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Enhance the Activities of Hydrogen Production by Changing the Sequence of Preparation the Ternary Composite Pt -TiO_2/MWNT

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Abstract

Two types of ternary Pt-TiO_2/MWNT were synthesized by Sonochemical/Hydration–Dehydration methods which include photoplatinazation and supporting with MWNTs. The synthesized materials (Pt-TiO_2)/MWNT and Pt-(TiO_2/MWNT) were characterized by X-ray diffraction, Raman spectroscopy, UV-Vis diffuse reflectance spectroscopy, scanning electron microscopy and transmission electron microscopy. The activity of (0.65 g/L) MWNT/TiO_2/Ptwere estimated by H_2 production from (7.5 vol %) aqueous methanol solution. The results showed that platinizationof TiO_2 than create hybrid with MWNTs was more efficient in hydrogen production than platinazationofMWNT/ TiO_2.The preparation method, homogenous distribution and localized of MWNTs with Pt onto TiO_2 shows sensitively influence in the achieving the best efficient charge separation and transfer in exist the platinum under UV- light (< 420 nm) irradiation.

Keywords: MWNT, TiO_2; Hydrogen Production; Ternary composite; Sequences of Preparation

1-Introduction:

The use of nanotechnology in the field of energy aims to provide energy with taking care on the source of energy, cost, and environmental risks as well as get the maximum amount of energy which can be obtained. Hydrogen gas is an ideal technology of energy for the future to produce clean and friendly sources without any damages for the environmental [Chiari, &Zecca, 2011]. Hydrogen as sources of energy started with electrolysis of water thus the real orientation towards of sustainable technology for hydrogen production [Hashimoto et al., 2005] was developed for a long time ago. Nanomaterials in pristine or compounds and composites showed positive orientations in this field such semiconductors SC, metals M, and carbon nanotubes CNTs [Chen et al., 2010; Ong et al. 2010]. The binary and ternary composites commonly used for synthesizing catalyst used in hydrogen production reactions. The activities of composites depend on nature of bonding which

produces maximum value for active sites. The ternary composites represent the ideal case for produce many active sites such Pt-TiO_2/CNTs. TiO_2 is semiconductors with three phases, Rutile, Anatase and Brookite. The first two phases of TiO_2 are both in a tetragonal structure and the last type in an orthorhombic [Nadtochenko et al., 2006].Carbon nanotubes CNTs is graphite or graphene sheets rolling from side to side to forming a tubular structure with specific properties such chiral, armchair and zig-zag with nanometer in diameter [Falah et al., 2018]. Carbon nanotubes can be classified two single-walled SWNTs, double walled DWNTs, few walled FWNTs and multi-walled carbon nanotubes MWNTs [Falah et al., 2018]. Pt as noble metals with specific physical and chemical behavior which encourage widely used activation and enhance the activities of semiconductors [Shaoet al., 2010; Stefano et al., 2012]. The ternary composites Pt-TiO_2/CNTs were used in many applications such Sensors [Stefano et al., 2012] hydrogen production [Firas et al., 2016] converted agent for CO to CO_2 [Lin et al., 2009] degradation of many pollutants [Shih et al., 2017]. The method of synthesized ternary composite technically influences with of preparations methods and the sequence of adding the three materials which rarely studied. This studies concern with the sequences effect for the out- sito addition of Pt and MWNTs in activates of TiO_2 towards hydrogen production. TiO_2 did not show any activities towards the hydrogen production in alcohol/water solution while existing of CNTs or Pt showed abilities to evolve the H_2 gas [Firas et al., 2016].The results from many literature had shown that exits CNTswith TiO_2 increasethe surface area of TiO_2. The contact between the surface of the TiO_2 particle and CNTs or Pt became one of the most important reasoned to accrue the reaction and increase the rate of reaction. The presence of the CNTs or Pt prevents for the recombination the photoexcited electron [Valentin, 2004]. The effect of Pt with TiO_2 in the reaction of hydrogen production [Ren et al., 2007] was shown more effective than two types of CNTs, which is less activates as compare with Pt-TiO_2/MWNT. The greater synergic effect of Pt -TiO_2/ MWNT can be related to the better charge transfer between TiO_2 and Pt and best distribution for three materials [Yang et al., 2012]. In this studies, two types of Pt-TiO_2/MWNTs were synthesized with changing the sequence of addition which characterized by UV-vis reflectance, X-ray diffraction, Raman spectroscopy, TEM images and BET. Activates were tested by using the hydrogen production reaction form 7.5% of methanol aqueous solution.

2-Experimental

2.1 Materials

Multi-walled carbon nanotubes MWNTs, were purchased from Aldrich, which fabricated by chemical vapor deposition method. Thepurities of MWNTs 95% and mode diameter 5.5nm. The TiO_2 sample was purchased from Degussa, Germany (TiO_2-P25) consist of 20% Rutial and 80% Anatase. The source of Pt was hexachloro

platonic (IV) acid hexa hydrate ($H_2PtCl_6.6H_2O$) where purchased from Riedel-De-Haen AG, Seelze, Hannover, Germany. Methanol(A.R quality, 99.9%) was supplied from Hayman, England. The work was done in Institute of Technical Chemistry, Leibniz Universität Hannover\Germany.

