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Hybrid TiO_2/ZnO Nanopowder for Several Dyes-Sensitized Solar Cell

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Abstract: ***In this research, hybrid solar cells created on the basis of (TiO_2/ZnO), where the performances of two kinds of the semiconductor are similar to make paste that is applied as electrode dye molecules absorb photons of falling light rays.These solar cells have preferred an alternative to traditional photovoltaic cells that rely on dyes due to improved properties performance. The dyes solar cell usually consists of four parts: conductive glass (FTO) , an electrolyt solution, dyes and TiO_2/ZnO electrode. solar cell depends on some characteristics, including technique and preparation of paste (TiO_2/ZnO) , which is important to obtain the best efficiency and used the method of Doctor blade. We proved that mixed dyes give higher conversion efficiency than if they were alone such as ruthenium dye (Ru) has better photovoltaic properties compared to other two dyes eosin (EO) and methyl red (Mth). Photovoltaic parameters like, Overall conversion efficiency (η) of glass substrate solar cell film thickness (16 µm) with efficiency three dyes of ruthenium, eosin and meth red were found (2.11 % , 0.84 %and 0.43 %) respectively, while best efficiency (2.29%) was found when mixing the together dyes with each other 3ruthenuim dye +7methyl red dye at percentage 75 % / 25% under 40 mW/cm^2 illumination .***

Keywords: Hybrid TiO_2/ZnO electrode, Dyes mixing, DSSC

1. Introduction

The dye-sensitized solar cell (DSSC), as a potential marketing renewable energy device, has attracted great interest due to its low cost, compared with the traditional Si solar cell [1,2]. The structure of a DSSC is made of three main parts; counter electrode, photo anode and an electrolyte. Counter electrode, normally conductive glass and a fluorine- doped tin oxide (FTO) the most commonly used, coated with few atomic layers of carbon or platinum, in order to catalyse the redox reaction of (I^-/I^{3-}) reaction with the electrolyte. Photo anode is constructed from semiconductor oxide porous film on a conductive glass substrate anchored amono layer of dye. The electrolyte can be made from organic solvent containing a red-ox couple such as iodide/tri-iodide [3]. Sensitizing dye plays an important role in the absorption of the photons and generation of electron and hole pairs; the charge carriers are transferred to the photoelectrode and the electrolyte. It is well known that the number of sensitizing dye molecules adsorbed on a photoelectrode is one of the key factors in determining the short circuit current density (Jsc) and hence the efficiency in DSSCs [4]. The quality and anchoring of the dye to the surface of semiconductor oxide porous film are important processes determining the photo conversion efficiency PCE of the cell[5].The huge mesoporous surface allows for an adsorption of a sufficiently large number of dye molecules for efficient light harvesting[5,6]. The highest efficiency of DSSC was observed for cells sensitized by ruthenium complexes adsorbed on naocrystalline TiO_2, which reached 11%–12%, but they are still not suitable due to the high cost [7].

Ru (II) is the most efficient dye due to its numerous advantageous features, such as good absorption, long excited-state lifetime, and highly efficient metal-to-ligand charge transfer. Ru bipyridyl complexes are excellent photosensitizers due to the stability of the complexes' excited states and the long-term chemical stability of oxidized Ru (III) [8]. the maximum certified efficiency for DSSCs is much lower compared to silicon based solar cells. Much research has been focused on enhancing the performance of DSSC with different anode materials such as TiO_2, ZnO, SnO_2, Nb_2O_5 etc. while TiO_2 is dominated most of times [9]-[10]. Recently, ZnO, with similar band gap to that of TiO_2, appears to be an alternative material for the fabrication of high efficiency DSSCs. It possesses high environmental stability and high electron mobility, providing a direct conduction pathway for rapid collection of electrons at the substrate of the photoanode [11]-[12]. Though power conversion efficiency of solar cells based on ZnO is lower than that of TiO_2, ZnO is still regarded as a prominent competitor due to its ease of synthesis and flexibility on the nanostructure morphologies. In addition, the electron mobility of ZnO is higher than that of TiO_2, the charge recombination rate of ZnO is lower than that of TiO_2, and the electron lifetime of ZnO is longer than that of TiO_2 [13, 14]. Those characteristics are beneficial for solar cell applications. The efficiency limitation of theDSSCs is considered as a big challenge to be In commercial application widely.Various strategies are being employed to overcome such intrinsic limitation**[15]**.

