Photocatalytic Hydrogen Production on Nanocomposite of Carbon Nanotubes and TiO$_2$

Firas H. Abdulrazzak$^a$ and Falah H. Hussein$^b$

$^a$Chemistry Department, College of Education for Pure Sciences, Diyala University, Diyala, Iraq. $^b$College of Pharmacy, Babylon University, Hilla, Iraq.

Corresponding author’s E-mail: firas_habeb2000@yahoo.com

Abstract. Sonochemical/hydration–dehydration techniques were used to synthesize binary composites CNT/TiO$_2$ consisting single wall carbon nanotubes (SWNTs) and multiwall carbon nanotubes (MWNTs) with TiO$_2$. Different percentages of CNT/TiO$_2$ were prepared (0.25, 0.5, and 1%). The morphological and physiochemical properties were investigated by powder X-ray diffraction (XRD), Raman spectroscopy and UV–vis diffuse reflectance spectroscopy. It was found the TiO$_2$ nanoparticles were more homogenized with SWNTs compared with MWNTs. 7.5% methanol solution was used as a sacrificial agent to produce hydrogen gas with 65 mg of synthesized binary composites at light intensity 40 mW cm$^{-2}$. The results show that SWNTs increased the activity of TiO$_2$ more than for MWNTs. The hydrogen production shows higher activity for TiO$_2$ with lower ratio of SWNTs, while the activity was raised for TiO$_2$ with increasing ratio of MWNTs.

1. Introduction.

Energy sources are one of the most important studies that interest researchers not to produce energy but to looking for clean and renewable energy for all the world. Recently, fossil fuels represent the main source, which used in all fields of life for a long time ago. May be the combustion of fossil fuels which produce CO and CO$_2$ with the risk of depleted completely cause bearing the world to search for alternative sources and environmentally friendly [1]. Hydrogen represents the ideal for the world due to easily produce a large amount of energy which equals to 122 kJ/g without any harmful product [2]. Many research reported that hydrogen as a source of energy for huge applications [3]. As we reported in our previous work hydrogen can produce by photocatalytic water splitting and photocatalytic reforming of biomass by semiconductor [4].

Photocatalysis reaction, used to produce hydrogen when the chemical reaction was induced by the catalyst in existing a convenient source of irradiation. Semiconductors are the common materials behave as a catalyst in the photocatalytic reaction such TiO$_2$, ZnO, and CdS [5]. The efficiency of semiconductors depend on three parameters, absorption of photons, prevent recombination and consuming of the excited electrons [6]. The energy of absorption photons responsible to translate the electrons from valence band (VB) to conduction band (CB), and forming positive charge h$^+$ while CB produces negative charge e$^-$. The prevention of e$^-$ to recombine with h$^+$ and consuming the excited electrons at the CB by acceptance species together, that produce the abilities of semiconductor towards hydrogen production.

Titanium dioxide (TiO$_2$) represent the ideal semiconductor for many applications due to inexpensive, higher activity and friendly to the environment [7]. The limitation for use TiO$_2$ related to reacting with less than 4% of solar light which represent by UV–light [8]. Many attempts were done to enhance the activity of redox reaction. All the strategies depend on addition different species such as metal/nonmetal doping, photosensitization with dyes and coupling with semiconductors [9]. After 1991 the attentions were brought toward using carbon nanotubes CNTs in hydrogen production research when characterized by rarer and amazing physiochemical properties [10]. Carbon nanotubes CNTs realize as graphene or graphite sheets wrapped in forming cylindrical structures such single—
walled carbon nanotubes SWNTs or multi–walled MWNTs [11]. The TiO$_2$/CNT composite can be prepared by sol-gel [12], chemical vapor deposition [13] and electro-spinning methods [14] which characterized by specific properties for the synthesized product. Herein, titanium dioxide was doped with SWNTs or MWNTs by a sonochemical/hydration–dehydration process. The synthesized binary composites were characterized by X-ray diffraction (XRD), Raman spectroscopy and UV–vis diffuse reflectance spectroscopy. The activity of synthesized different ratios and types of CNTs in composites were tested in hydrogen production from aqueous alcohol solution.