2.2**Preparation of Binary and ternary composite**

TiO_2/MWNT were prepared by a simple evaporation methodbased on our previous works[Firas et al., 2016a]. Firstly,100mg of MWNTs was treated with 60 ml of mixture HNO_3/H_2SO_4 (1/3) with the assist of ultra-sonic water bath for 7h [Dirk et al., 2010] then washing and drying at 100^{o}C. The required amount of activated MWNTs was dispersed in 200 ml of distilled water by using ultra-sonic system for 20 min then adding the equivalent amount of TiO_2 powder which produces TiO_2/0.5%MWNT. The suspension was filtered by vacuum evaporator (Rota vapor re121 BUSHI 461 water Bath) at 45 °C, then dried overnight in an oven at 100 °C. TiO_2 was platinized, by photo-depositionmethodwhenmixture of 37% formaldehyde: absolute ethanol (4:1) was added to the aqueous suspension of TiO_2 and an equivalent amount of ($H_2PtCl_6.6H_2O$)[Falah et al., 2016]. The deposition was accrued with UV light irradiated for 3hour at 40^{o}C, using a 200-W mercury lampto produce 0.5%Pt-TiO_2. Two types of ternary composites were prepared: the first (0.5%Pt-TiO_2)/0.5%MWNT, while the second 0.5%Pt-(TiO_2/0.5%MWNT). The first ternary composite (0.5%Pt-TiO_2)/0.5%MWNT was prepared by platinized the TiO_2 then loaded with MWNTs under the same conditions of preparation. The second composite 0.5%Pt-(TiO_2/0.5%MWNT) was prepared by loaded MWNTs than platinized process.

2.2.Hydrogen production

The activity of the composites was evaluated by H_2 production from 70 ml of an aqueous methanol solution (7.5 vol %) with (0.65 g/L) of catalyst which was stirred in a Pyrex-glass reactor (ca. 110 ml volume) equipped with a quartz disc for light penetration. Before to irradiation, Argon gas was purged through the suspension for 30 min. A solar simulator equipped with (SUX 1450) Xenonlampenversorg UNG, Muller, was used as a light source. To avoid thermal effects, the reactor was cooled to room temperature with a cooler system Land Nds. Uni Han. 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.

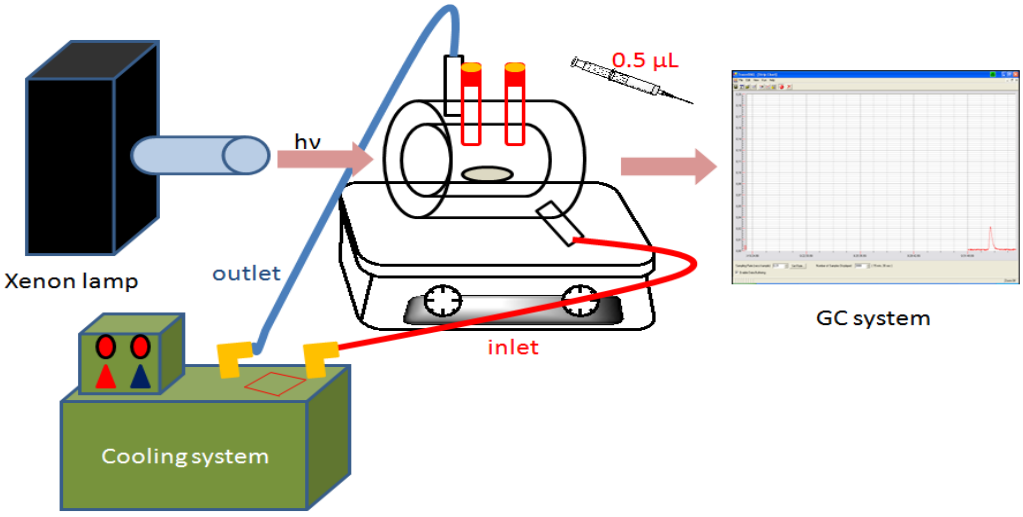

Figure 1. Schematic diagram for the system of hydrogen production

2.3 **Characterization**

UV-Vis diffuse reflectance spectra were recorded over the range of 200–800nm in the absorption mode using a CARY 100 Bio UV-vis spectrophotometer which calibrated with $BaSO_4$. Kubelka–Munk function [Kauffman & Star, 2008] were depend to calculate the band gap energy (E_g) from diffuse reflectance data. The E_g value was determined using the theory of optical absorption for allowed direct transitions: {$h\nu = A\ (h\nu - E_g)^{1/2}$ }where A is the absorption coefficient which relative to the material, (hv) is the discrete photon energy. The linear portion of extrapolating $(FR \times h\nu)^{1/2}$ vs. hν curves to FR = 0 refer to the E_g as reported in Fig. 2. The important consideration for TiO_2 was absorbance occurred at 380 nm, while MWNTs observed broad peaks between 450-1000 nm [Firas, 2016b,c]. In the same time the combined effect of both carbon nanotubes and Pt in the band gap value of TiO_2 will increased[Luma et al., 2014]. Surface area estimation of the TiO_2 has been performed by the Brunauer-Emmett-Teller 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 as shown in table 1.

Table 1. Summaries of, surfaces area, particle size and band gap, for pure MWNTs, TiO_2, and modified TiO_2 with Pt and MWNTs.

Samples	BET (m^2/g)	Particle size (nm)	Band gap (e V)
MWNT	282	04.37	0.50
TiO_2	51	23.09	3.18
TiO_2/0.5%MWNT	56	15.41	2.80
0.5%Pt-TiO_2	47	23.13	2.75
(0.5%Pt-TiO_2) /0.5%MWNT	61	18.60	2.60
0.5%Pt-(TiO_2 /0.5%MWNT)	50	25.76	2.80