2. Experimental

2.1 Materials

Titanium dioxide powder anatase (25 nm) is purchased from MK nano Canada), ZnO (50 nm)) is purchased from China , Conductive glass (Fluorine doped tin oxide, FTO, sheet resistance 7sq−1 transmission (80%) and Ethylene glycol from GCC England, acetic acid solution-from SCR-china, iodine (I_2) and potassium iodide (KI) and e (H2PtCl6) were purchased from Erftstadt Germany. And N719 stands for di-tetrabutylammoniumcisbis (isothiocyanate) bis (2,22 -bipyridyl-4,42 - dicarboxylate) ruthenium complex both supplied by [Solaronix] . A dye eosin- Y was bought from SCR-china as sensitizers and methyl red dye purchased from

Germany. Distilled water and Ethanol purchased from Fluka. multimeter is dvice used to measure short circuit current and open circuit voltage Which directly connects to electrodes solar cell. It is also used to find out conductive side of the glasses from China.

2.2 Preparation of the TiO_2/ZnO solution

First start by making the mixture TiO_2/ZnO paste with powder preparation ZnO and TiO_2 according to the following steps: (1) material TiO_2 powder and ZnO powder are weighed, (2) the mixture of w/w: TiO_2/ZnO were nanoparticles according to the following percentages : 100% TiO_2 + 0% ZnO , 75% TiO_2 + 25% ZnO , 50% TiO_2 + 50% ZnO , 25% TiO_2 + 75% ZnO, 0% TiO_2 +100% ZnO or (100/0, 75/25, 50/50, 25/75,0/100) respectively.(3) The (TiO_2 / ZnO) powder have been grinding by using mortar and pestle for 20 minut in order to prevent powder aggregation. (4) into the mixed solvent composed of 75mL of ethanol and 25mL of water, The solution was mixed until it became uniform and lump-free and Suspension is then stored and allows equilibrating for 15 minutes,then after that we follow the way doctor blade method [16]. (5) two clean FTO glass substrates were used as positive and negative electrodes with a 1 cm^2 space between the two electrode surfaces; (6) the sample film was immersion in the dyes; (7) finally, Annealing temperature above 723 K (450 ^oC) for 0.5 h, has a significant effect on the film morphology as well as more TiO_2 paste cohesion of the substrate [17].

2.3 Dye sensitization of TiO_2 / ZnO films

Dyes have a significant and significant effect on solar cells and the intensity of lighting also has a clear effect on cell performance with TiO_2 / ZnO films prepared by the above procedure on FTO glass substrates was immersed into an organic dyes , ruthenium dye N719 (5×10^{-4} M) ,eosin dye (2×10^{-4} M) methyl red dye (3×10^{-3} M) . In the case of mixing pigments left immersed for a period of 2.5 hours . The dye-coated electrodes were copiously washed with ethanol before their use in DSSC, the electrodes were left in the oven (100 ^0C) for 5 min to remove any ethanol or humidity that could be present in the pores of the films. Therefore, it is highly recommended that the prepared TiO_2 / ZnO films must be annealed at a temperature of 723 K (450 ^oC) before being immersed into the sensitizing dyes.

3. DSSC Performance

Fill factor for DSSC was calculated from equation (1). The conversion efficiency of solar cell can be calculated from the output of short circuit current and open circuit voltages according to the following relationship:

$$FF = (J_{max} \times V_{max}) / (J_{sc} \times V_{oc}) \quad ....(1)[18]$$
$$\eta = (J_{sc} \times V_{oc} \times FF) / P_{in} \times 100\% \quad ....(2)[18]$$

where Pin is the total is solar power incident on the cell. Where is the power incident light equal 40 mW /cm^2 for air mass (AM) 1.5. The fill factor (FF) is the ratio of the maximum power from the solar cell to the product of open-circuit voltage (V_{oc}) and the short-circuit current density (mA/cm^2) (J_{sc}) , Where is the current at maximum output power and voltage at maximum output power (J_{max} , V_{max}) respectively.