2. Experimental.

**Materials.**
Two types of carbon nanotubes were used, SWNTs and MWNTs which purchased from Aldrich and fabricated by chemical vapor deposition. The SWNTs consist of more than 90% carbon and 77%wt SWNTs, with a diameter 0.7–1.1 nm, while the MWNTs are 95% carbon nanotubes with a mode diameter 4.5 nm. The TiO$_2$ sample was supplied as Degussa, Germany (TiO$_2$-P25) (consisting of 20% Rutile and 80% Anatase, with a BET area 51 m$^2$/g). Nitric acid (65 wt% HNO$_3$) and sulfuric acid (37 wt% H$_2$SO$_4$) were obtained from Fluke and Sigma- Aldrich, respectively. Methanol with purities (99.99%) as the sacrificial agent was purchased from Fluke.

3. Preparation of Binary composite.
The binary composite CNT/TiO$_2$ were prepared as reported in our previous work [7]. Briefly; an ultrasonic water bath was used for 7 hours when the two types of SWNTs and MWNTs were dispersion in (1/3) a mixture of two concentric nitric and sulfuric acid. The TiO$_2$ was suspended in 100 mL of required weight of CNTs aqueous solution using an ultrasonic water bath. The two suspensions were washed and dried by a vacuum evaporator (Rota vapor re121 BUSHI 461 water Bath) at 45 °C then thermal treatment overnight in an oven at 90 °C.

4. Characterization of SWNT/TiO$_2$ and MWNT/ TiO$_2$.
Energy sources are one of the most important studies that interest researchers not to produce energy but to looking for clean and renewable energy for all the world. Recently, fossil fuels represent the main source, which used in all fields of life for a long time ago. May be the combustion of fossil fuels which produce CO and CO$_2$ with the risk of depleted completely cause bearing the world to search for alternative sources and environmentally friendly [1]. Hydrogen represents the ideal for the world due to easily produce a large amount of energy which equals to 122 kJ/g without any harmful product [2]. Many research reported that hydrogen as a source of energy for huge applications [3]. As we reported in our previous work hydrogen can produce by photocatalytic water splitting and photocatalytic reforming of biomass by semiconductor [4].

Figure 1 shows the XRD patterns for SWNTs with two characteristic peaks at 23.7°, 42.9° and many noises which related to the structure of SWNTs. In the same figure reflection planes of MWNTs were (002) and (100) which related to 26.3° and 43.7° respectively with more regular and less noise as compared with SWNTs.
Figure 1 shows the XRD patterns for SWNTs with two characteristic peaks at 23.7°, 42.9° and many noises which related to the structure of SWNTs. In the same figure reflection planes of MWNTs were (002) and (100) which related to 26.3° and 43.7° respectively with more regular and less noise as compared with SWNTs.

The XRD patterns of pristine TiO$_2$ and modified with different ratios of CNTs are shown in Fig.2 and 3. The anatase crystallites were determined by the (200) reflection at (2θ= 48.1°), which there is no interference from CNTs. Table 1, shows the particle sizes of composites catalyst were estimated using Scherrer’s equation which decreases gradually with the increasing the ratios of CNTs, and showed less intense and wider for binary composite CNTs/TiO$_2$ [15].

| Ratios of CNTs | SWNT Particle size (nm) | MWNT Particle size (nm) |
|----------------|-------------------------|-------------------------|
| 0.0%           | 23.09                   | 23.0                    |
| 0.25%          | 19.97                   | 22.14                   |
| 0.5%           | 15.41                   | 20.84                   |
| 1.0%           | 14.19                   | 19.07                   |

The change for peaks in intensity and area were occurred with SWNTs more than MWNTs while the shift was more with MWNTs, which may related to influence number of layers in MWNTs. The low ratios of CNTs causing limited change in peaks which covered by the much more intense peaks for the large ratio of TiO$_2$. 
Figure 2. X-ray patterns of pristine and modified TiO$_2$ with SWNTs a. total figure from 15-65$^\circ$, b. 24-28$^\circ$, c. 35-65$^\circ$.

