Comparison study on making dye sensitive solar cell using nanomaterials

Abdulkareem Mohammede Ali Alsammarraie and Noor Abdullah Al-Attar

Department of Chemistry, College of Science, University of Baghdad, Jadiriyah, Baghdad, Iraq

_____

ABSTRACT

Dye sensitized solar cells (DSSCs) have emerged as a promising device to meet the energy needs as an environmentally friendly alternative for the development of sustainable power generation. In this study different types of DSSCs were fabricated using mixed combination between four kinds of Titania (TiO_2) semiconductors ,and three kinds of counter electrodes while the sensitized dye was natural pomegranate seeds and the electrolyte was I^-/I_3^- for all assembled DSSCs.TiO_2 semiconductors includes; bulk TiO_2 powder ($>20\mu m$), 50nm TiO_2 powder, hydrothermally nanotubes (HT) TiO_2 powder ,and anodized TiO_2 nanotubes arrays (TNTs).The counter electrodes include; carbon, electrodeposited platinum (Pt), and electro polymerized polyanilne. The I-V plots and all cell parameters were established using two electrodes potentiostat, the results showed that the activity of anode materials follow the order;
TNTs on Ti foil > 50nm TiO_2 /ITO glass> HT TiO_2/ITO glass > Bulk TiO_2/ITO glass
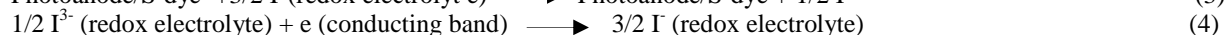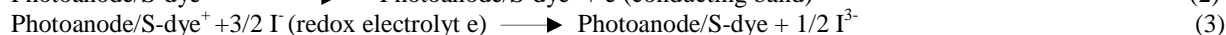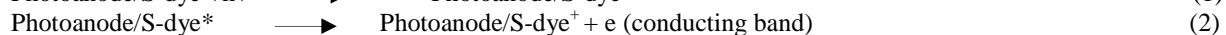*While the effectiveness of the counter electrodes obey the order;*
Pt > PANI > Carbon
The best Efficiency (3.27%) achieved using TNTs on Ti foil as active anode and Pt on ITO glass as counter electrode.
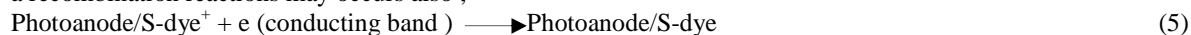
Keywords: DSSc, TiO_2, Titania nanotubes, polyaniline, hydrothermal

_____

INTRODUCTION

After the invention of the dye sensitized solar cell (DSSC) in 1991 by O'Regan and Gratzel.[1],it has become a hot topic in the area of solar cell research because it has many advantages such as low cost, a simple manufacturing process, and low environmental loads , but with limited efficiency in converting solar energy into electricity [2]. A typical composition of DSSC is shown in Fig. 1, is assembled placing in succession a transparent dyed-photoanode, an electrolyte solution containing a redox mediator system and a catalized counter-electrode [3,4] ,the reactions take place to generate the electricity is explained in the following equations;

Photoanode/S-dye +hv $\longrightarrow$ Photoanode/S-dye*   (1)
Photoanode/S-dye* $\longrightarrow$ Photoanode/S-dye$^+$ + e (conducting band)   (2)
Photoanode/S-dye$^+$ +3/2 I$^-$ (redox electrolyt e) $\longrightarrow$ Photoanode/S-dye + 1/2 I^{3-} (3)
1/2 I^{3-} (redox electrolyte) + e (conducting band) $\longrightarrow$ 3/2 I$^-$ (redox electrolyte)   (4)

a recombination reactions may occurs also ;
Photoanode/S-dye$^+$ + e (conducting band) $\longrightarrow$ Photoanode/S-dye   (5)
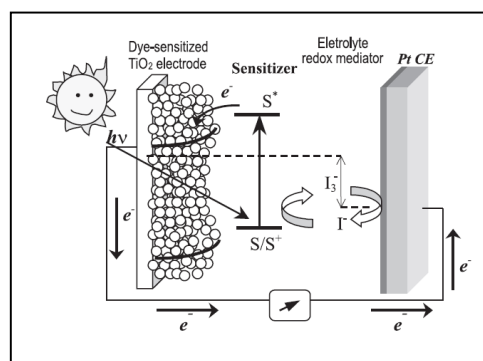
Figure 2. Representation of a dye-sensitized TiO2 solar cell (S represents the dye-sensitizerand I⁻//I³⁻ is the charge mediator)

Four types of numerous studies to improve the efficiency of DSSCs have been recorded; a- the sensitized dyes[5] ,b- the active semiconductor anodes[6], for easy charge transfer through the conduction band ,c-the electrolytes with efficient redox couples[7] ,and d-the catalyzed counter electrode systems for maximized electron transport [8] .

In this paper, mixed combination of different nanostructured TiO$_2$ as anode and three types of catalyzed counter electrode materials were selected to investigate their effect on the performance of the DSSC ,while the electrolyte and the dye are same for all the prepared cells.