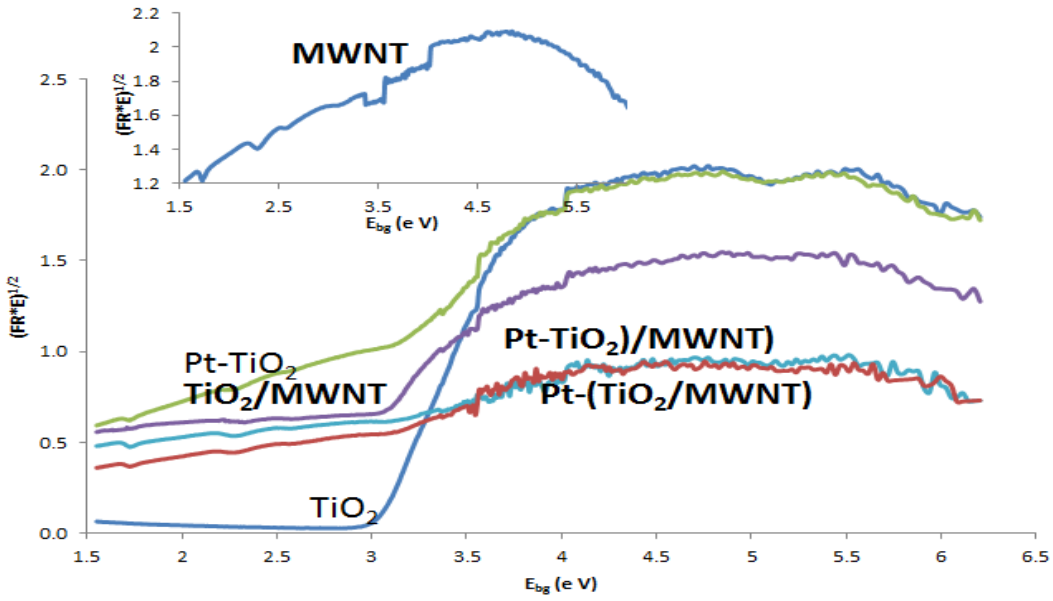

Figure 2. Band gap for pristine and modified TiO2 with MWNTs and Pt in binary and ternary composites.

Table 2. Summaries for activities of binary and ternary composites towards hydrogen productions.

Samples	r (µ mole/h)	Compare r**		k (s^{-1})	R
0.5%Pt-TiO_2	226	TiO_2		4.42	1
		0.00			
(0.5%Pt-TiO_2)/0.5%MWNT	263	2.17	TiO_2/0.5%MWNT	4.83	1.12
0.5%Pt-(TiO_2/0.5%MWNT)	208			3.94	0.89

The binary and ternary composites were characterized by X-ray diffraction (XRD) on a (RigakuRotalflex) (RU-200B) X-ray diffractometer using Cu Kα radiation at 0.15405 nm) with a Ni filter. The tube current was 100 mA with voltage 40 kV. The

2θ angular regions between 15 and 65° were explored at a scan rate of 5°/min. For all XRD tests, the resolution of the 2θ scans was kept at 0.02°.Fig. 3 shows the XRD patterns of the crystallographic structures of the binary and ternary composites. The influence was limited to the small change in the width of peaks with the shift towards higher 2θ. The 0.5%Pt-TiO_2 , there is only TiO_2 in the anatase form and rutile while no peaks of Pt at 2θ = 40 and 48◦ can be notes, maybe can be attributed for low ratios of Pt which used or the homogenous dispersion for Pt on TiO2 [Stefano et al., 2012]. Debye–Scherrer equation (d = K λ / β cosθ) [Luma et al., 2014] were depended to determine the average crystallite size (d) which estimation by line broadening measurements. When λ refers to X-ray wavelength which equals to 0.15405 nm, β is the peak width at half maximum height resulting in radians and K mostly equal to 0.9 which related to crystallite shape. The peaks at 25.3° and 27.4° are the characteristic reflection for anatase and rutile, respectively for TiO_2, which did not change in the binary and ternary composite [Stefano et al., 2012]. From Fig. 4, for MWNTs appears two characteristic peaks 2θ=25.9° and 43.2°, from C(100) and C(002) planes of the carbon nanotubes, [Fias et al., 2016a,b].The two peaks for MWNTs disappears in binary and ternary composites because the overlapped for these peaks with the anatase peak of TiO_2 at 25.2° and 43.9◦ [Firas et al., 2016b]. The results show that TiO_2 crystallite size of the binary compound did not significantly affect by Pt [Shao et al., 2010] while with MWNTs there is reduces in size. The ternary composite shows the two properties in crystallite size of Pt and MWNTs with TiO_2. The two types of ternary composites appear variance in particle size which represent less broadening of the XRD peaks found for 0.5%Pt-(TiO_2/0.5%MWNT) compared to (0.5%Pt-TiO_2)/0.5%MWNT. These phenomena make the particle size for pristine and modified TiO2 arranged as the following:Pt-(TiO_2/MWNT)>P25 ≈ P25/Pt > (Pt-TiO_2)/MWNT > TiO_2/MWNT.

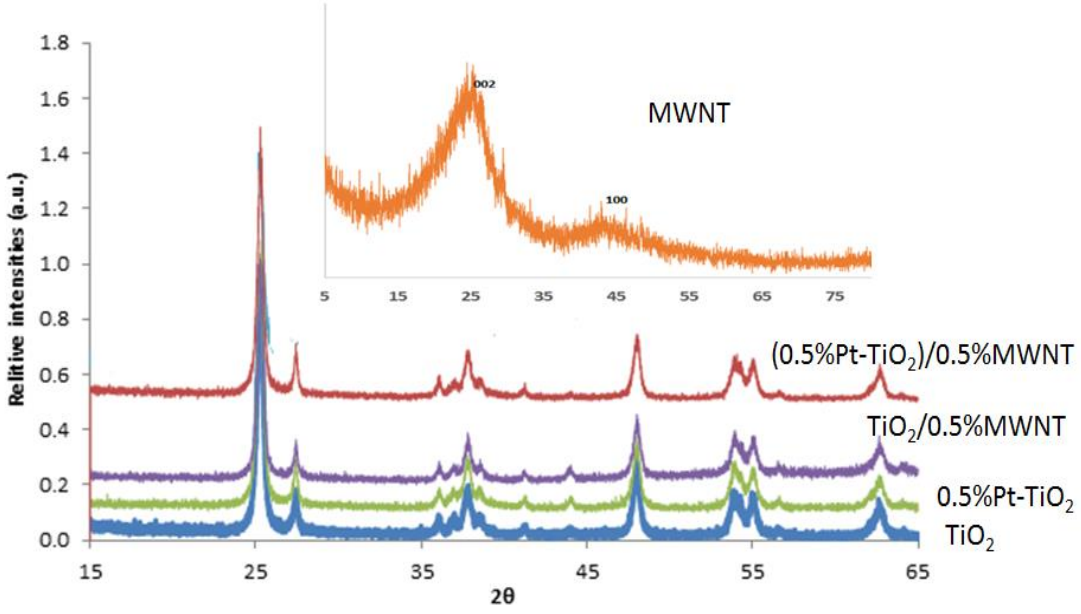

Figure 3. XRD pattern for pristine and modified TiO2 by loading with MWNTs and platinized in binary and ternary composite.