Figure 3. X-ray patterns of pristine and modified TiO$_2$ with MWNTs a. total figure from 15-65$^\circ$, b. 24-28$^\circ$, c. 35-65$^\circ$.

The Raman spectra in Fig.4, explains the Raman spectrum for SWNTs when characterized with five peaks such RBM, G, D, G', and RBM+G while with MWNTs shows three peaks. The pristine TiO$_2$ recognize two phases' Anatase and Rutile which represent the continents of this type. The region at 150 cm$^{-1}$ ($E_g$), 395.1 cm$^{-1}$ ($B_{1g}$), 512.5 cm$^{-1}$ ($A_{1g} + B_{1g}$), and 636.7 cm$^{-1}$ ($E_g$) which refer to orientations ($E_g$), ($B_{1g}$), ($A_{1g} + B_{1g}$), and ($E_g$) respectively represent the modes of Anatase. The Rutile phase appears in two peaks at 143, 235 cm$^{-1}$, for the $B_{1g}$, and 445 cm$^{-1}$, and 612 cm$^{-1}$ for Eg and $A_{1g}$, respectively [16]. The last behavior indicates that as expected the nano-composite preserved the structures of both the MWNTs and anatase TiO$_2$. Figure 5 with four parts a, b, c, and d refer to Raman spectroscopy of SWNT/TiO$_2$ which shows red shift for all anatase and rutile peaks with increase the
width more than the effect of MWNT in composites. Fig. 6, for MWNT/TiO\textsubscript{2} composites, distinguish with bands of anatase and MWNTs when did not change, except that the anatase [16] are slightly broadened compared to the pure TiO\textsubscript{2}. This peak broadening is consistent with the decreasing in the average of crystallite size. It is worth noting that the peaks assigned to CNTs within the composites exhibit broadening and a slight blue-shift relative to the acid-treated CNTs, indicating the interfacial interaction between the TiO\textsubscript{2} and acid-treated CNTs [15].

![Raman spectroscopy for pristine and modified TiO\textsubscript{2} with SWNTs](image1.png)

**Figure 4.** Raman spectra of SWNTs and MWNTs from 100 to 2900 cm\textsuperscript{-1}.

![Raman spectroscopy for pristine and modified TiO\textsubscript{2} with SWNTs](image2.png)

**Figure 5.** Raman spectroscopy for pristine and modified TiO\textsubscript{2} with SWNTs, a. total skim 50-2650 cm\textsuperscript{-1}, b. for (110-170) cm\textsuperscript{-1}, c. (300-700) cm\textsuperscript{-1}, d. (1200-1700) cm\textsuperscript{-1}.
Figure 6. Raman spectroscopy for pristine and modified TiO$_2$ with MWNTs, a. total skim 50-2650 cm$^{-1}$, b. for (110-170) cm$^{-1}$, c. (300-700) cm$^{-1}$, d. (1200-1700) cm$^{-1}$.

The band gap measurements were done for pristine TiO$_2$ and with different ratios of CNTs (0.25%, 0.5%, and 1% of SWNTs or MWNTs) which plotted in figure. 7 and 8.