MATERIALS AND METHODS

2. Experimental
The flow diagram of all experimental procedures is represented in figure 2;

2.1. Preparation of TiO$_2$/ITO electrode from bulk TiO$_2$(B) and nanosized TiO$_2$(NS) powders;
The TiO2 paste was prepared by grinding 2g of TiO$_2$ (TiO$_2$(B) ,Sigma Aldrich or TiO$_2$(NS) <50nm ,MTI) with 10ml of deionized water and adding few drops of dilute solution of acetic acid for 10 min. The deposition of the TiO$_2$-layer was done by doctor blade technique and spread on well cleaned and dry indium –tin oxide conductive (ITO) glass, the washed glass is masked on its four sides by a scotch tape of thickness 30μm to unify the layer thickness in all samples to give active area of $2 \times 1.5cm^2$ then left to dry naturally for 30 min and sintered in atmospheric muffle furnace for 60 min at 450°C then left to cool down, and rinsed with water and ethanol afterwards.

2.2. Preparation of hydrothermal TiO$_2$(HT) / ITO electrode ;
2gm of TiO$_2$ (NS) powder was mixed with 10M NaOH for 15 min at room temperature then put into homemade Teflon-lined stainless steel autoclave at 180°C for 48 hr, After the autoclave was gradually cooled down to room temperature ,the obtained product was washed with 0.1M hydrochloric acid solution and deionized water until pH reaches 7.5 followed by drying at 100°C using drying oven for 2 hours then left to cool down to room temperature. The same procedure mentioned in the previous paragraph was used to apply the TiO$_2$(HT) on ITO glass.

2.3. Synthesis of anodized TiO$_2$ nanotubes (ATNTs) electrode;
Highly ordered TiO$_2$ nanotube arrays were grown on titanium foil (to serve as active anode for dye-sensitized solar cell (DSSC)) ,by an anodization process in a two-electrode electrochemical Plexiglas cell, Ti foil (99.5% purity, 0.25 mm thick, Alfa Aesar) with rectangular dimensions of (1.8*2.5 cm) was used as a working electrode. Platinum foil was used as the counter-electrode. The voltage was applied by a DC power supply (GW Instek, PSP-603). A thin TiO$_2$ nanotube array layer was produced by anodizing the Ti foil in a solution of ethylene glycol (99.8%, BDH) containing 0.5% ammonium fluoride (NH$_4$F, 98%, Aldrich) and 4% DI water at 60 V for 60 min. After the end of anodizing period ,the anodized foil was rinsed in deionized water then with ethanol , dried with flow of nitrogen gas ,and annealed at 450°C for 120 min in air.
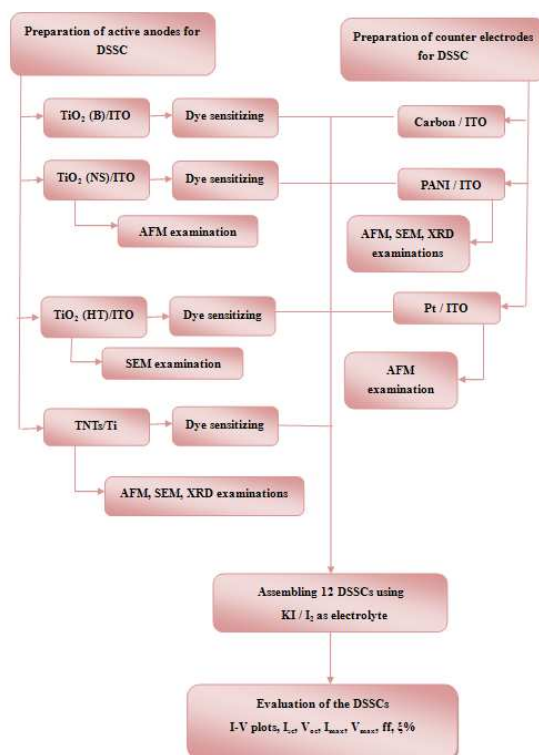
Figure 2. The flow diagram of all experimental procedures

2.4. Dye sensitizing of TiO₂(B) /ITO , TiO₂(NS) /ITO, TiO₂(HT) / ITO ,and TiO₂(ATNTs)/Ti electrodes;

All types of TiO_2 electrodes mentioned above were immediately sensitized by immersing in fresh prepared pomegranate seed syrup for about 24 hours (overnight).

2.5. Preparation of polyaniline (PANI)/ITO electrode

Polyaniline (PANI) films were synthesized on a conducting ITO glass bycyclic potentiostatic techniques to construct counter electrode for dye-sensitized solar cell (DSSC).the electrolyte composed of 0.1M aniline monomer (purity 99.4%,BDH) and 0.3M sulfuric acid(99.8%,BDH), the voltage scan range was -200 to 1500 mV with scan rate of 40mV/sec and cycle repetitions of 6.

2.6. Preparation of platinum (Pt) / ITO electrode

The fabrication of Pt counter electrode was conducted by cyclic electro deposition method using three electrodes potentiostat, the three electrodes(ITO, Pt, and Ag/AgCl) were immersed into a 500 ml solution of (5mM $NaNO_3$,H_2PtCl_6 5mM all purchased from Sigma Aldrich) the voltage scan range was -1000 to 200 mV with scan rate of 30 mV/sec and cycle repetitions of 6.

2.7. Preparation of carbon (C) /ITO electrode;

The Carbon black electrode was fabricated by an easy way with moving the conductive side of ITO glass above the flame of candle till it get black, then let the ITO to cool for 5 mints and   few drops of ethanol was added to diffuse across the carbon film and dried by heat gun.

