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Influence of grain size, electrode type and additives on dye sensitized solar cells efficiency

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ABSTRACT

In the present work; there are some parameters affected the dye sensitized solar cell efficiency such as: different grain size of TiO_2 nanopowder paste on two types of electrodes, glass and polymer, in addition to some additives added. The optimum thickness utilized for TiO_2 paste is (15μm) on a conductive glass, (rigid electrode), which is coated with fluorine doped tin oxide (FTO). The best efficiency achieved with grain size (10nm) of TiO_2 is (1.95%). While the thickness is (12μm) spread over a polyethylene terephthalate (PET) plastic, (flexible electrode), film coated with indium tin oxide (ITO). The best efficiency achieved is (1.62%). Microwave heating operating at a frequency (2450 MHz) and (1.15 Kw), were applied for drying the TiO_2 polymer electrodes paste whereas, a furnace at (450 ºC) was utilized for glass electrode. Several additives were tested and, the best additive chosen which gives the best efficiency was Copper (II) nitrate.

Three particle sizes of TiO_2, (10nm, 38nm and 50nm) were considered and, the best efficiency achieved was with TiO_2 (10nm). All the tests were done under illumination of (40 mW/cm^2) mercury lamp.

KEYWORDS

DSSC;
Flexible DSSC;
Additives;
TiO_2 grain size;
FTO and PET.

INTRODUCTION

During the last few decades, there have been intensive research activities to explore green sources of energy. An alternative solar cell technology is the dye sensitized solar cell (DSSC) also known as "Grätzel cell", which is characterized as light-weight, portable, inexpensive, and transparent relative to conventional solid state solar cells.

A major component of (DSSC) is nanocrystalline TiO_2 deposited as a film on conductive glass electrodes. So far, these films are usually sintered at relatively high temperature; 450ºC. However, a considerable effort has been made recently to obtain TiO_2 films on flexible (plastic) electrodes, since this will increase the range of (DSSC) applications. Therefore, it is necessary to develop procedures of low-temperature TiO_2 deposition so as to protect the plastic substrate. The structure of a (DSSC) is made of three main parts; counter electrode, photo anode and an electrolyte[1]. Plastic (DSSCs) based on

the substrates of indium tin oxide (ITO) coated polyethylene-terephthalate (PET), or polyethylene-naphthalate (PEN) instead of a rigid glass substrate, are regarded as possible breakthrough in the field of (DSSC) in terms of commercialization since plastic (DSSCs) have advantages of low cost production and wide applications. Large scale roll-to-roll printing process can be applied to fabricate a plastic substrate (DSSC), making its commercialization more viable[2].

Number of methods has been done concerned with the preparation of nanoporous TiO_2 films at low temperature. These methods were; low temperature heating, compression, microwave irradiation, electron-beam annealing, chemical-vapor deposition with UV irradiation, and hydrothermal crystallization[3,4]. A photoplatinization technique was proposed on a thin TiO_2 layer modified (ITO/PEN) substrate at low temperature (about 50°C after 1 hr. of UV irradiation) for the first time[5]. By replacing the glass substrates with flexible plastics, mesoporous TiO_2 films have to be prepared at low temperature and also with nanocrystalline dimensions for better efficiency to energy conversion[6]. One of the problems with plastic substrate (DSSCs) is that, they have lower efficiency than that of glass substrate. The plastic substrates have thermal instability at high temperature (450–550)^{0}C which is required for sintering of TiO_2 photo electrodes of DSSC[7]. The transparent conductive oxide (TCO) at the counter electrode is coated with few atomic layers of carbon or platinum in order to catalyze the redox reaction with the electrolyte[8].

The DSSCs effecinicies are thickness limited, typical film thicknesses are 5–20 μm, with TiO_2 mass 1–4 mg cm^{-2},

It is essintily known that, the position of the CB in the TiO_2 depends strongly on the surface charges as well as the adsorbed dipolar molecules. These additives in the electrolytes are expected to be adsorbed onto the TiO2 surface, thus affecting the CB in the TiO2 strongly associated with the photocurrent and photovoltage. Therefore, the introductions of additives into the liquid electrolytes have been effective strategies to enhance the photovoltaic performances of DSSC [62]. The difference is that the function of electric additive for optimizing the photovoltaic performance of DSSCs is more efficient than that of the donor number of solvent[9].