4. Results and Discussion

4.1. Absorption spectrum of three dyes

Figure (1) three dyes were used as sensitizers in solar cells, the most important of which is the dye of Ruthenium because it occupies a wide range of the spectrum with three absorption peaks at (350 nm, 382nm, 533 nm), Its spectrum does not exceed the limits of the red zone where the efficiency of the dye is limited. While eosin dye, it is less efficient to occupy part of the visible spectrum and have two peaks at (525nm,410 nm). The third type of methyl red dye which is the least efficient possession of only one peak at (422nm) , This means weak to absorb most of the solar spectrum.

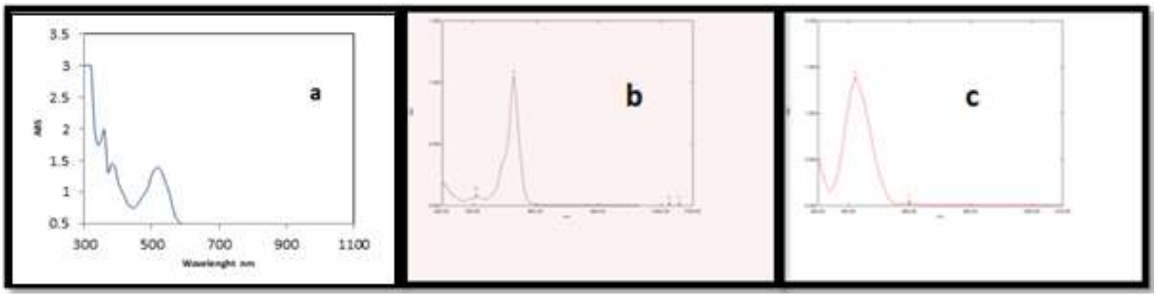

Figure (1) : Absorption spectrum for three dyes (a) Ruthenium dye (Ru) (b) Eosin dye (EO) (c) Methyl red dye (Meth)

4.3 Effect of thickness on efficiency

Film thickness layer on the electrode influences the efficiency of the solar cell because this layer absorbs the dye and thus the transition time of the electron. The higher thickness layer made on the pole the less permeability according to the Lambert Bear law as well as the dispersion of light because of the surface roughness and the aggregation particles, and may get cracks in the layer due to this increase film layer [19] .After several tests it was found that the highest efficiency was found when thickness of film (16 μm)This is within the thickness preferred [20]. As shown in fig (2).

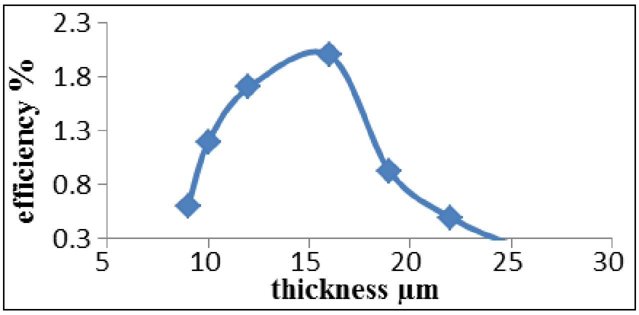

Figure 2: Thickness film vs efficiency

Figure (3) we observe increase current as the thickness layer increases until it reaches the thickness (16µm) where the current is the greatest value and the best efficiency as in the following results

I_{sc} =2 mA ,I_{max} =1.7 mA ,V_{oc} = 0.55 mV , V_{max} = o.47 mV, FF = 0.75 , η = 2 % .

After this point begins to descend due to increased thickness of the layer that leads to slow electron transmission.

