) (consisting of 20% Rutile and 80% Anatase, with a BET area 51 m<sup>2</sup>/g). CyanoCobalamin C<sub>63</sub>H<sub>88</sub>CoN<sub>14</sub>O<sub>14</sub>P purchased from Sigma with purities more than 98.5%.

## 2.2 Preparation of Binary composite

TiO<sub>2</sub>/SWNT binary composites were prepared by a impregnation method. Firstly, SWNTs were treated with mixture of acid HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> (1/3) with ultrasonic water bath for 7h [24] washing and drying at 100°C overnight. One gram of TiO<sub>2</sub> has been suspended by ultrasonic water bath in 100 ml of distils water for 30 min which containing the desired percent weight of SWNTs. The mixed suspension was filtered by using vacuum evaporator (Rota vapor re121 BUSHI 461 water Bath) at 45 °C to accelerate the evaporation of water. After the water evaporated, the composite was dried overnight in an oven at 104 °C.

## 2.3 Characterization

Raman analysis was done by using Sentara infinity 1 Bruker with using laser light at 530 nm, intensity 2m W for 5 lops per 2s and resolution equal to 3-5 cm. Spectrofluorophotometer RF-540 Shimadzu was used to analyze the photoluminances for TiO<sub>2</sub> and composites in the range of 350-650 nm. The X-ray diffraction (XRD) patterns were made on a (Rigaku Rotaflex) (RU-200B) X-ray diffractometer using Cu K $\alpha$  radiation (wavelength 0.15405 nm) with a Ni filter. The tube current was 100 mA with a tube voltage of 40 kV. The 2 $\theta$  angular regions between 15 and 65° were explored at a scan rate of 5°/min. For all XRD tests, the resolution in the 2 $\theta$  scans was kept at 0.02°.

The change in absorbance for TiO<sub>2</sub> within SWNTs were done by UV-Vis diffuse reflectance spectra using a UV-Vis spectrometer (CARY 100 Bio). Surface area estimation of the TiO<sub>2</sub> powders has been performed by the Brunauer-Emmett-Teller (BET) method, performed on a Micrometrics Automate 23 apparatus. The samples have been previously heated to 125 °C for 30 min to remove possible contaminants and humidity adsorbed on their surfaces. The measurements have been performed using a gas mixture containing 30 % nitrogen and 70 % helium.

The Raman spectra in Figure.1 show Both spectra G band at 1582 cm<sup>-1</sup> corresponding to the -C-C- bond in the wrapped graphene plane, and D band at 1330 cm<sup>-1</sup> corresponding to the C-related defects of SWNT. The 2D and G+D bands were typical shown for the SWNTs[25].

From Figure.1 the peaks in the 100-700 cm<sup>-1</sup> region confirmed the presence of anatase TiO<sub>2</sub> with a dominating at 150 cm<sup>-1</sup> (E<sub>g</sub>), 395.1 cm<sup>-1</sup> (B<sub>1g</sub>), 512.5 cm<sup>-1</sup>

(A<sub>1g</sub> + B<sub>1g</sub>) and 636.7 cm<sup>-1</sup> (E<sub>g</sub>), respectively. The rutile phase at 143, 235 cm<sup>-1</sup> which refer to the B<sub>1g</sub>, two-phonon scattering, 445 cm<sup>-1</sup> E<sub>g</sub>, and 612 cm<sup>-1</sup> A<sub>1g</sub>, respectively[26]. In the case of TiO<sub>2</sub>/SWNT composites, all the Raman bands for anatase still remain with slightly broadened as compared to the pure TiO<sub>2</sub>. In addition, it is noteworthy the peaks assigned to SWNTs within the composites exhibit broadening and more clear as compare with TiO<sub>2</sub> due to real connections' across the interface between SWNTs and TiO<sub>2</sub> [27].