2.8. Fabrication of dye sensitized solar cells;

12 DSSCs were assembled using the prepared photoanodes and counter-electrodes by putting any couples of two electrodes together into a sandwich cell type structure and sealed with hot-melt gasket. The cell's internal space was filled with electrolyte prepared by dissolving (0.5M) of KI and (0.05M) of I_2 in Ethylene glycol to obtain an (I^- / I_3^-) ions which served as acceptor and donor for electrons through an oxidation redaction reaction with anode and counter electrode, then the cell was placed in a vacuum chamber to remove the air from inside the cell space and allow the electrolyte to enter.

_____

2.9 Characterization
The surface morphology of the most prepared electrodes were determined using scanning electron microscope (SEM, Hitachi FE-SEM model S-4160, Japan) ,and atomic force microscope (AFM,AA3000 of Angstrom Advanced Inc.USA), and x-ray diffraction used to identify the phase structure of ATNTs and electropolymerized polyaniline. The photocurrent density–voltage (I–V) curves were measured using two electrodes potentiostat by applying biass potentials from-200 mV and 1200 mV under a 250 W xenon lamp the illumination intensity (90 mW/ cm^2) was calibrated by a standard Si cell.

RESULTS AND DISCUSSION

3.1 Electropolymerization of aniline on ITO glass counter electrode
Figures 3. shows the cyclic voltammograms of PANI films recorded at 0.3 M distilled aniline and 1 M sulfuric acid, the polymerization takes place by oxidation at (900-1300) mV while potential is increasing followed by a de-protonation at (300- 0) mV in the reverse direction of potential . It is observed that the current density in 1st cycle was four times of the current in 6th cycle, the deposition yielded a green film of polyaniline.
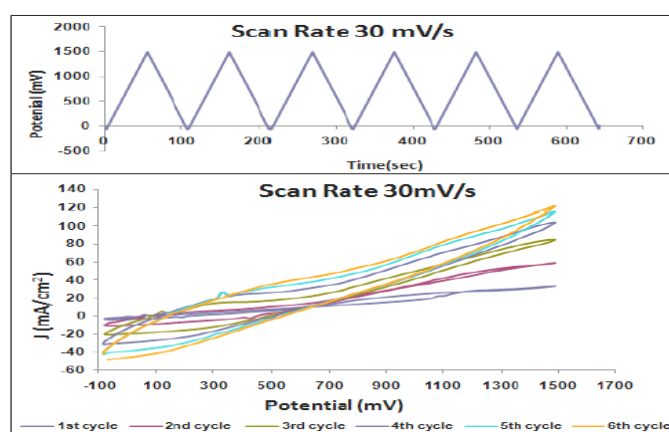

Figure 3. cyclic voltagram of PANI fabricated in 0.1 M aniline and 0.3 M H_2SO_4 scan rate 30 mV/s with 6 rep. at room temperature

Figures 4 and 5 show the SEM and AFM images of PANI ,they revealed a film of nanofibers structure with diameter around 70 nm.
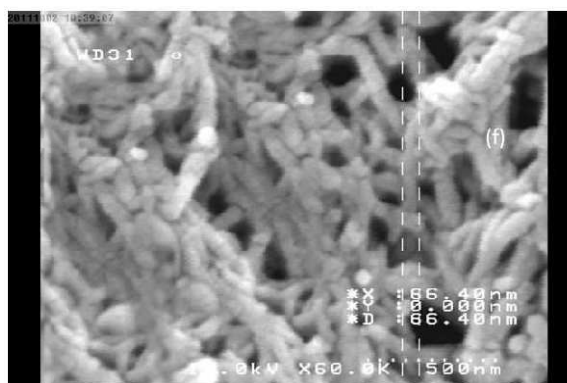

Figure 4. SEM image of electropolymerized PANI films obtained in 0.1M aniline and 0.3 M H_2SO_4 electrolyte
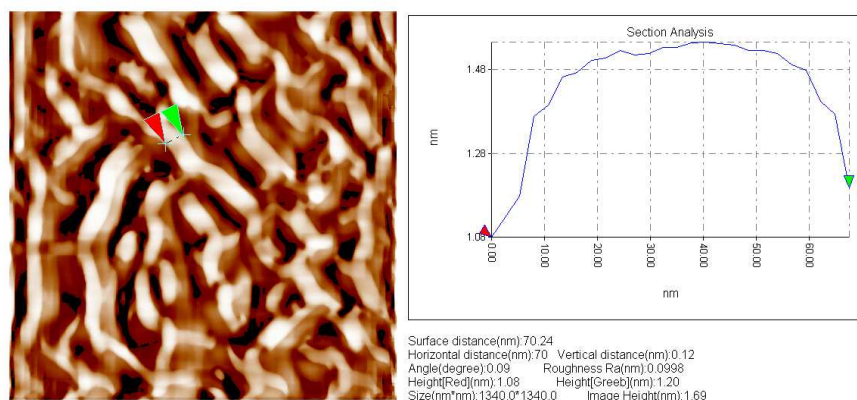
Figure 5. AFM image show the section line analysis of electropolymerized PANI films obtained in 0.1M aniline and 0.3 M H₂SO₄ electrolyte