Figure 7. Band gap $E_{bg}$ for pristine and modified with 0.25, 0.5, and 1% SWNTs.
The Kubelka–Munk function [17] were used to estimate the band-gap energies $E_g$ for the synthesized binary composites. Theories of optical absorption for direct transitions which depend on the using equations:

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

where $A$ is refer to the absorption coefficient which related to the nature of the material, $(h\nu)$ refer to photon energy. The extrapolating $(FR \times h\nu)^{1/2}$ vs. $h\nu$ curves to $FR = 0$ within linear portions showed the value of $E_g$ as shown in Figure 7 and 8. The TiO$_2$ absorbance occurred below 400 nm, whereas for SWNTs and MWNT broad peaks of absorption can be observed between 450-1000 nm. The absorbance of composites TiO$_2$/CNT appeared red shifted in absorbance towards the visible light which increases with increase ratios of CNTs. The redshift can be related to an intrinsic property of CNTs which more shifted for composite with SWNT due to higher conductivity as compared with MWNTs.

### 5. Hydrogen Production

Figure 9, shows the reactor that used for hydrogen production. Briefly a xenon lamp (Osram XBO) with a 1000-WattUV-B light at the 240-1000nm wavelength was use as source of energy which fixed horizontally in the direction of the reactor. The light source was switched on 15 min before irradiation to reach stability for the lamp with light intensity 40 mW cm$^{-2}$. The reactor vessel consisting of a double-jacket Pyrex-glass reactor (110 mL volume) equipped with a quartz disc for light penetration. Prior to irradiation, Argon gas was purged through the suspension for 30 min. the reactor was cooled to room temperature with a Land Nds. Uni Hancooker system to keep the temperature of reaction at 298.15K. During irradiation, the headspace gas (40 mL) of the reactor was intermittently sampled (0.5 μL) and analyzed for H$_2$ using a gas chromatograph (Shimadzu GC – 8A) equipped with a thermal conductivity detector and a carboxen 1000 packed column. The photocatalytic reactions of hydrogen production from 7.5% of an aqueous methanol solution (0.131mol methanol) were carried out using 65 mg of different binary composites of TiO$_2$ with SWNTs or MWNTs. It is obvious that pristine TiO$_2$ without CNTs did not give any activity for producing hydrogen under dark or illuminated conditions.
The work was include studied the effect types and ratio of CNTs. The results were plotted in figure 10 for different binary composites of TiO$_2$ with SWNTs and MWNTs.

From figure 10, and table 2 presence of CNTs directly affect the activities of TiO$_2$, when producing hydrogen gas in all ratios and types of CNTs. According to the results, CNTs were succeeded to behave as ideal captures for excited electrons causing reduce the recombination of the electrons from conduction band to valence band [18].
Table 2. The rate of H2 production for different ratio of (a)- MWNT, (b)-SWNT with TiO2.

| a-%MWNT | k(µmole/min) | b-%SWNT | k(µmole/min) |
|---------|--------------|---------|--------------|
| 0.25    | 0.0007       | 0.25    | 0.6381       |
| 0.5     | 0.0363       | 0.5     | 0.3366       |
| 1.0     | 0.2297       | 1.0     | 0.1081       |

The influence of CNTs types in the value of emitted hydrogen gas can be related mainly to two causes: the first represent by distribute of SWNTs with TiO2 more than MWNTs. The second related to lower densities and diameters of SWNTs than MWNTs (1:3) make SWNTs with TiO2 particles more regular with homogenizing and more darkness [4] than MWNTs as shown in figure 11. The activities of TiO2/SWNT were reduced with increasing the ratio of SWNTs due to shielding effect which prevents UV-light to reach for the surfaces of TiO2. This behavior was reduce with MWNTs, however; the increases in H2 gas were shown with an increase in the ratios of MWNTs, causing reduce in shielding effect.

Figure 11. Schematics structures of (a) TiO2/ 1%SWNTs, (b) TiO2/ 1%MWNTs.