Figure 2 shows the XRD patterns of SWNTs, which includes two characteristic peaks 2 $\theta$ =25.9° and 43.2°[28]. Figure 2 refer to TiO<sub>2</sub> peaks at 25.3° and 27.4° are the characteristic reflection for anatase and rutile, respectively [29]. diffraction peaks of SWNTs didn't observe clearly, probably due to the composites are covered by the much more intense peak for large ratio of TiO<sub>2</sub>.

Generally the first peak of SWNTs disappears in binary composites due to overlap with the anatase peak of TiO<sub>2</sub> at 25.3° causing increase the width of the peaks which increase with increasing the ratio of SWNTs [30]. The second peak of SWNTs at 43.2° seems weak, which appeared strongly with high ratio of SWNTs.

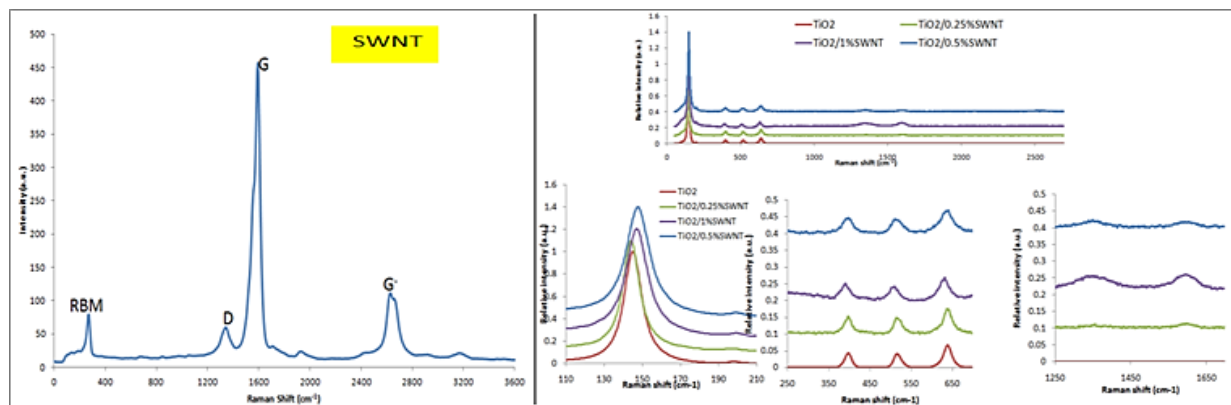
The band-gap energies E<sub>g</sub> were calculated by the Kubelka–Munk function [31]. The E<sub>g</sub> value was determined using the theory of optical absorption for allowed direct transitions:

$$h\nu = A (h\nu - E_g)^{1/2} \quad (1)$$

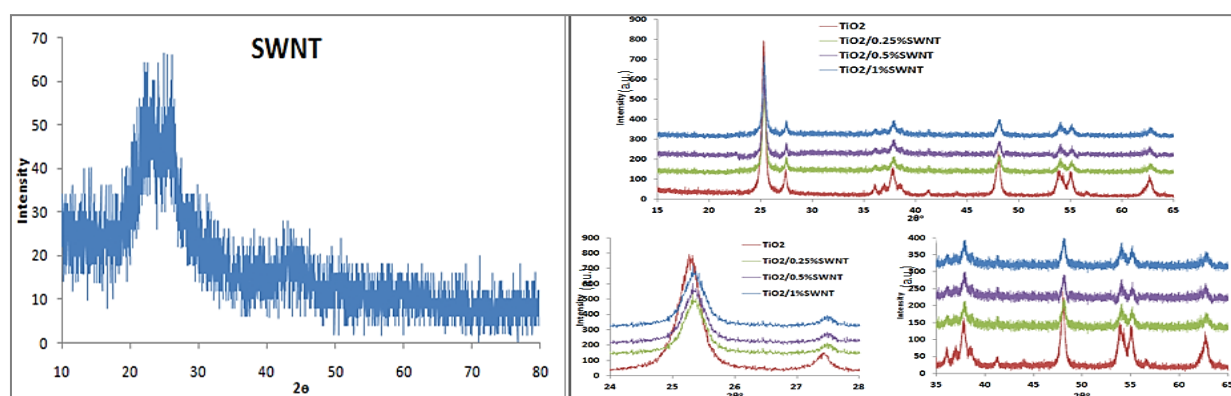
Where A is the absorption coefficient that constant relative to the material, (h $\nu$ ) is the discrete photon energy. The extrapolating linear portion of the (FR  $\times$  h $\nu$ )<sup>1/2</sup> vs. h $\nu$  curves to FR = 0 which refer to the value of band gap energy E<sub>g</sub> as shown in Figure 3.