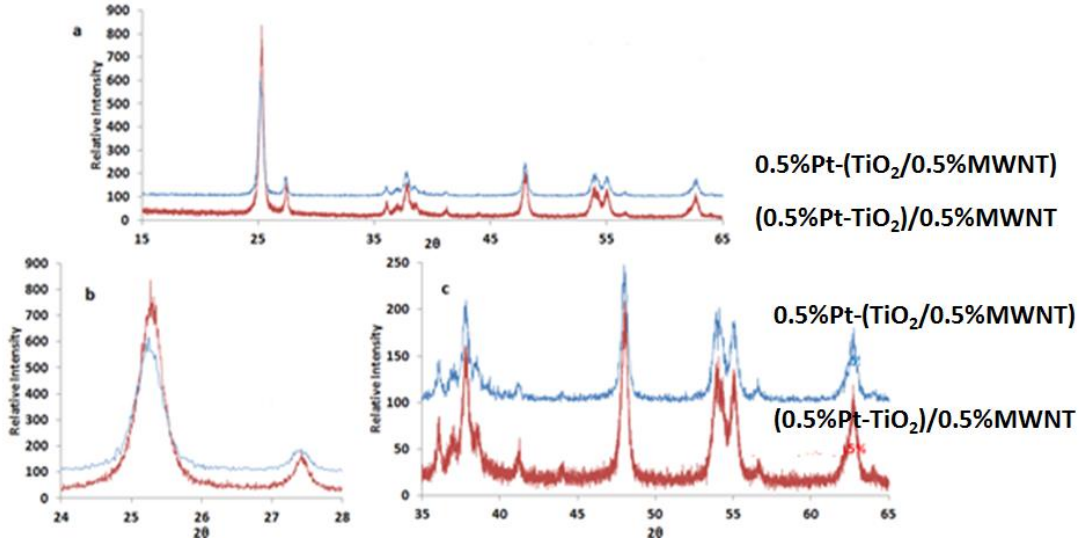

Figure 4. XRD pattern for ternary composite Pt-TiO2/MWNT with different sequence of preparation.

Raman spectroscopy for pure TiO_2 was plotted in Fig. 5, characteristic bands for two phases' anatase and rutile. Anatase modes appears at 150 cm-1 (Eg), 395.1 cm^{-1} (B1g), 512.5 cm^{-1} (A1g + B1g) and 636.7 cm^{-1} (Eg) respectively[Hashimoto et al., 2005 &Firas et al. 2016a]. rutile phase appears at 143, 235 cm-1 which can be ascribed to the B1g, two-phonon scattering, 445 cm^{-1}Eg, and 612 cm^{-1} A_1g, respectively [Zhenhai et al., 2013].The Raman spectra for both binary and ternary composite with MWNTs showed a G band at 1582 cm^{-1} corresponding to the wrapped graphene plane and a D band at 1330 cm-1 for the C-related defects of MWNTs [Falah et al.,2018]. In the case of TiO_2/0.5%MWNT composites, all the Raman bands for anatase and MWNTs remain, except slightly broadened. Table 1 and Fig. 5 shows the peak broadening which is consistent with their decease in the average crystallite size. From the Fig.5, it is seen that Raman spectroscopy for 0.5%Pt-TiO_2, the spectrum shows distortion for TiO_2 between 100-700 cm^{-1} which refer to precipitation Pt on the surfaces of particles TiO_2. The ternary composite shows the two effects for MWNTs and Pt with

less distortion for anatase phase before 700 cm^{-1}.

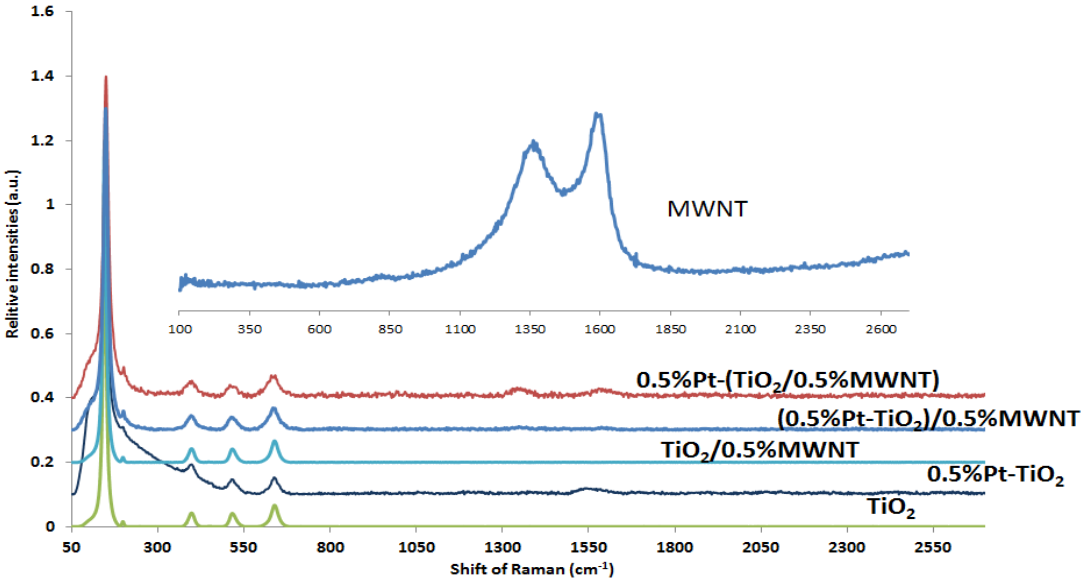

Figure 5. Raman Shift for pristine and modified TiO2 by loading with MWNTs and platinized in binary and ternary composite.