6. Recovery of Titanium Dioxide.

TiO2 Degussa P25 physically consists of nano powder which is impossible to remove from solution easily and as mention before there is no activity for hydrogen production. Figure 12, refer to the results which produced from this work when referring to the quantities of hydrogen production efficiency (HPE) with the ability to reuse the catalyst. Under the same experimental conditions, the modified TiO2 catalyst with CNTs appears to be much easier to separate than pristine TiO2. The reason behind that can be related to large agglomerate particle precipitation was observed and to complete separation was achieved approximately less than 30 min.
7. **Mechanism of Hydrogen Production.**

The activity of binary composite were plotted in figure 13 which shows maximum rate of hydrogen gas evolved with TiO$_2$/0.25%SWNT and TiO$_2$/1% MWNT. The mechanism of activity for TiO$_2$ with SWNTs or MWNTs depend on transferring the electrons from TiO$_2$ to CNTs, which agree with reported in many literature [18-19]. The active site in the binary matrix stimulates under UV-light, to transfer the excited electrons from the TiO$_2$ surface to the graphitic network of CNTs. Increase photocatalytic activity produce from synergistic effect between TiO$_2$ and CNTs and on finding the optimum weight ratios of TiO$_2$/CNTs to create the best arrangement for the ideal behavior of composites [20].

![Figure 12. Schematic diagram of the HPE% to reuse TiO$_2$/CNTs.](image)

![Figure 13. Schematic diagram of the proposed mechanism for the activity of TiO$_2$/CNTs.](image)

It should be referred to the work function of TiO$_2$ $\approx$ 4.3 eV [21] and 3.12 eV for the band gap [8-9], while the work function of CNTs is 4.8 eV and band gap is 0.5 eV [22,18]. The composites, a N-/p-type hetero-junction can form an ideal bridge for withdrawing and transferring the electrons from TiO$_2$...
to a network of carbon nanotubes. The behavior refers to increase the electric charge on the surface of semiconductor oxide with catalysts composite as a result of large surfaces area of higher conductivity CNTs as carrier electrons [23].

8. Conclusions.
Binary composite TiO$_2$/ CNTs were successfully prepared, by impregnated SWNT and MWNT with TiO$_2$. The high conductivity and low density of SWNTs enhance the activity of TiO$_2$ more than MWNTs. Increase the ratios of SWNTs to 1% with TiO$_2$ reduce the activity of semiconductor due to shielding effect which prevents UV-light reach to TiO$_2$. The Raman and XRD analysis for TiO$_2$/ SWNTs show clear change in intensity and area of the peaks than TiO$_2$/ MWNTs which shows less average crystallite size. The Raman spectroscopy for Anatase and CNT did not change significantly only the Anatase Raman bands for TiO$_2$/ MWNTs composites are slightly broadened as compared to the pure TiO$_2$, which in agreement with XRD analysis that shows the decreasing in the average crystallite size. The ideal method of preparation and ratios with types of CNTs can produce the best binary catalyst can behave excellent activities towards hydrogen production reaction.