4.4. Effect of thickness on the current for solar cell

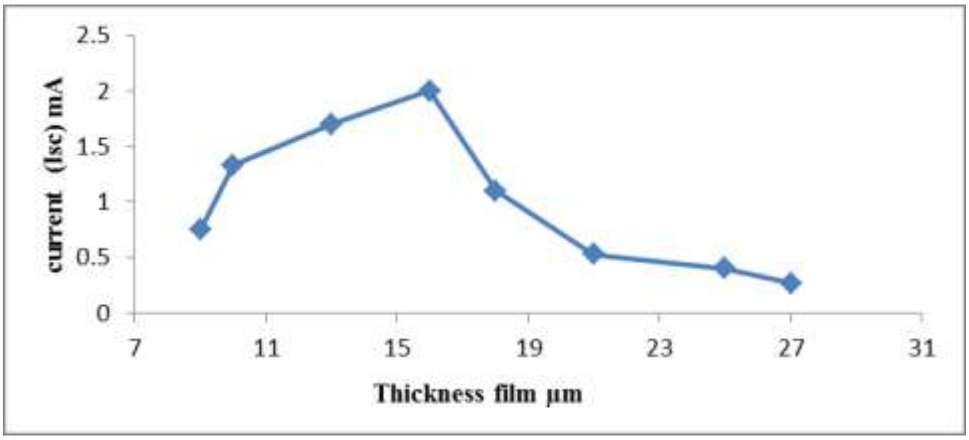

Figure 3: Effect thickness on the current

4.5. Effect of dyes on efficiency

Dyes play a major role in the work of solar cells as shown in table (1). The first model (without ZnO) is the efficiency of the second place in terms of preference dyes (Ruthenium Ru, Eosin EO, Methyl red dye Mth), while the second model efficiency is better after mixing the ratio (TiO_2 / ZnO) is (75/25) in the three dyes.Zinc oxide increased open circuit voltages, This ratio was sufficient to improve the efficiency solar cell . In the following models , Zno increase , over (25%) led to a decrease in efficiency as indicated in the table because particles size of zinc oxide is more than titanium dioxide, great molecules size lead less surface area of the dye absorption therfore , decreases efficiency and the electron transfer process is available. As shown figure (4) .

Table 1: Effect dyes on efficiency

TiO_2 / ZnO w/w	Ru dye η%	Eosin dye η%	Red dye η%
100/0	2	0.79	0.4
75/25	2.11	0.84	0.43
50/50	1.65	0.65	0.3
25/75	1.5	0.51	0.24
0/100	1.32	0.38	0.19

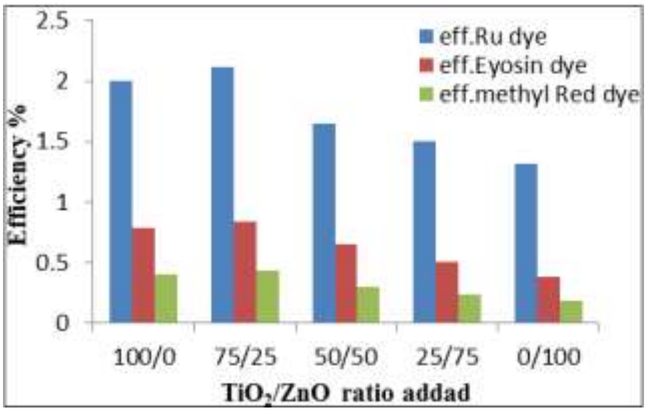

Figure 4: Effect dyes on efficiency

4.6 Effect of mixing dyes on the efficiency

T**able (2)** shows the absorption spectrum of the mixed dyes ruthenium (Ru), eosin (EO) and methyl red (Mth) with the absorbability range of 200 - 700 nm. The same method was used to determine the efficiency. When examining the absorption of the dyes after blending. I had two groups terms of number peaks because increasing the peaks means their absorption spectrum is high especially in the visible light area. First set with three peaks figure (5). From the result in Table 2, the DSSC of the combined dye mixture had improved photoelectric conversion efficiency. This is attributed to a synergistic sensitization by the dye mixture leading to higher efficiency [21]. The peak of pigments mixed in this table showed that mixed blended dyes showed different wavelengths because of the difference in their absorption and composition .

Table 2: Effect mixing dyes on efficiency

TiO_2/ ZnO (dyes ml)	100/0 (eff%)	75/25 (eff%)	50/50 (eff%)	25/75 (eff%)	0/100 (eff%)
1)5Ru+1EO+4Mth.red	2.15	2.25	1.88	1.72	1.5
2)3Ru+7Mth.red	2.21	2.29	2	1.7	1.6
3)1Ru+9Mth.red	2.17	2.2	1.9	1.62	1.5
4)4Ru+5EO+1Mth.red	2.13	2	1.85	1.65	1.42
9)8Ru+2Mth.red	1.8	1.87	1.62	1.46	1.26
10)2Ru+2EO+6Mth.red	1.7	1.9	1.4	1.25	1.16
11)6Ru+4EO	2.2	2.27	2.13	2	1.44
12)7Ru+2EO+1Mth.red	1.8	1.96	1.5	1.37	1.2
13)2Ru+5EO+3Mth.red	1.4	1.52	1.15	1.1	0.9
14)8Ru+2EO	1.3	1.6	1.14	1	0.84

Figure (5) we observe the best model for mixture of dyes are models (2,11,1) respectively with the best efficiency (2.29%, 2.27% , 2.25%) respectively for having three peaks (305nm, 389 nm ,492 nm), (299 nm , 397 nm , 519 nm) ,(300 nm, 385 nm, 513 nm) respectively.