EXPERIMENTAL

Materials

Anatase titanium dioxide powders (10nm) and (50nm) were purchased from (MK nano, Canada). Conductive glass, fluorine doped tin oxide (FTO), with sheet resistance (7 Ω/cm^2), and Indium Tin Oxide / polyethylene-terephthalate (PET/ITO) with sheet resistance (60 Ω/sq) were supplied from (Solaronix S.A, Switzerland). Ethylene glycol was purchased from (Sigma-Aldrich). Acetic acid solution from (SCR, China), Iodine (I_2) and Potassium Iodide (KI) were purchased from (Erftstadt, Germany). Nitric Acid (HNO_3), purity 65%, supplied from (Merck Co.). Dye [Ruthenium (RU) (N719)] was purchased from (Solaronix S.A., Aubonne, Switzerland) which is used as a sensitizer. Ethanol was purchased from (Fluka Co.). Titanium tetraisopropoxide (TTIP), $Ti[OCH(CH_3)_2]_4$, purity 97% was purchased from (Sigma-Aldrich Co.).

Procedure

The synthesis procedure for nano TiO_2 sol is as follows: Titanium tetraisopropoxide (TTIP) was mixed with ethanol then distilled water was added drop wise under vigorous stirring for one hour. This solution was peptized using nitric acid and refluxed at (80ºC) for (8 hours). After this period, the TiO_2 sol had been prepared. The nonporous TiO_2 films were dye-sensitized by soaking the films for (5.5 hrs.) in a dye solution of ruthenium (II) (N719) suspended in ethanol. TiO_2 (10nm and 50nm) powders have been grinding by using mortar and pestle for (20 minutes) in order to reduce powder aggregation.

Suspensions of TiO_2 powders were prepared as follows:

Adding drops of nitric acid solution to (6ml) of distilled water until the solution becomes acidic with pH (3-4). This solution is added to (6 gm) of colloidal TiO_2 powder, then a drop of transparent surfactant was added to ensure coating uniformity, adhesion to electrodes, and to avoid cracking of the deposited film. Finally, we follow doctor blade method for coating TiO_2.

Dye sensitization of TiO_2 films

The TiO_2 films prepared by the above procedure on (FTO) glass or (ITO-PET) plastic substrates were

immersed into an ($5x10^{-4}$) [M] ethanol solution of [Ru (N719)] dye and were kept there for (5.5) hours. The dye coated electrodes were carefully washed with ethanol.

The electrodes were left in the oven at (50^0C) for (1hour), before use them in DSSC, to remove any ethanol or humidity that could be exist in the pores of the films. Finally, the electrodes were dried through two categories; the glass electrode using 450°C hot plate device, whereas the plastic electrode drying was achieved using 1.15 Kw, 2450 MHz microwave oven.

RESULTS AND DISCUSSION

The TiO_2 sol prepared by the above procedure was coated on both electrodes and then tested by XRD which shows that its grain size was (38nm).

AFM test

Analysis of AFM images confirmed that the root mean square (Rms) values for the TiO2 films (10nm), (38nm) and (50nm) are (11.2nm, 3.6nm, and 1.15nm) respectively as shown in Figure (1). The highest value of (Rms) associated with the lowest TiO_2 grain size, since the surface area was increased with the increasing of (Rms) value as a result of reduction in the grain size, yielding enhancement of the dye adsorption capacity on TiO_2 and hence, enhancing the solar cell efficiency.

Absorption spectrum of ruthenium (N719) dye

The ruthenium dye has an intense absorption band at (355 and 385) nm. Both of them are in the UV region of solar spectrum. The interested absorption peak of (N719) dye is at (535 nm) because of its big matching with the solar spectrum. The ruthenium (N719) dye has absorption spectrum extends only to (700nm); so that it has nearly no absorption band in the infrared region which causes limited solar cell efficiency[1].