References
[1] Liao C. H., Huang and C.W. Jeffrey C. S. 2012. Hydrogen Production from Semiconductor based Photocatalysis via Water Splitting, *Catalysts* 2 490.
[2] Prakash D. V. and Jose A. L. 2017. Review of Hydrogen Production by Catalytic Aqueous-Phase Reforming. *Chemistry Select.* 2(22) 6563.
[3] Sharif S.A., Barbir F., and Vizroglu T.N. 2003. Principles of hydrogen energy production, storage, utilization. *Journal of scientific and industrial research* 62 46.
[4] Firas H. A., Falah H. H., Ayad F. A., Irina I,Alexei V. E. and Detlef W. B. 2016. Sonochemical/hydration–dehydration synthesis of Pt–TiO$_2$ NPs/decorated carbon nanotubes with enhanced photocatalytic hydrogen production activity. *Photochem. Photobiol. Sci.* 15 1347.
[5] Adel A. I. and Detlef W. B. 2014. Photochemical splitting of water for hydrogen production by photocatalysis: A review. *Solar Energy Materials & Solar Cells* 128 85.
[6] Chi-Hung L., Huang C.W. and Jeffrey C. S. 2012. Hydrogen Production from Semiconductor-based Photocatalysis via Water Splitting. *Catalysts* 2 490.
[7] Firas H. A. 2016. Enhance photocatalytic Activity of TiO2 by Carbon Nanotubes. *International Journal of Chem Tech Research.* 9 (3) 431.
[8] Hoffmann M. R., Martin, S. T., Choi, W. and Bahnemann, D. W., 1995. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.*, 95 69.
[9] Kumar S.G. and Devi L.G. 2011 Review on modified TiO$_2$ photocatalysis under UV/visible light: selected results and related mechanisms on interfacial charge carrier transfer dynamics. *J Phys Chem A.* 115(46) 13211.
[10] Iijima S, 1991. Helical Microtubules of Graphitic Carbon. *Nature* 354 56.
[11] Kauffman D. R. and Star A., 2008. Carbon nanotube gas and vapor sensors. *Angew. Chem., Int. Ed.* 47 6550.
[12] Feng W., Feng Y., Wu Z., Fujii A., Ozaki M. and Yoshino K, 2005. Optical and electrical characterizations of nanocomposite film of titania adsorbed onto oxidized multiwalled carbon nanotubes. *J. Phys.:Condens Matter.* 17 4361.
[13] Fan W, Gao L, Sun J, 2006. Anatase –TiO$_2$ coated multi-walled carbon nanotubes with the vapor phase. *J. Am. Ceram.Soc.* 89 731.
[14] Frontera P., Trocino S., Donato A., Antonucci P. L., Lo F. M., Squadrito G., and Ner G. 2014. Oxygen-sensing properties of electrospun CNTs/PVAc/TiO$_2$ composites. *Electron. Mater. Lett.* 10 305.
[15] Xie Y., Heo S. H., Yoo S. H., Ali G., and S. O. Cho. 2010. Synthesis and Photocatalytic Activity of Anatase TiO\textsubscript{2} Nanoparticles-coated Carbon Nanotubes. *Nanoscale Res Lett.* 5 603.

[16] Firas H. A. and Falah H. H. 2015. Effects of Nanoparticle Size on Catalytic and Photocatalytic Activity of Carbon Nanotubes-Titanium Dioxide Composites. *Environmental Analytical Chemistry* 12 2.

[17] Kokhanovsky A., 2007. Physical interpretation and accuracy of the Kubelka–Munk theory. *J. Phys. D: Appl. Phys.* 40 2210.

[18] Chai B., Peng T., Zhang X., Mao J., Li K., and Zhang X. 2013. Synthesis of C60-decorated SWCNTs (C60-d-CNTs) and its TiO\textsubscript{2}-based nanocomposite with enhanced photocatalytic activity for hydrogen production. *Dalton Trans.* 42 3402.

[19] Xu Y. N., Zhuang Y. N., and Fu X. 2010. New insight for enhanced photocatalytic activity of TiO\textsubscript{2} by doping carbon nanotubes: A case study on degradation of Benzene and Methyl Orange. *J. Phys. Chem. C.* 114 2669.

[20] Khan G., Kim Y. K., Choi S. K., Han D. S., Wahab A. A., and Park H. W. 2013. Evaluating the Catalytic Effects of Carbon Materials on the Photocatalytic Reduction and Oxidation Reactions of TiO\textsubscript{2}. *Bull. Korean Chem. Soc.* 34 (4) 1137.

[21] Bickley R., Carreno G. T., Lees J. S., Palmisano L., and Tilley R. 1991. A structural investigation of titanium dioxide photocatalysts. *J. Solid State Chem.*, 92 (1) 178.

[22] Santangelo S., Faggio G., Messina G., Fazio E., Neri F., and Neri G. 2013. On the hydrogen sensing mechanism of Pt/TiO\textsubscript{2}/CNTs based devices. *Sensors and Actuators B*, 178 473.

[23] Kiselev N., Hutchison J., Ryabenko A., Rakova E., Chizhov P., Zhigalina O., Artemov V., and Grigoriev V. 2005. Two structural types of carbon bi-filaments. *Carbon*, 43 1897.