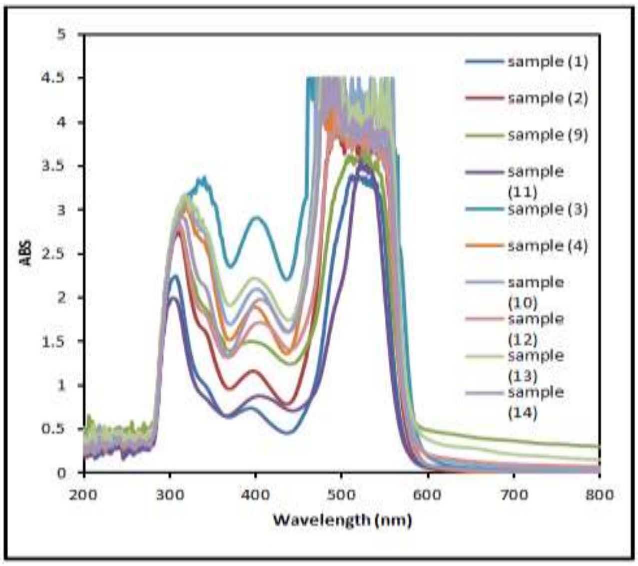

Figure 5: Absorption mixture dyes

Second group table (3), which has two peaks, means the amount of absorption of the solar spectrum less than the first group. Under conditions illumination intensity has stronger influence on the performance of cell with TiO_2- ZnO nanoparticles when volum (75/25). Under the illumination intensity of 40 mW/ cm^2, Where efficiency is shown in the following figure (6) .

Table 3: Effect mixing dyes on efficiency

TiO_2/ ZnO (dyes ml)	100/0 (eff%)	75/25 (eff%)	50/50 (eff%)	25/75 (eff%)	0/100 (eff%)
5)1Ru+9EO	2.1	2.15	1.63	1.44	1.21
6)6Ru+4Mth.red	2	2.5	1.8	1.6	1.4
7)2Ru+2EO+6Mth.red	1.91	2.10	1.75	1.61	1.5
8)1Ru+3EO+6Mth.red	1.85	1.93	1.53	1.42	1.21

In Figure (6) the best model for mixxing dyes was observed (model 6,5) because they contain more ruthenium in the second group, the best efficiency (2.5%,2.15%) for having two peaks (290 nm ,411nm), (294nm , 393nm) respectively.

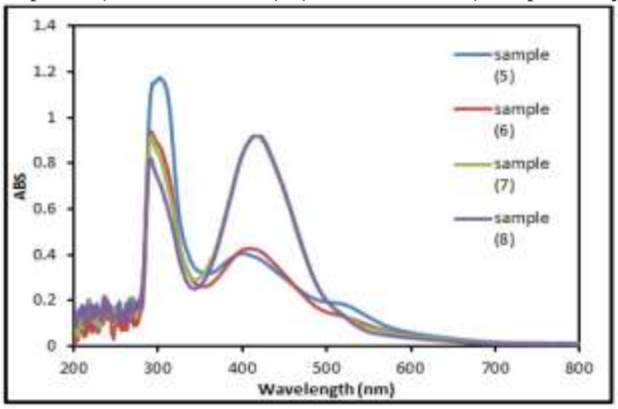

Figure 6: Absorption spectrum for mixing dyes

4.7. Surface morphology of TiO_2/ ZnO paste film using (AFM) and Scanning probe microscope (spm)

Table (4) the results extracted from samples (a,b,c,d,e) worked in the manner of a doctor bled these films are usually sintered at relatively high temperature; 450°C for different mixing percentages of zinc oxide with titanium dioxide . With increasing surface area, the value of root mean squer (R.m.s) increases due to lower particle size and increased surface roughness. This increases the absorbability of the dye and thus increases efficiency as in the first mode. The variations of roughness with prepared samples were shown in Table (4) .