In order to investigate the reasons for different activities among binary composite between SWNT and TiO<sub>2</sub> must take into consideration the absorbance ability of materials. The TiO<sub>2</sub> absorbance occurred below 400 nm ,whereas for SWNTs broad peaks of absorption can be observed between 450-1000 nm. Figure 3 shows the UV-Vis diffuse reflectance spectra of P25/SWNT composites. Gradual increases of absorbance in visible light region ( $\lambda$  > 400 nm) may be ascribed to intrinsic property of SWNTs and the slight differences of absorbance among the composites are likely due to exist SWNTs with TiO<sub>2</sub>.

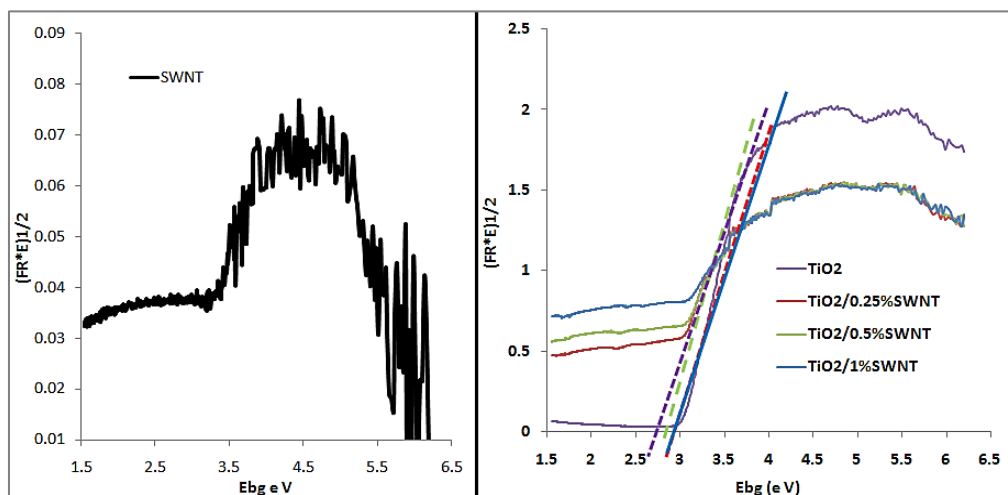
The enhancement for the absorption increase with high SWNTs content in the composites. The behavior refer to increase the electric charge on the surface of semiconductor oxide with catalysts composite as a result of large surfaces area of higher conductivity SWNTs as carrier electrons [32-33].



**Figure 1** Raman spectrum for pristine TiO<sub>2</sub> and different ratios of O-SWNT with TiO<sub>2</sub> (TiO<sub>2</sub>/SWNT)