Influence of thickness on efficiency

The DSSC performance largely depends on the thickness of TiO_2 film because changing the film thickness will change the amount of dye adsorbed on TiO_2. Increasing the thickness of the film leads to reduce transparency and hence reduce light harvesting. The optimum thickness adopted in glass electrode was (15μm), while for the polymer electrode was (12 μm)

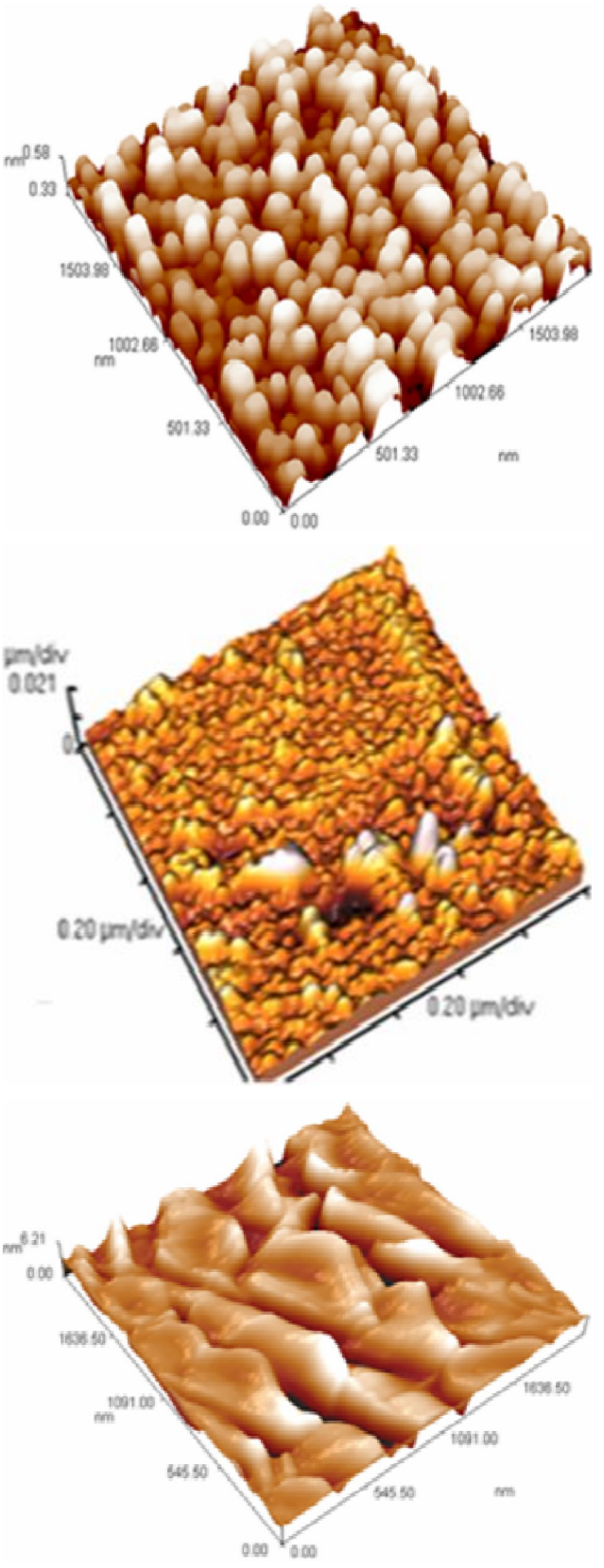

Figure 1 : AFM images for: a) TiO_2 (10 nm) after annealing at 450°C b) TiO_2 (38 nm) after annealing at 450°C c) TiO_2 (50 nm) after annealing at 450°C

which gives best efficiency as shown in Figure 2.

Influence of additive on efficiency

Additives play an important role to enhance the photovoltaic parameters in liquid electrolyte-based DSSC. It has been found that the photovoltaic performance of DSSC can be enhanced substantially by adding a small amount of different additives[1]. The enhancement in both current and voltage is due to the increasing in electron transfer speed, since adding Copper (II) nitrate will increase the electrical conductivity of the electrolyte. TABLE 1 shows the effect of added additive solar cell for both plastic and glass using TiO_2 (10nm, 38nm and 50 nm).

Copper nitrate Cu $(NO_3)_2$ as a new electric additive for enhancing photovoltaic performance of dye-sensitized solar cell (DSSC) was studied. It showed high efficiency for enhancing both open-circuit voltage and short-circuit current density of DSSC when the suitable amount of $Cu(NO_3)_2$, 0.002 (g/10ml), was added in liquid electrolyte.