Table 4: effect mixing dyes on efficiency

TiO_2/ZnO W/W	Avr.Diameter nm	R.m.s nm	Surface . Avr Ratio	Roughness Avr(nm)
100/0	44.35	12.5	34.7	10.5
0/100	67.25	1.17	0.632	1.46
25/75	56.47	0.993	0.0999	0.86
50/50	45.53	1.12	0.27	0.948
75/25	75.57	1.25	0.253	1.07

In order to evaluate the surface roughness and morphologies of the optimized samples for each group, atomic force microscopy technique has been used. Figures (7, 8) show the (2D) image and the histogram of the sample (a,b) respectively. Figure (7) show that the film has got large value of (Rms) (12.5nm) and with an average diameter of 44.35 nm . The image clarified that the surface of this film was homogenous nanostructured and the particles are uniformly distributed with crack free, than that (b) sample; it is equal to (1.17nm) and with an average diameter of 67.25 nm . It can be seen the TiO_2 / ZnO particles are stuck together forming a large cluster. The result indicates that this sample (a) has got a larger photocatalytic activity than sample (b).

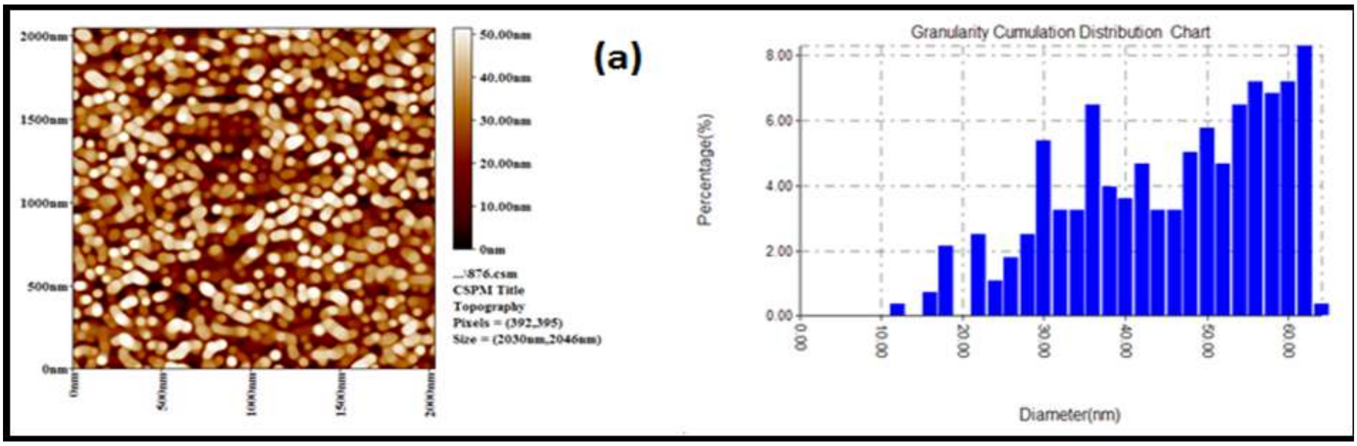

Figure 7: (2D) image and histogram of TiO_2 / ZnO (100/0 %)