**Figure 2** XRD patterns for TiO<sub>2</sub> (P25) and series ratios of xSWNT/TiO<sub>2</sub> (x=0.25, 0.5, 1%).



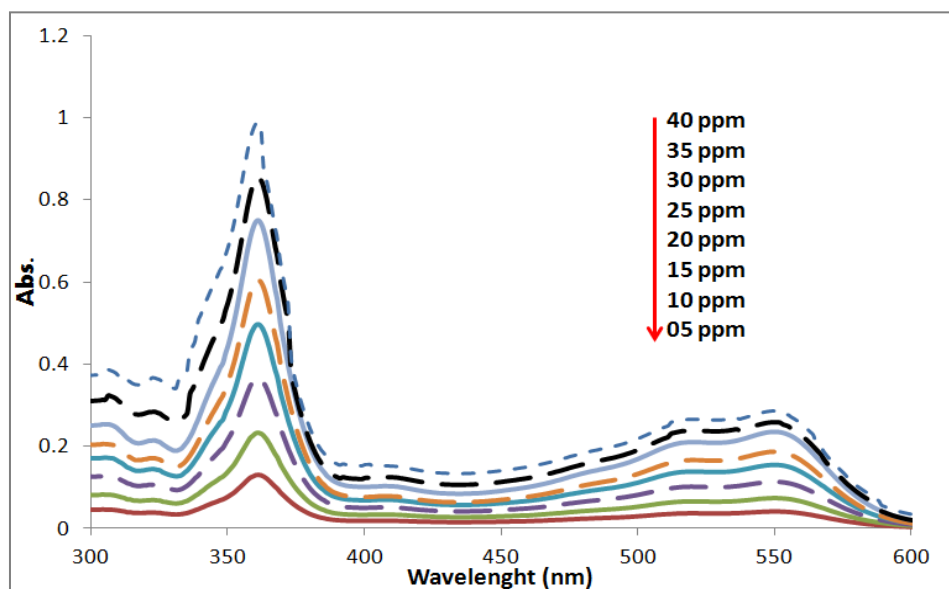
**Figure 3** UV-Vis diffuse reflectance spectra for pristine TiO<sub>2</sub> (P25) and different ratios of SWNT in binary composites SWNT/TiO<sub>2</sub>

#### 2.4 Measured the activity of composite

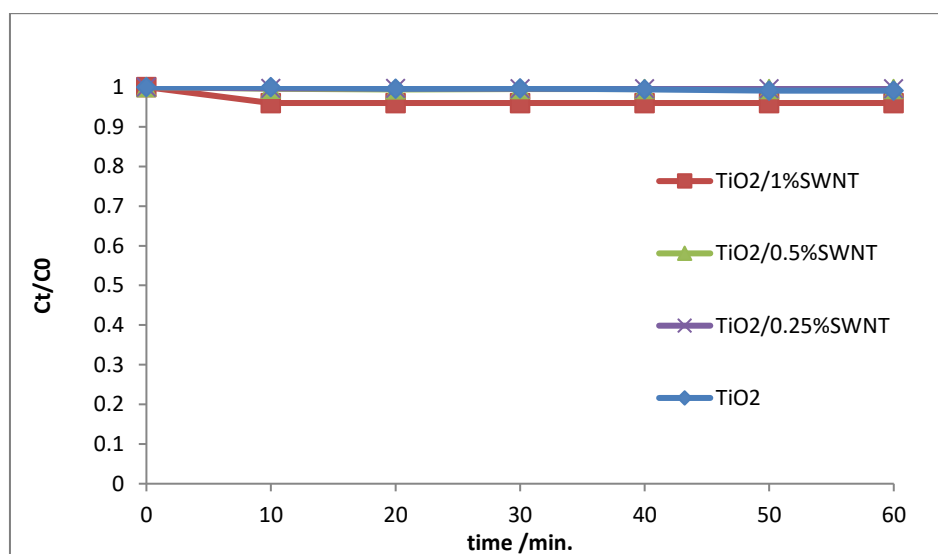
The photocatalytic activities of the P25/SWNT and TiO<sub>2</sub> (P25) were determined by the decolorization of Cobalamin in an aqueous solution under UV-light. Figure 4, showed the absorbance spectra of different concentrations of Cobalamin which depend to found the maximum wavelength of absorbance and to measure the concentrations. The catalysts (175mg) were suspended in

100 mL of 40 ppm Cobalamin solution in a glass vessel in atmospheric oxygen.