The Fourier Transformation Infrared spectra (FT-IR) of electropolymerized PANI was investigated ,as shown in figure 6 the spectra show a typical Infrared spectra of the PANI, The main absorption peaks shows 3468 cm-1 it is possible assign asymmetric stretching vibration of NH_2. The N-H stretching in benzoid-NH-benzoid (B-NH-B) ,the broad band at 3310 cm-1 to hydrogen bonded NH and 3178 cm^{-1} to terminal quinoid =NH (Q=NH). The 2943 cm^{-1} represented C-H stretching region. The absorption peak observed at 1647.21 cm^{-1} were attributed to C=C stretching in aromatic nuclei Absorption bands at 1477.4 cm^{-1} evidenced to C=N stretching in aromatic compounds. absorption bands at 1300-1200 cm^{-1} which confirms the C-N stretching of primary aromatic amines . The 1141 cm^{-1} band is vibrational mode of (B-NH=Q) and (B=NH-Q) which is formed in doping reaction . this band is very intense and broad which may be attributed to an existence of positive charges [9].The absorption peaks at 1546.91cm^{-1} assigned to the quinoid structure does not revealed any significant changes for all polymer samples, that concludes that the polymers were prepared using di and tri basic acids. It has been reported that H_2SO_4 may interact with PANI   by donating either hydrogen sulfate, $(HSO_4)^-$ or sulfate, $(SO_4)_{-2}$ anions as dopant anions. Many authors agreed that $(HSO_4)^-$ dopant anions are present in PANI/H_2SO_4 [10].
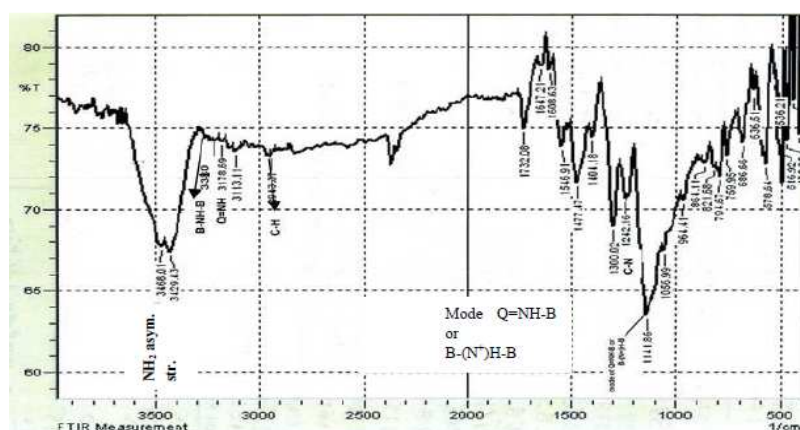

Figure 6. Infrared spectra of electropolymerized PANI in (0.1 M aniline +0.3M H₂SO₄) at scan rate 30 mV/s with 6 repetition

The XRD patterns of prepared PANI is shown in figure 7 revealed orientation   at 2θ   of (43,50, and 74) this information have no standard card for matching the data.
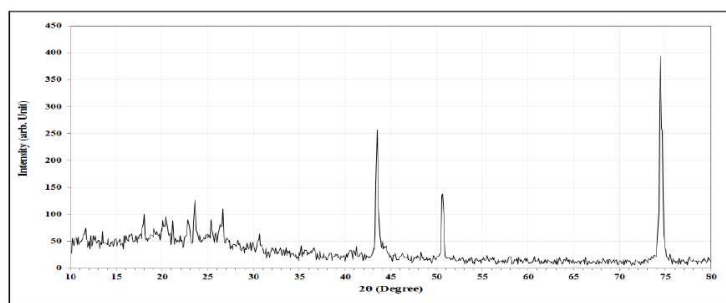
82

_____

Figure 7. XRD spectra of electropolymerized PANI in(0.1 M aniline + 0.3M H$_2$SO$_4$) at scan rate 30 mV/s with 6 repetition

3.2 platinum electrodeposition on ITO glass couter electrode

Figure 8 show the topographic views of the Pt layer formed by cyclic deposition (CD) from chloroplatinic acid solution   using scan range started at -1000 mV and ended at 200 mV with repetition cycles of four .The particles size of the deposited Pt   were measured using AFM scans they are between   20 and 50 nm , and the average particle size is around 37 nm, as shown in figure 9 .

3.3 Preparation of titanium oxide nanotubes by anodizing

TNT photoanode was prepared by anodizing process which is an electrochemical process that convert Ti to TiO$_2$ according the following chemical reaction:
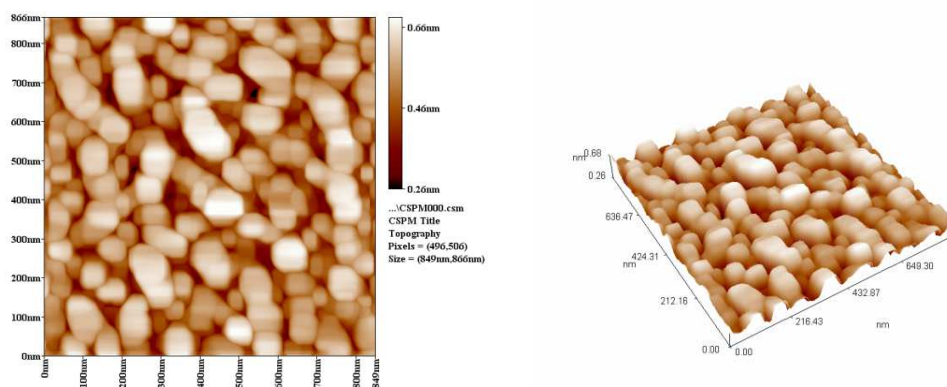
$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$$