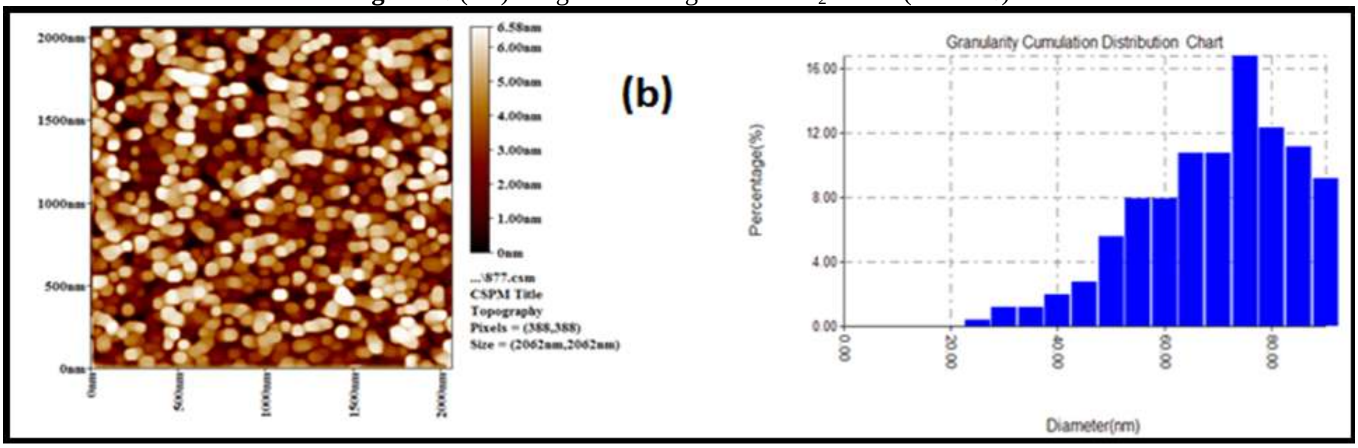

Figure 8: (2D) image and histogram of TiO_2 / ZnO (0% /100 %)

Figures (9,10,11) shows the (2D) image and the histogram of (TiO_2 / ZnO) composite samples. Film (e) becomes more efficiency than (c,d) films because the addition of (ZnO) changes the surface area of the (TiO_2) nanoparticles in the composite paste. It is believed that the (ZnO) nanoparticles increase current open circuit. The film (c) has got a very small roughness (Rms = 0.99nm), Therefore this sample will show a very low photocatalytic activity. Aggregates generate (TiO_2 / ZnO) an effective light scattering and thus significantly increasing traveling distance of the light within the photoelectrode film.

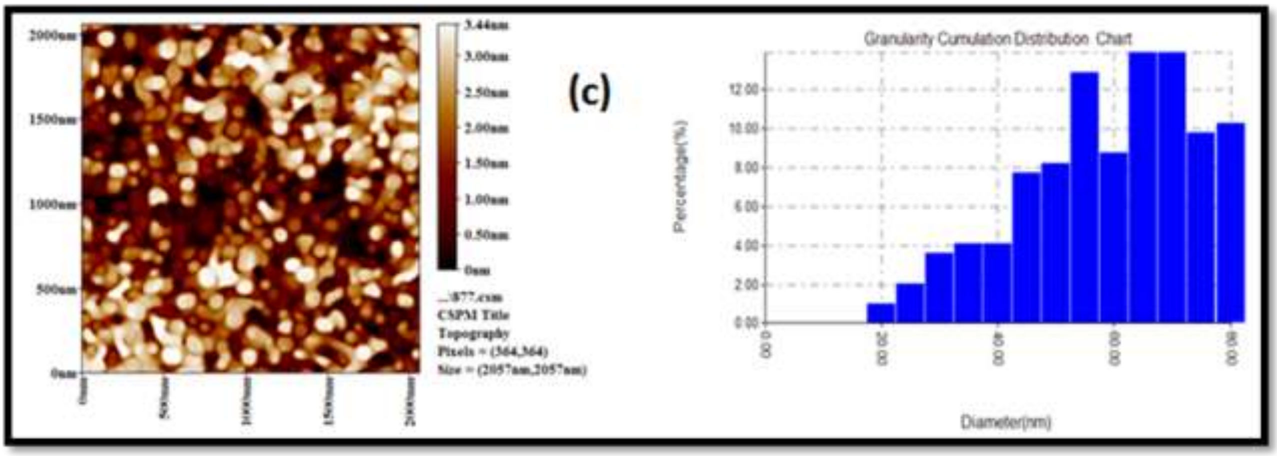

Figure 9: (2D) image and histogram of TiO_2 / ZnO (25 % /75 %)