Prior to irradiation, the suspensions were magnetically stirred in the dark to 60 min to ensure the establishment of an adsorption/desorption equilibrium among the photocatalyst, which considered the initial concentration. Photocatalytic degradation was tested using TiO<sub>2</sub> and TiO<sub>2</sub>/SWNT catalysts under UV light irradiation.



**Figure 4:** Absorbance for different concentrations of Cobalamin in A UV



**Figure 5** Dark reaction for TiO<sub>2</sub>, 0.25,0.5, and TiO<sub>2</sub>/1%SWNT with 40ppm Cobalamin at 298K

The light irradiation with intensity 1.3 m W/cm<sup>2</sup> were applied to the reactor for 60 min and the removal of the dispersed powders through centrifuge. The clean transparent solution was analyzed using a UV–Vis spectrophotometer. The spectra (300–700 nm) for each sample were recorded and the absorbance was determined at the characteristic wavelength 550 nm.

### 3. Results and Discussion

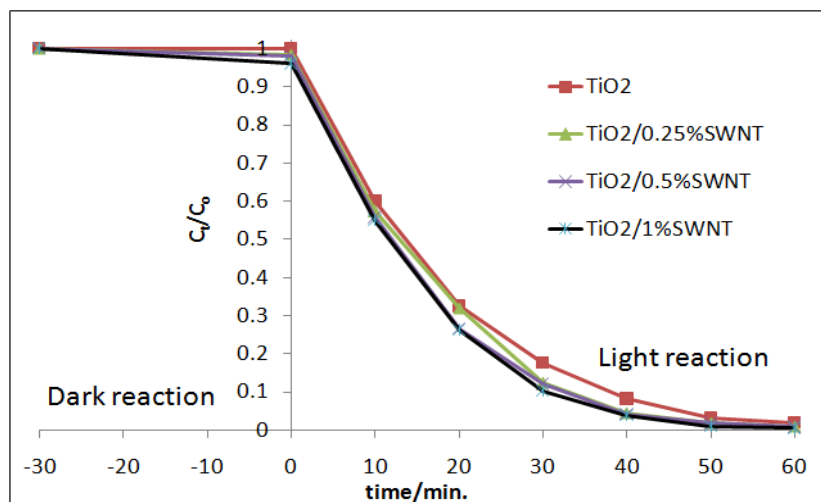
#### 3.1 Effect of SWNTs on the adsorption property of TiO<sub>2</sub>

Figure 5 shows the adsorption dynamics for the Cobalamin onto different photocatalysts. The amount of the Cobalamin adsorbed onto photocatalyst from aqueous solution increases quickly with time, for

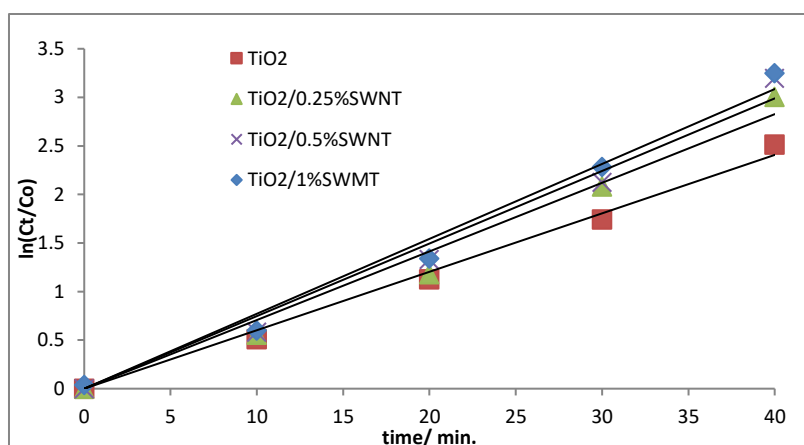
composite of TiO<sub>2</sub>/SWNT with equilibrium being achieved within 30 min for the three ratios of photocatalysts. When the adsorption reaches equilibrium, the amount of Cobalamin adsorbed onto materials arranged as: TiO<sub>2</sub>/1%SWNT > TiO<sub>2</sub>/0.5%SWNT > TiO<sub>2</sub>/0.25%SWNT > TiO<sub>2</sub>. The results of adsorption were listed in table 1 which shows that adsorption activity increase 2.20, 2.47 and 4.02% for TiO<sub>2</sub>/0.25%SWNT, TiO<sub>2</sub>/0.5%SWNT and TiO<sub>2</sub>/1%SWNT respectively compare with pristine TiO<sub>2</sub> (P25).