The SEM images in Fig.6(a,b) shows the surface from a TiO_2 agglomerate. The marked area is shown in the micrograph to the right at higher magnification, a single carbon fillement is visible. The Fig.6c shows the TiO_2 particle surface, which were decorated by a lot of small particles (Platinum) with a single carbon nanotube is visible. The interesting imager which shown in Fig. 6d when seen that particles of Pt in the surface of CNTs , and that may reffer to the to increasd the activity of ternary composite as compaer with Pt- TiO_2.

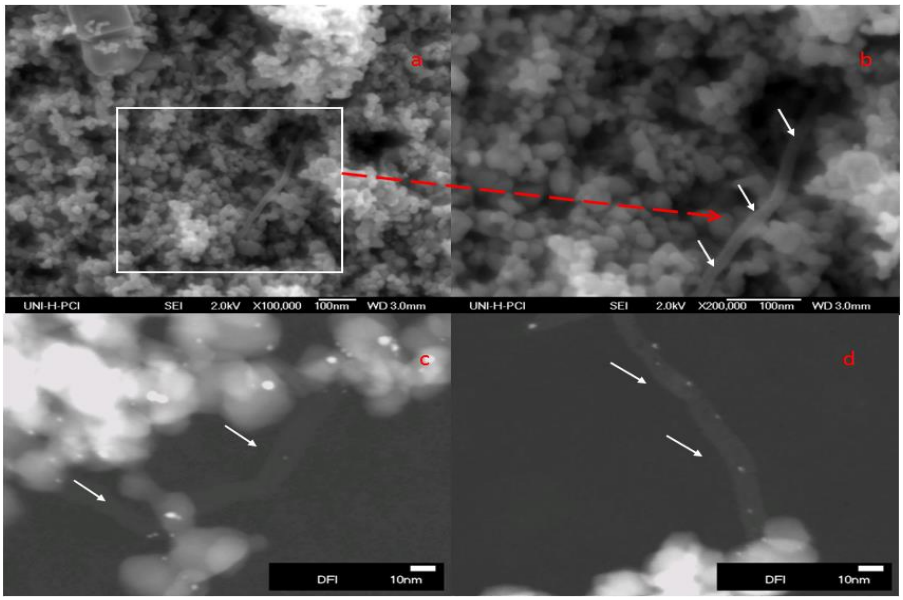

Figure 6. SEM (a,b) and HR-TEM images (c, d) for ternary (Pt-TiO2)/MWNT composites.

3-Results

The activities of synthesized binary and ternary composites were tested in hydrogen production from 7.5 vol % aqueous methanol solution. The catalysts include binary

TiO_2 composites which platinized with 0.5% of Pt or loaded with MWNTs. The last two binary composites were used as control groups against ternary composites. The ternary composites which the aims of this work include two composites with the same ratios and continent but different from each other in the strategy of preparation. The first ternary composite was prepared from platinization of TiO_2 than loaded with MWNTs which is (Pt-TiO_2)/MWNT. The second ternary composite Pt-(TiO_2/MWNT) was loaded with MWNTs than platinized. The brackets refer to the first process of preparations and slash refer to support or impregnated surfaces MWNTs while (-) refer to impregnation Pt onto TiO_2. The results were plotted in Fig.7 and listed in table 1 which shows that pristine TiO_2 without platinization or loading with MWNTs do not show any activity to produce hydrogen under dark or illumination conditions. The results show that effect of Pt towards hydrogen production was larger than MWNTs in binary composites.

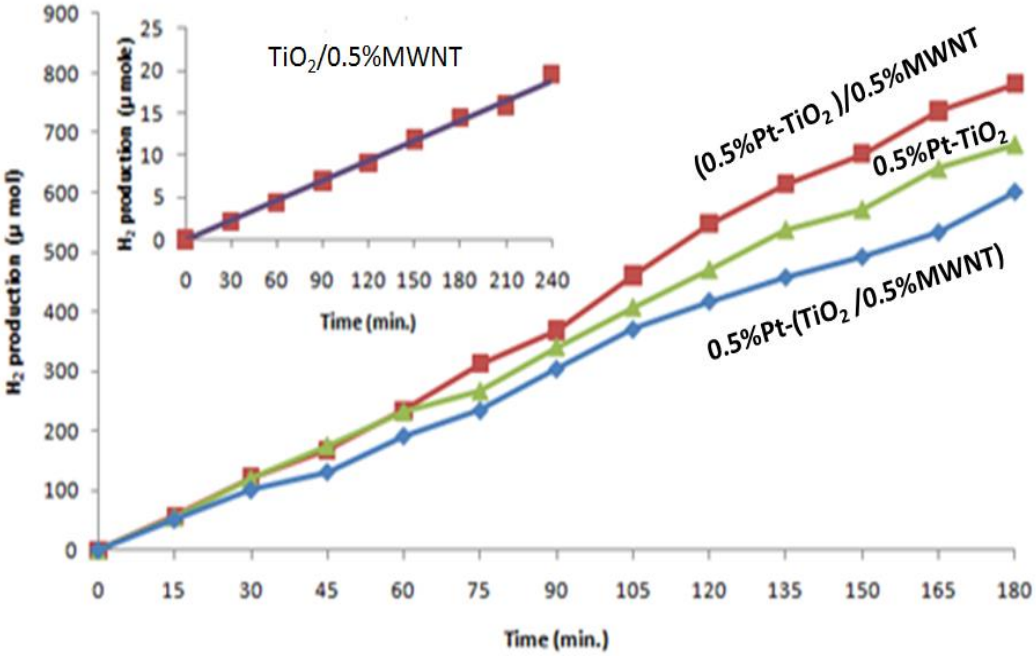

Figure 7. The photocatalytic H_2 production from 7.5vol% methanol aqueous suspended with 65 mg of Pt-TiO_2, TiO_2/MWNT, (Pt-TiO_2)/MWNT and Pt-(TiO_2/MWNT) using 300 W xenon arc lamp as the light source.