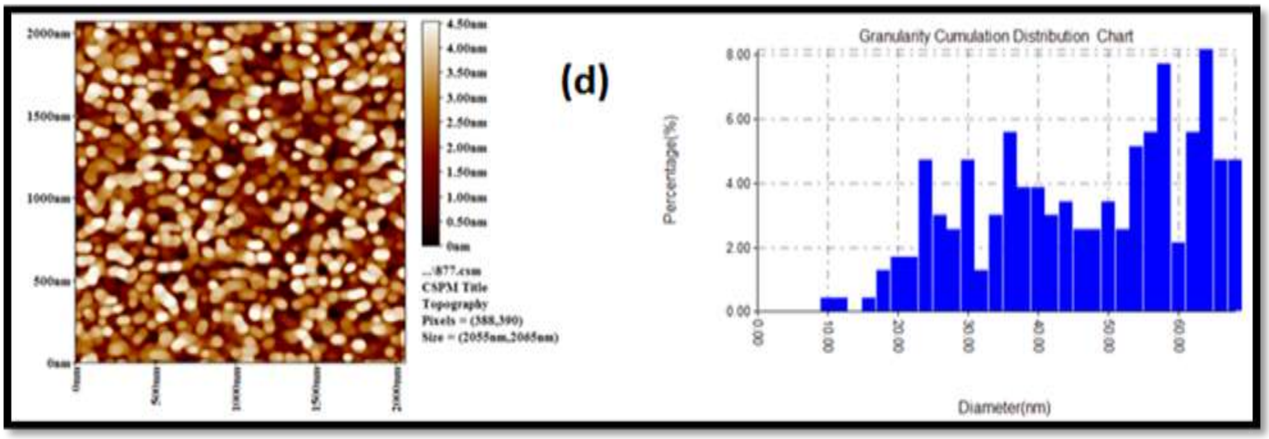

Figure 10: (2D) image and histogram of TiO_2 / ZnO (50 % /50 %)

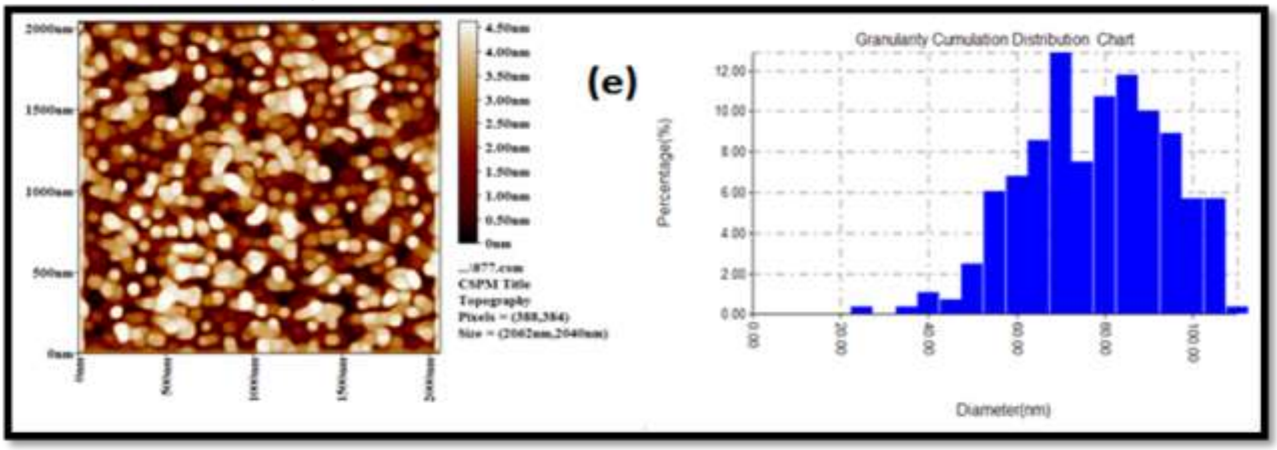

Figure 11: (2D) image and histogram of TiO_2 / ZnO (75 % /25 %)

5. Conclusion

Hybrid TiO_2 / ZnO photo- anodes were prepared using doctor bled method , Our results reveal that at an optimal thickness16µm . Photovoltaic performance of cell with ZnO-TiO_2 nanoparticles is superior to that of cell with pure ZnO or pure TiO_2 nanoparticles. The illumination intensity has stronger influence on the performance of cell with ZnO-TiO_2 nanoparticles. Under the illumination intensity of 40 mW cm-2. The best efficiency of solar cell with TiO_2- ZnO equal 75% /25% nanoparticles is 2.29 % , while 1.32 % and 2 % in case of cell with TiO_2 and ZnO, respectively. We conclude that the mixed dye has a higher conversion efficiency than the dye, which is on its own. So they provide higher efficiency than dye on their own. The mixed dye has higher conversion efficiency than dyes prepared by either ruthenium dye , eosin dye or methyl red dye. Therefore, the mixed dye in this study provides a more efficient incident photon-to-electron conversion. From table (4) increase titanium doxide leads to increasing of the roughness situation. There is not much difference in the microstructures except that .agglomeration has increased in the film sintered at 450^0C which has led to degradation in the performance of DSSC as obvious from the electrical studies due to increased particle size.

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