#### 3.2 Measurement of Photocatalytic Activities for composites

The photolysis of Cobalamin without catalyst shows that the sources of illumination did not make any photolysis



**Figure 6** Degradation reaction for TiO<sub>2</sub>, 0.25, 0.5, and TiO<sub>2</sub>/1%SWNT with 40ppm Cobalamin at 298K gas and light intensity 1.3 m W/cm<sup>2</sup> in exist of O<sub>2</sub> gas



**Figure 7** Rate constant for different ratios (175mg) TiO<sub>2</sub> and , 0.25, 0.5, and TiO<sub>2</sub>/1%SWNT with 40ppm Cobalamin at 298K gas light intensity 1.3 m W/cm<sup>2</sup> in exist of O<sub>2</sub> gas

**Table 1** Summary of UV- light photodegradation of Cobalamin on different composites TiO<sub>2</sub>/SWNT

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	Band gab eV	C <sub>0</sub> ppm	K /s <sup>-1</sup>	R	TOC <sub>8h</sub>
TiO <sub>2</sub> (P25)	50	3.18	40	0.0692	-	77.58
TiO <sub>2</sub> /0.25%SWNT	59	2.9	39.11	0.0771	1.19	81.02
TiO <sub>2</sub> /0.5%SWNT	65	2.8	39.01	0.0796	1.23	86.11
TiO <sub>2</sub> /1%SWNT	71	3	38.39	0.0868	1.34	88.28

for Cobalamin. The photodegradation experiments by UV irradiation of the Cobalamin solutions follow the pseudo-first-order kinetics with respect to the concentration of dyestuff in the bulk solution (C):

$$-\frac{dC}{dt} = k_{app} C \quad (2)$$

When made Integration for this equation and by using the same restriction of  $C = C_0$  at  $t = 0$ , and  $C_0$  being the initial concentration in the bulk solution before starting the light reaction), thus the equation become

$$\ln\left(\frac{C_0}{C}\right) = k_{app} t \quad (3)$$

Where  $k_{app}$  is the apparent reaction rate constant. A plot of  $\ln(C_0/C)$  versus  $t$  for Cobalamin degradation with different composite of SWNT/P25 photocatalysts is presented in Fig.6. The value of  $k_{app}$  can be obtained directly from the slope of the respective linear curves in the plot which listed in Table 1.

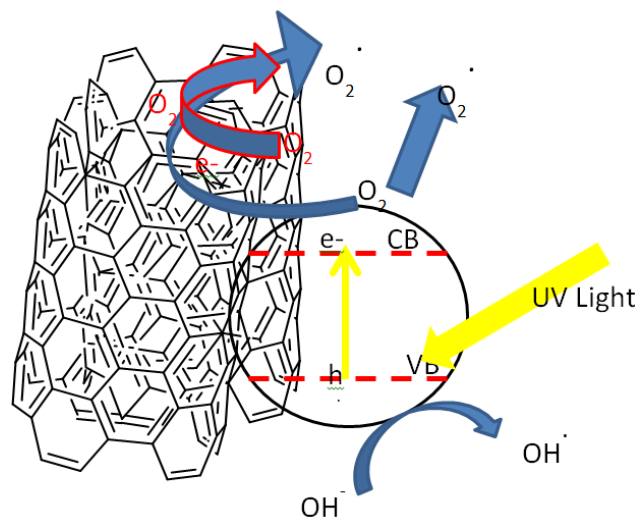
The synergy factor (R) [34] is defined as the following equations