Table 2, shows that ternary composite (Pt-TiO_2)/MWNT was succeeded to increase the hydrogen production more than Pt-TiO_2 while Pt-(TiO_2/MWNT) was failed. The evaluations for the results of hydrogen production in two types of ternary composites compare with binary composites, can estimated synergy factor (R). The increase and reduce were calculated by apparent rate constant for Pt-TiO_2/MWNT with Pt-TiO_2 {R = k_{app}Pt-TiO_2/MWNT/ k_{app}Pt-TiO_2}. The R represent the best calculus to valuation

effect of loading MWNTs and platinazation towards achievement maximum activities for hydrogen production.

*** These values refer to the rate of hydrogen evaluate for TiO_2/0.5%MWNT which insert with these tables for compare with the same ratios of Pt in Pt-TiO_2 and with Pt-TiO_2 /MWNT.*

4. Discussion The efficiency of Pt-TiO_2/MWNT [Bo et al., 2013] increases with increasing the direct connections between TiO_2 and Pt with interference MWNTs for creating the best transfer of the electrons from TiO_2 to methanol/H_2O mixture. The strong connections between TiO_2/MWNTs occurred when MWNTs penetrated through TiO_2 under the influence of ultrasonic when succeed to break Van Der Waals interaction for MWNTs bundles [Yi et al., 2010]. The results of UV-visible reflectance and XRD refer to change in band gap and particle size which shows variance in size of groups as explain in Figure 8. The activities of Pt- TiO_2 can be related to Pt when removed photoexcited electron from hole because reduce the space charge [18] and forming Schottky barrier for TiO_2 electron in CB to the CB of Pt. the role of MWNT in binary TiO_2/MWNTs was the same action of Pt with less activities which shows in value of product. The different between Pt- TiO_2 and TiO_2/MWNTs were shown in reducing the agglomerations and increase the surface area with MWNTs as compare with Pt as represented in Fig. 8 and table 2.

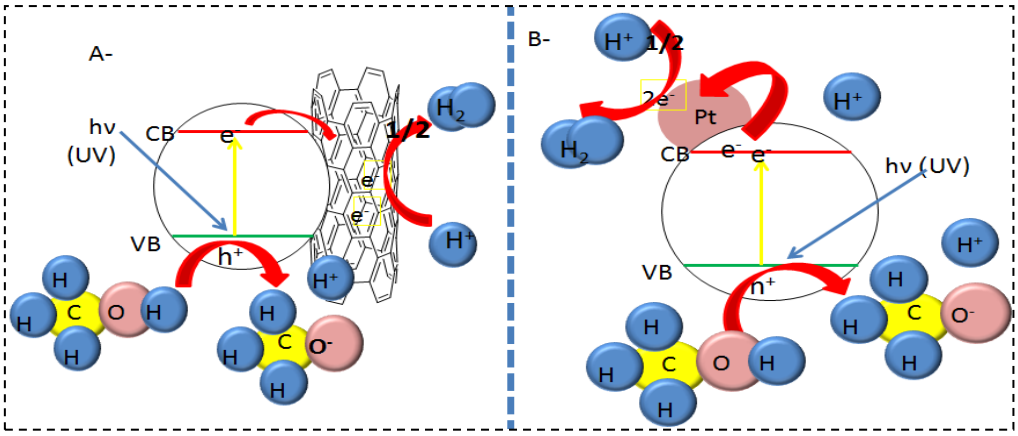

Figure 8.Schematics of synthesized -1, (Pt-TiO2)/MWNT, by platinized than loading by MWNTs -2, Pt-(TiO2/MWNT), by loading with MWNT than platinized.

Fig. 8 refer to the behaviors of ternary composites when accumulations for effect of Pt and MWNTs reduce the surface area SBET for (Pt-TiO_2)/MWNT and increase SBET with Pt-(TiO_2/MWNT). The process of platinization was added many active sites to produce many agglomerations that covered most of the active sites causing reduce the activity. Loading MWNTs within ultra-sonic water bath at least reduce the agglomerations which encourage to shows more active site. All of this change in morphology can be seen in Fig9. When TEM images show redistribution for Pt onto MWNTs and TiO_2 surface under the effect of ultra-sonic [Jimmyet al., 2002].The

ternary composite as mentions before shows variance on activities for evaluating hydrogen gas, which appears as a result of appearing or disappears the active site which responsible for activities.

4.1 Mechanism of the reaction

The mechanism depends on transfer of the electrons from TiO_2 to MWNTs as mentions in many works of literature [Rowan & Aidan, 2009] and represents in Fig.9A. When TiO_2 was attached to the surface of MWNTs, the active site of the binary matrix within existing of UV lights, mostly stimulates the transfer of excited electrons from the surface of TiO_2 to the network of MWNTs [Baoet al., 2012] which become a source to convert H^+ to H_2. The effect of Pt was more activities for withdrawn the excited electron as compare with MWNTs as represented in Fig.9B.