(6)

Figure 8. 2D and 3D AFM views of Pt layers deposited on ITO glass by (CED)
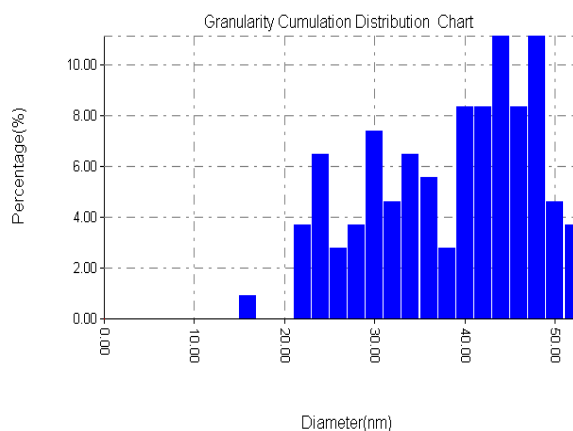

Figure 9. Particle size distribution plot of Pt layers deposited on ITO glass by (CED)

83

_____

This compact oxide layer on the titanium surface leads to a rapid reduction in the current density, due to its poor electrical conductivity. The current density then reaches a quasi-steady state due to the chemical dissolution of the oxide layer forming soluble fluoride complexes according to the following reaction:

$$TiO_2 + 6F^- \rightarrow TiF_6^{2-}$$

(7)

As a result fine pits or pores are formed at the surface. Under sufficient applied voltage magnitude, field-assisted oxidation occurs at the TiO_2/Ti interface, where the oxygen ions (O^-) are transported from the solution to the oxide layer. At the same time, titanium ions (Ti^{4+}) are transported from the titanium to the oxide/solution interface and dissolve into the solution, leading to a continuous increase in the depth of the porous structure and thus the formation of ordered nanotubes oriented vertically to the substrate [10]. It was reported that several parameters effect the architectures including pore diameter, wall thickness, tube length, and surface roughness of prepared TNT such asanodizationvoltage, time and electrolyte composition [12] , figure 10 illustrate the current-time transit plot of the anodizing process .
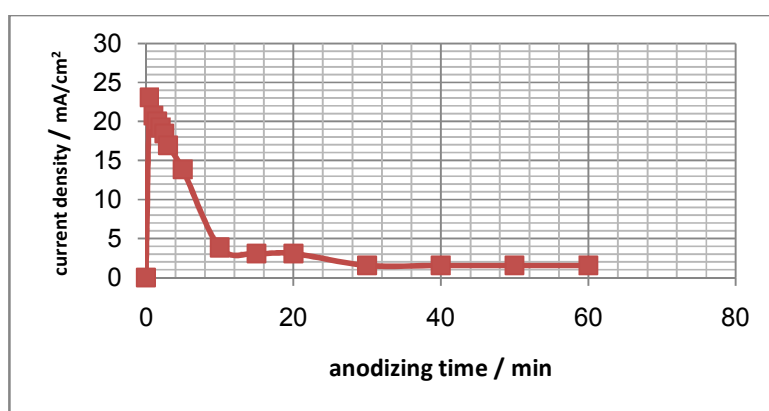

.

Figure 10 current/time plot of grown TiO₂ nanotubes via anodizing process in in (0.4% NH₄F, 3% H₂O and 87.8 % by wt ethylene glycol), with anodizing potential of 60 V for 1 hr

The I-time   behavior show that at first the current start to increases suddenly and reaches a maximum point at the first (1-4 min) ,then a fast decay of the current started until a steady   reading was recorded which remained nearly constant for the rest time of the process.

This behavior is expected to occurs according to ohm's low (I=V/R) , this stage of anodizing process is responsible for making full coverage of TiO2 on the Ti surface .Table 1 show the maximum and steady stat currents and times reaching them.

Table 1. Time of reaching maximum and steady currents of the anodizing of Ti foils in electrolyte consist of 0.4% NH4F, 3% H2O and 87.8 % by wt ethylene glycol at 60 V for 1hr

Anodizing Potentially/volt	Max, Current density mA/cm²	Time minutes	Steady Current density mA/cm²	Time minutes
60	23	1.5	2	10

The prepared TNT's was subjected to SEM and AFM examination as shown in figures 11 and (12,13) respectively, the measurements of the tube parameters (length, diameter, wall thickness) were conducted on SEM images using (Imager J) software   they revealed the length nearly 8 microns   ,the tube diameter around   65 nm while the wall thickness about 30 nm.

Somehow similar results achieved using AFM images, and highly accurate cell dimensions measured as shown in figure 12 for 2D and 3D views, and figure 13 for roughness report;
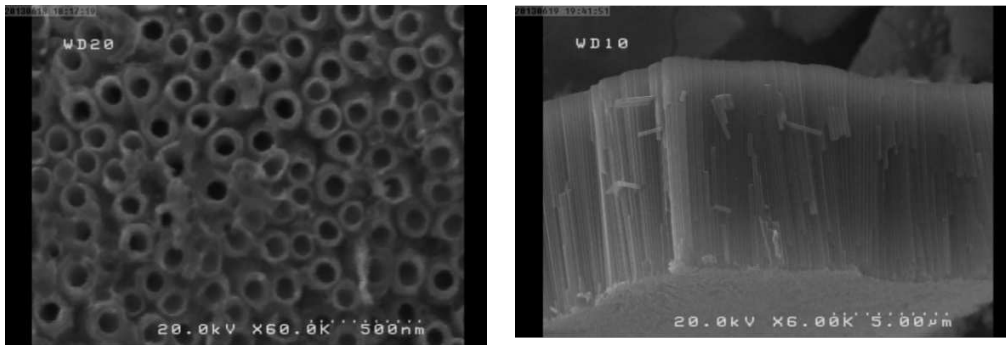
_____