$$R = k_{app}(\text{TiO}_2/\text{SWNT}) / k_{app}(\text{TiO}_2) \quad (4)$$

When  $k_{app}(\text{TiO}_2/\text{SWNT})$ ,  $k_{app}(\text{TiO}_2)$  refer to the aberrant rate constant for decolorization in exist of composite and TiO<sub>2</sub> respectively. Increase the ratios of SWNTs causing increased in decolorization rate, Which listed in table 1, shows increased adsorption ability of TiO<sub>2</sub> in exist SWNTs. The synergetic effect of SWNTs with TiO<sub>2</sub> represent by the value of R which increase from 19, 23 and 34% with increase SWNTs from 0.25, 0.5 and 1% respectively. In the same time the efficiency remaining total carbon for 8h was change from 4.43, 10.99, 13.79 with increase SWNTs from 0.25, 0.5 and 1% respectively as compare with pristine TiO<sub>2</sub>.

### 3.3 Mechanisms of reaction

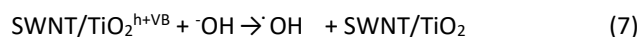
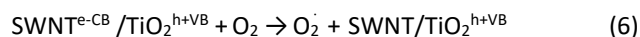
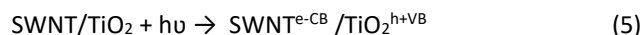
A proposed mechanism for the enhanced the photocatalysis of composites P25/SWNT is shown schematically in figure (8). The SWNTs have a higher surface area of 1232 m<sup>2</sup>/g which can be a co-adsorbent to improve the adsorption ability of TiO<sub>2</sub> [30-34]. It may be attributed to the small internal diameter for SWNTs and the large size of the molecule Cobalamin and strong interaction between SWNTs and TiO<sub>2</sub> particles, caused limitation in active site of adsorption.



**Figure 8** Schematic of a proposed model for TiO<sub>2</sub>/SWNT

Under UV illumination electron are excited from valences band to the conduction band of TiO<sub>2</sub> that leads to forming positive hole  $h^+$  in the valance band and negative position for  $e^-$  in conduction band. The two active sites without SWNTs mostly recombination quickly with losing most site which may react chemically, only <1% of electron and hole will react, which is explain value of reactivity [35]. The band gab for P25 about 3.18 e V [36], while for SWNT less than 0.1e V, [37], thus when SWNTs attached to the surfaces of TiO<sub>2</sub> the exited electron in the conduction band will be transfer to the surfaces of SWNTs. The last action induces to make separation  $e^-/h^+$  (equation 1) and reduce the recombination for the

charges [38-39]. However, the live time for the hole will increases which produce more of  $OH^\cdot$  radical from react  $h^+$  with  $OH^-$  (equation 2). In the same time the exited electron on the surface of SWNTs will react with  $O_2$  (equation 3) to forming superoxide [40].



### Conclusion

The impregnation of series ratios of single walled carbon nanotubes with TiO<sub>2</sub> as co-doped TiO<sub>2</sub> was successfully synthesized by the impregnation method. The SWNT /TiO<sub>2</sub> samples exhibited lager surface area. The increase ratio of SWNT in composite P25/SWNT sample exhibited the highest adsorption compare with pristine TiO<sub>2</sub>. Also photocatalytic activity of degradation Cobalamin showed the same behavior with increase SWNTs. The enhanced activity of TiO<sub>2</sub> could be attributed to the SWNTs doping, which causing synergistic effects , large surface area, red shift in adsorption edge of the prepared sample in addition to reduce the recombination of  $e^-/h^+$ . The mixing between adsorption and high conductivity make the composite more active when the SWNTs adsorbed the organic molecules and increase the free radical of  $OH^\cdot$  and  $O_2^\cdot$  on the surface of SWNT and TiO<sub>2</sub>.

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