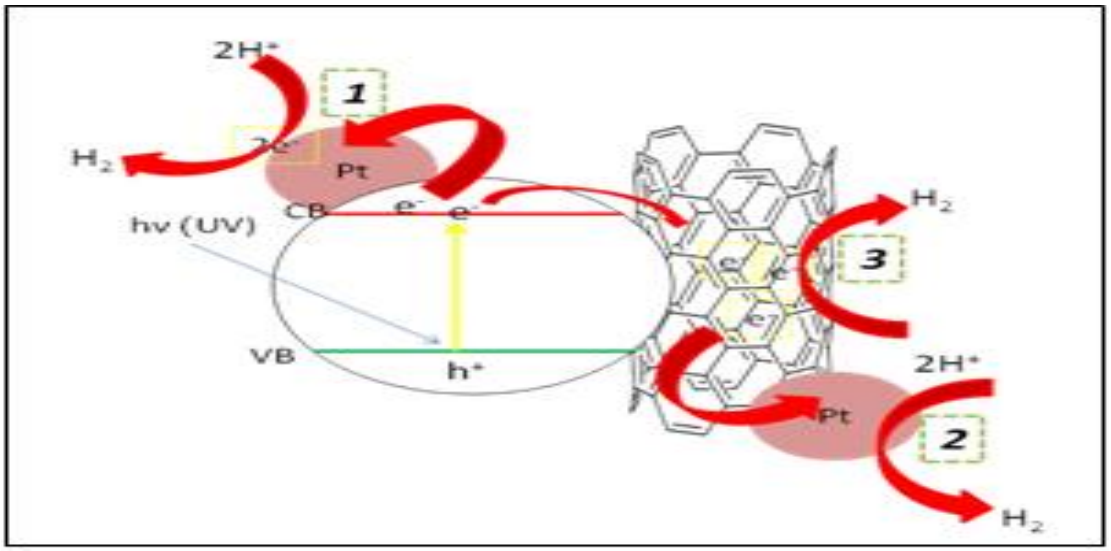

Figure 9.Sckematic diagram for proposal mechanism of A- TiO2/MWNT, and B- Pt-TiO2.

The mechanism depends on transfer of the electrons from TiO_2 to MWNTs as mentions in many works of literature [Rowan & Aidan, 2009]. When TiO_2 was attached to the surface of MWNTs, the active site of the binary matrix removed the exited electrons which forming H_2 gas. In the cases of Pt- TiO_2/MWNT, under the irradiation the electrons were excited to the conduction band CB from valence band VB of TiO_2. The Pt- TiO_2/MWNT, raises two routes for electrons to transfer, the first is from the conduction band of TiO_2 to Pt, and the second is to transfer the electrons to MWNTs. The second routs appear two probabilities, one of them include indirect ways for transfer the electron to Pt which adsorbed on the surfaces of MWNTs. The ether which represents direct ways from the surfaces of MWNTs to H^+ and all of this state causing evaluate the hydrogen gas as shown in Fig. 10. The efficiency of Pt-TiO_2/MWNT may relate to the Pt particles on TiO_2 aggregates were isolated the electrons transport which limited in activity by the insufficient local electronic conductivity of TiO_2 [Lin et al., 2009].The UV lights, mostly stimulates transfer of

excited electrons from the surface of TiO_2 to the network of MWNTs [Baoet al., 2012] which become a source to convert H^+ to H_2as shown in Fig.10.

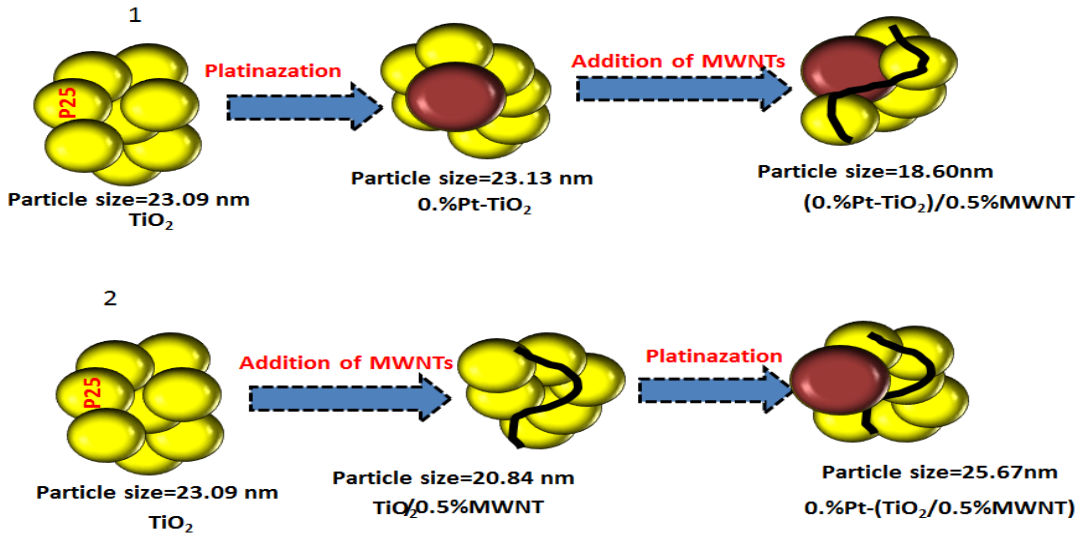

Figure 10. Schematic diagram for the mechanism of ternary composite Pt-TiO2/MWNT.

Conclusion

The binary and ternary composite was successfully synthesized by using simple evaporations methods and platinazation to forming Pt- TiO_2, TiO_2/MWNT and Pt-TiO_2/MWNT. The ability of Pt to evaluate hydrogen in binary composite was more active than MWNTs although, reduce the activities of Pt- (TiO_2/MWNT) when platinazation were done after loading with MWNTs.Ternary composite Pt- (Pt-TiO_2)/MWNT showed the best abilities to increase the activities due todouble effectof MWNTs when reduces the agglomeration, and make with Pt as a bridge to move the electrons from TiO_2freely. Thus chose the best ways for preparations toachieve the ideal transfer of electron can produce the best activities for hydrogen production.

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References:

Bao Y. X., Shujiang D., Hao B. W., Xin W. &Xiong W. D.(2012). Hierarchically structured Pt/CNT@TiO_2nanocatalysts with ultrahigh stability for low-temperature fuel cells, *RSC Advances*, 2,792–796.

Bo C., Tianyou P., Xiaohu Z., Jing M., Kan L. & Xungao Z.(2013).Synthesis of C60-decorated SWCNTs (C60-d-CNTs) and its TiO2-based nanocomposite with

enhanced photocatalytic activity for hydrogen production", Dalton Transactions, 42(10), 3402-3409.