Figure 11. A-top view, B-side view, of TNTs prepared by anodizing in (0.4% NH$_4$F , 3% H$_2$O and 87.8 %　by wt ethylene glycol), with anodizing potential of 60 V for 1 hr
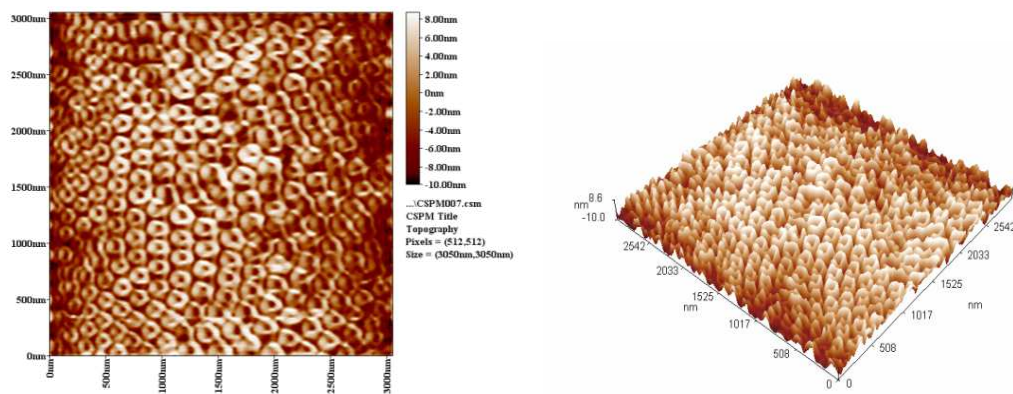

Figure 12. 2D & 3D AFM images of TNT's prepared via anodizing in (0.4% NH$_4$F , 3% H$_2$O and 87.8 % by　wt ethylene glycol), with anodizing potential of 60 V for 1 hr
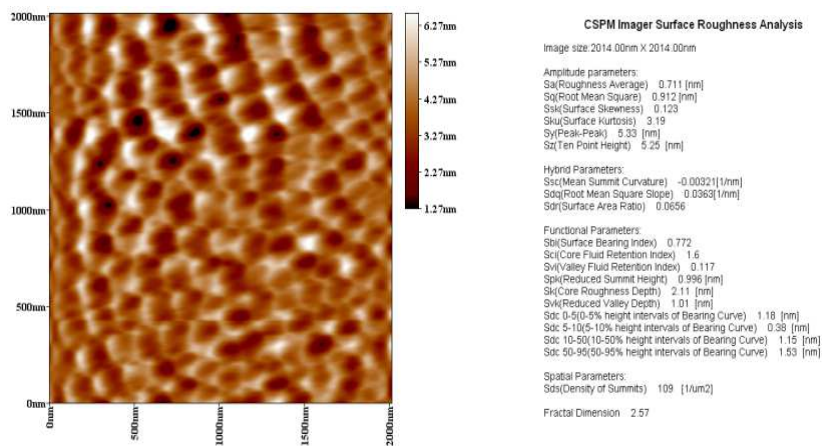

Figure 13. AFM roughness report of TNT prepared via anodizing in (0.4% NH$_4$F , 3% H$_2$O and 87.8 % ethylene glycol), with anodizing potential of 60 V for 1 hr
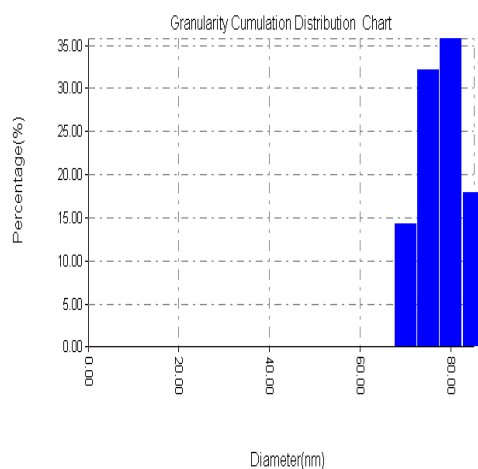
Figure 14. pore size distribution ,of TNT prepared via anodizing in (0.4% NH₄F , 3% H₂O and 87.8 % ethylene glycol), with anodizing potential of 60 V for 1 hr