Chen X., Shen S., Guo L., & Samuel S. M. (2010). Semiconductor-based Photocatalytic Hydrogen Generation.*Chemical Reviews*, 110 (11), 6503–6570.

Chiari, L. &Zecca A. (2011). A. Constraints of fossil fuels depletion on global warming projections. Energy Policy, 39(9), 5026–5034.

Dirk M. Guldi& Martín N.(2010). Carbon Nanotubes and Related Structures Synthesis, Characterization, Functionalization, and Applications. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Kauffman D. R. & Star A.(2008).Carbon nanotube gas and vapor sensors. AngewandteChemie International Edition, 47,6550-6570.

Falah H. Hussein, Firas H. Abdulrazzak, and Ayad F. Alkaim, (2018). Nanomaterials: Biomedical and Environmental Applications, chapter 1: Nanomaterials: Synthesis and Characterization,1 ed. Welly .

Firas H. Abdulrazzak , Falah H. Hussein , Ayad F. Alkaim , Irina Ivanova , Alexei V. Emeline & Detlef W. Bahnemann. (2016a) Sonochemical /hydration–dehydration synthesis of Pt–TiO_2 NPs/decorated carbon nanotubes with enhanced photocatalytic hydrogen production activity. Photochemical &PhotobiologicalSciences., 15(11),1347-1357.

Firas H. Abdulrazzak(2016b). Enhance photocatalytic Activity of TiO2 by Carbon Nanotubes. International Journal of ChemTech Research., 9(3) 431-443.

Firas H. Abdulrazzak, Shahad K Esmail, Halimah A. Dawod, Ahmed M. Abbas & Mustafa K. K. Almaliki. (2016c).X-ray Analysis for Purification Process of Synthesized Multi-Walled Carbon Nanotubes by Chemical Vapor Deposition. International Journal of Theoretical & Applied Sciences, 8(1), 432016-432037 .

Hashimoto K., Irie H., &Fujishima A, (2005). TiO_2photocatalysis: a historical overview and future prospects. *Japanese Journal of Applied Physics* , 44(12),8269–8285.

Jimmy C. Yu, Jiaguo Y., Lizhi Z. &Wingkei H.(2002).Enhancing effects of water content and ultrasonic irradiation on the photocatalytic activity of nano-sized TiO2 powders. Journal of Photochemistry and Photobiology. A: Chemistry, 148,263–271.

Lin K.N., Liou W.J., Yang T.Y., Lin H.M., Lin C.K., Chien S.H., Chen W.C.& Wu S.H.(2009). Synthesis of hybrid Pt/TiO2 (anatase)/MWNTs nanomaterials by a combined sol–gel and polyol process. Diamond and Related Materials . 18,312–315.

Luma M. Ahmed, Irina I., Falah H. Hussein, &Detlef W. Bahnemann. (2014). Role of Platinum Deposited on TiO2 in Photocatalytic Methanol Oxidation and Dehydrogenation Reactions. International Journal of Photoenergy.(3):1-9.

Nadtochenko V., Denisov N., Sarjusiv O., Gumy D., Pulgarin C. & Kiwi J.(2006). Laser kinetic spectroscopy of the interfacial charge transfer between membrane cell walls of E. coli and TiO2. *Journal of Photochemistry and Photobiology A: Chemistry*, 181,401–408.

Ong Y. T., Ahmad A.L., Hussein S. Z. & Soon H. T. (2010). A review on carbon nanotubes in an environmental protection and green engineering perspective. *Brazilian Journal of Chemical Engineering*

Ren W. J., Ai Z. H., Jia F. L., Zhang L. Z., Fan X. X. & Zou Z. G. .(2007).Low temperature preparation and visible light photocatalytic activity of mesoporous carbon-doped crystalline TiO2. Applied Catalysis

Rowan L.& Aidan W.(2009). Carbonaceous nanomaterials for the enhancement of TiO2 Photocatalysis. Diamond and Related Materials

Shao F. C., Jian P. L., Kun Q., Wei P. X., Yang L., Wei X. H. & Shu H. Y. (2010). Large Scale Photochemical Synthesis of M@TiO_2 Nanocomposites (M = Ag, Pd, Au, Pt) and Their Optical Properties, CO Oxidation Performance, and Antibacterial Effect. *Nano Res*earch, 3(4),244–255.

Shih-Y. L., Ya-Chu Y., Sheng-Hsin H., & Jon-Yiew G.(2017). Synthesis of Pt@TiO_2@CNTs Hierarchical Structure Catalyst by Atomic Layer Deposition and Their Photocatalytic and Photoelectrochemical Activity",*Nanomat*. (Basel). 7(5)97-112.

Stefano T., Andrea D., Mariangela L., Nicola D., Salvatore G. L. & Giovanni N. (2012). Pt-TiO_2/MWNTs Hybrid Composites for Monitoring Low Hydrogen Concentrations in Air, *Sensors*, 12(9), 12361-12373.

Valentin N. P.(2004). Carbon nanotubes: properties and application. Materials Science and Engineering. R, 43, 61–102.

Yang Z, Du G., Meng Q., Guo Z., Yu X., Chen Z., Guo T. & Zeng R.(2012). Synthesis of uniform TiO2@carbon composite nanofibers as anode for lithium ion batteries with enhanced electrochemical performance. Journal of Materials Chemistry. 22(12), 5848–54.

Yi-Jun X., Yangbin Z. &Xianzhi F.(2010). New insight for enhanced photocatalytic activity of TiO2 by doping carbon nanotubes: A case study on degradation of Benzene and Methyl Orange", The Journal of Physical Chemistry. C , 114, 2669–2676.

Zhenhai W., Suqin C., Shun M., Shumao C., Ganhua L., Kehan Y., Shenglian L.& Zhen H., Junhong C.(2013).TiO2 nanoparticles-decorated carbon nanotubes for significantly improved bioelectricity generation in microbial fuel cells", Journal of Power Sources. 234, 100-106.