TiO_2 layer was studied by XRD spectroscopy to identify the crystalline phases.   Figure 15 shows the XRD spectra of TiO_2 nanotubes formed before and after annealing. They revealed that the titania before annealing is a poly-crystalline nature with a combination of phases (Anatase and Brookite) but after annealing at temperatures 450°C for 1hr on Ti foil substrate, showed peaks present Rutile phase Because of the heat, disappeared phase (Anatase) due to its transformation completely into phase (Rutile) and transformation part of the phases (Brookite) also into (Rutile).Also, the intensity and sharpness of almost all the peaks increased considerably after annealing [13].
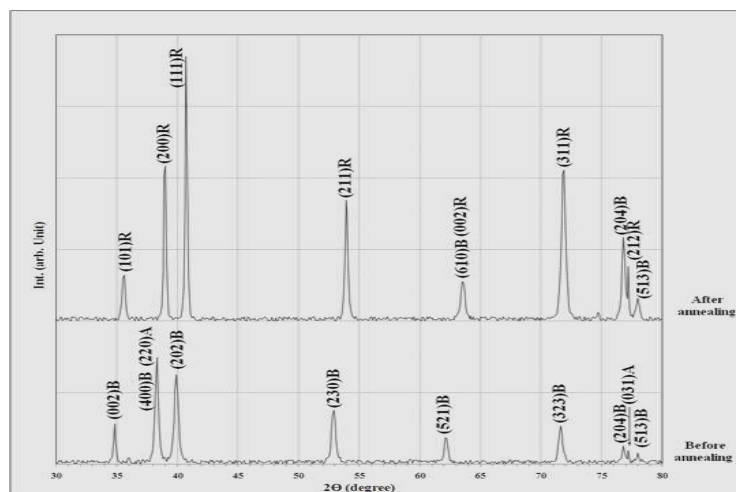

Figure 15. XRD pattern of TNT's prepared via anodizing in (0.4% NH₄F , 3% H₂O and 87.8 % ethylene glycol), with anodizing potential of 60 V for 1 hr., before and after annealing at temperatures 450°C for 3hr on Ti foil substrate

3.4. Preparation of titanium oxide nanotubes via hydrothermal procedure:

Starting from standard TiO_2 nanoparticles (50 nm) ,a hydrothermal process conducted as described in the experimental part, to investigate the possibilities of conversion the nanoparticles to other nanostructures at 180ºC for 48 hrs. Figure 16 show the   SEM image of the produced TiO_2which revealed that complete conversion of the TiO_2 nanoparticles to tube like forms achieved at 180ºC .The diameters of the produced tubes are equal or little smaller than the starting nanoparticles(50nm) which can be explained that the process is surface modification mechanism rather than dissociation-formation one.
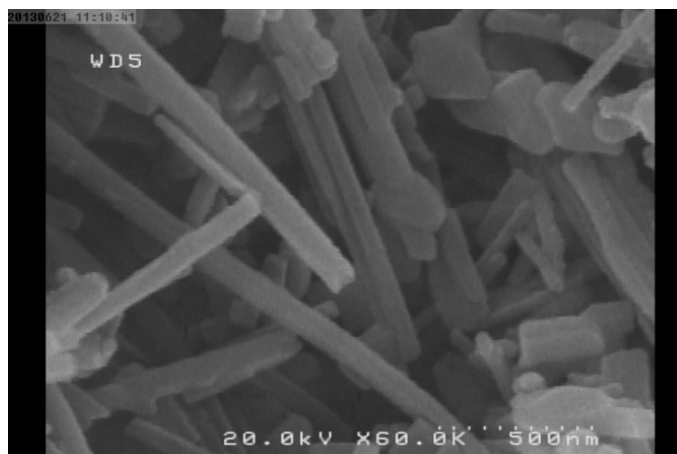
86

_____

Figure 16. SEM image of complete conversion of TiO₂ nanoparticles to nano tubes at 180°C for 48 hrs in hydrothermal bomb

3.5 Characterization of assembled DSSCs

All types of the assembled   DSSCs from mixed combination of different counter electrodes and different   active anodes were subjected to I-V characterization by fast scan with two electrodes potentiostat, to evaluate all parameters of   each of them ;current short circuit (I_{sc}), voltage of open circuit (V_{oc}),maximum cell power ($P_{max}=I_m*V_m$), were estimated using two electrodes potentiostatic measurements ,then the full factor (FF),and conversion efficiency(E%) were calculated using the following equations;

$$E\% = \frac{V_{OC}I_{SC}FF}{P_{inc}}$$

(8)

$$FF = \frac{I_m V_m}{I_{SC} V_{OC}}$$

(9)

All measurements are tabulated in table 2. The best efficiencies were achieved using Ti/TNTs as anode, and ITO/Pt and ITO/PANI they are 3.27 and 2.94 % respectively ,while the ITO/carbon with Ti/TNTs give very low efficiency (0.31 %) that may attributed to the absence of the transparency of the two faces of the DSSC body [14].

Table 2. values of assembled DSSCs with; a-standard TiO₂ NP's, b-anodized TNT's at 60 v, and c-hydrothermally prepared TiO₂ at 180°C

DSSC Cathode	Anode	V_{OC} mV	I_{SC} mA/cm²	V_{max} mV	I_{max} mA/cm²	ff	P_{in} mW/cm²	P_{max} mW/cm²	% E
ITO/carbon	TiO₂(B)/ITO	158	0.38	148	0.29	0.71	90	0.043	0.047
ITO/PANI	TiO₂(B)/ITO	160	0.77	159	0.70	0.90	90	0.111	0.123
ITO/Pt	TiO₂(B)/ITO	178	0.58	141	0.48	0.65	90	0.068	0.075
ITO/carbon	TiO₂(NP)/ITO	448	3.81	408	2.75	0.65	90	1.122	1.246
ITO/PANI	TiO₂(NP)//ITO	482	6.45	440	5.51	0.78	90	2.244	2.493
ITO/Pt	TiO₂(NP)//ITO	540	5.75	478	4.65	0.71	90	2.223	2.475
ITO/carbon	Ti/TNTs	280	1.52	255	1.11	0.66	90	0.283	0.31
ITO/PANI	Ti/TNTs	450	9.81	339	7.81	0.59	90	2.647	2.94
ITO/Pt	Ti/TNTs	518	8.02	440	6.70	0.71	90	2.948	3.27
ITO/carbon	TiO₂ (HT)/ITO	190	0.9	162	0.64	0.60	90	0.104	0.115
ITO/PANI	TiO₂ (HT)/ITO	202	1.31	194	1.00	0.73	90	0.194	0.215
ITO/Pt	TiO₂ (HT)/ITO	251	1.62	200	1.21	0.59	90	0.242	0.268

The micron sized MP TiO₂ reflected bad efficiencies in all types combination of counter electrodes, this results can be attributed to the low active surface area of the TiO₂semiconductor which led to the deficiency of the number of injected electrons by the dye [15]. Using the ITO/PANI as counter electrode gave very competitive substitute to the ITO/Pt which is more expensive and difficult to control the number of layers of Pt which may led to affect the

_____

transparency of the ITO glass, in addition to that the PANI has very attractive colors which give the DSSC a beautiful appearance.

The effectiveness of using nanostructure materials;PANI,TiO$_2$NP, and mono layers of Pt   in making the anodes or the cathodes are very clear and always gives a better efficiencies [16] ,the low efficiencies of using HT TiO$_2$ may attributed to a new factor related to the hydrophobic/hydrophilic properties of the semiconductor which directly affected the absorption of the dye on its surface [17,18].

CONCLUSION

The type of the anode materials play the major role in making the DSSC , a wide differences in the values of the cells efficiencies were noticed ,while the variation of the catalyst of the counter electrode play less important role. The electropolymerized polyaniline applied easily on ITO glass and the examinations revealed nanofiber structure with   a diameter around 70 nm and presents an efficient substitute for the platinum catalyzed counter electrode. TNTs grown successfully on Ti foil in electrolyte consist of 0.4wt% NH$_4$F, 3wt % H$_2$O and 87.8 wt % ethylene glycol at 60 V for 1hr., with length of about 8 micron and tube diameter around 60 nm ,the Ti/TNT serves as good anode materials in making DSSC . The hydrothermal conversion of TiO$_2$ NP to tubes like form is proceeded at 180 'C, but the new form of TiO$_2$ didn't show improvement for the efficiency of the assembled DSSC.

REFERENCES

[1] B.O'Regan and M. Gratzel, *Nature*, **1991**,353(6346): 737.
[2] K. Nithyanandam, R. Pitchumani, *Solar Energy* **2012**,86 351–368.
[3] J. Velten, Attila J Mozer, D. Li, D. Officer, G. Wallace, R. Baughman, and A. Zakhidov, *Nanotechnology* **2012**,23 085201.
[4] H. Shaaker ,H.Badran and W. Hussain, *Arch. Appl. Sci. Res*., **2012**, 4 (4):1804-1810.
[5] Ho Chang, Yu-Jen Lo, *Solar Energy* **2010**,84 ,1833–1837.
[6]M. Geetha, K. Suguna, P. M. Anbarasan, , *Arch. Phy. Res*, **2012**,3 (4):303-308
[7] H. Nusbaumer, J-E.Moser, S. Zakeeruddin, M. Nazeeruddin, and M. Gra1tzel, *J. Phys. Chem. B* **2001**,105, 10461-10464.
[8] LI Jing, SUN Ming-Xuan, Zhang Xiao-Yan, *Acta Phys. Chim. Sin*, **2011**,27 (10): 2255-2268.
[9] J. Vivekanandan,V. Ponnusamy, A. Mahudeswaran and P.Vijayanand, *Arch. Appl. Sci. Res.,* **2011**, 3 (6):147-153.
[10] M.Trchová, and J. Stejskal Polyaniline, *Pure Appl. Chem*., **2011**, 83(10),1803–1817.
[11] A-K M. Alsammarrai, Q.M. Al-Ittabi, and Y.Mohammed, Am*. J. Sci. Ind. Res.,* **2011**, 2(6): 852-859.
[12] A-K M. Alsammarrai, H.I. Jaafar and K.Abed, *Arch. Appl. Sci. Res.,* **2014**, 6 (2):115-121.
[13] M. Norani Muti, A. Dzilal, J. Dennis, *Journal of Engineering Science and Technology*., **2008**, 3(2),321.
[14] R. S. Dubey, *Arch. Appl. Sci. Res*., **2013**, 5 (5),28-32.
[15] W. Kubo,A.Sakamoto, T.Kitamura,; Y.Wada, and S. Yanagida, *J. of Photochemistry and Photobiology* A: Chemistry, **2004**,164, 33–39.
[16] Q. Li, J. Wu, , Q. Tang, Z. Lan, , P. Li, J. Lin, and L.Fan, *Electrochem. Commun*, **2008**, 10,1299- 1302.
[17] J.Akilavasan1, P.Chandrasekera, J.Bandara,International Conference on Sustainable Built Environment, Kandy ,**2010**,13-14 December,(ICSBE).
[18] K. A   Aduloju., A. T. Fatigun and T. O.Ewumi , *Arch. Appl. Sci. Res*., **2014**, 6 (2):1-4.