The energy conversion efficiency of DSSC increased from 1.6% to 1.8% for flexible type of solar cells, while the glass conductive type efficiency of DSSC increased from 1.95% to 2.3%. Therefore, it is considered as highly efficient electric additive for DSSC. The essential reason is owing to the special molecular structure of Copper nitrate, which contains two different polarity groups. As a surfactant, Cu $(NO_3)_2$ could form ordered arrangement in liquid electrolyte, which affects the diffusing ability and the redox reaction of (I^-/I_3^-), and further affects the photovoltaic performance of DSSC.

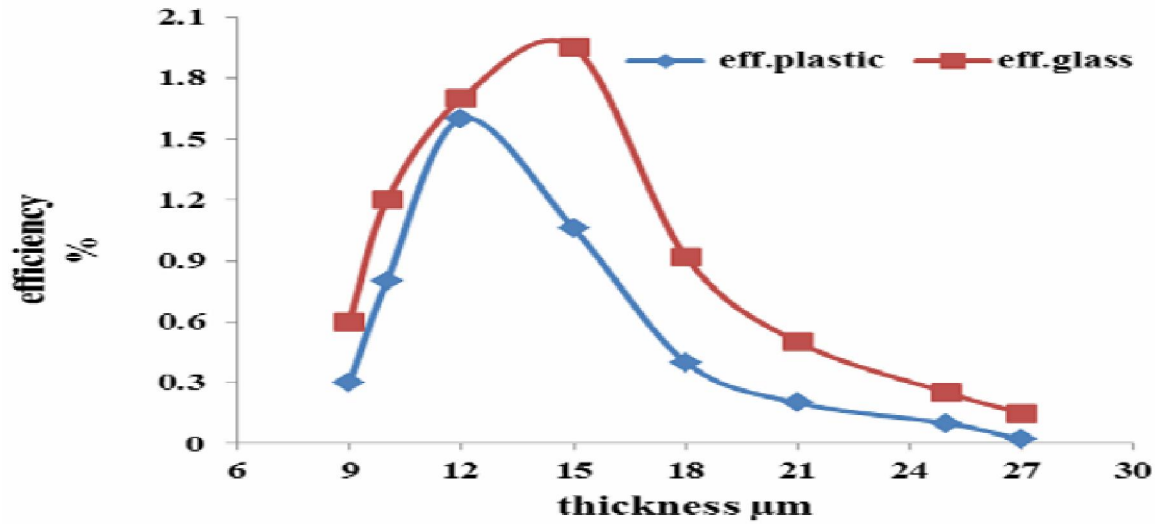

Figure 2 : Glass and plastic thickness film vs. efficiency

TABLE 1 : Solar cells film with and without additive of Cu $(NO_3)_2$

Type TiO_2 nm	PLASTIC CELLS 12µm				GLASS CELLS 15µm			
	I_{sc}	V_{oc}	FF%	η%	I_{sc}	V_{oc}	%FF	η%
10 nm (before Additive)	1.6	0.52	76	1.62	1.7	0.51	90	1.95
After Additive	1.8	0.55	74	1.8	2	0.57	80	2.3
38nm (before Additive)	1.4	0.52	64	1.16	1.6	0.55	73	1.6
After Additive	1.3	0.48	79	1.23	1.62	0.53	78	1.67
50nm (before Additive)	1.2	0.45	74	0.99	1.45	0.55	73	1.45
After Additive	1.3	0.51	68	1.13	1.49	0.55	77	1.58

Influence of additive concentration on efficiency

In order to study the additive concentration on the performance for both glass and plastic DSSC, Copper (II) nitrate at fixed concentration of (0.002 g/10ml) was selected. The efficiency for glass solar cell was (1.95%), and then improved to (2.3%), while the efficiency for plastic solar cell was (1.6%), and then improved to (1.8%), so it is better than the rest additives selected as shown in Figure 3.

The results summarized in TABLE 2 showed that the efficiency increased as the concentration gradually increased till (0.002 g/10ml). After that, any increase in the concentration causes a decrease in efficiency.

Influence of additive type on efficiency

Several metallic additives were tested in this work such as Cu $(NO_3)_2$, $AlCl_3$, $CO(NO_3)_2$, $CaSO_4$, Ni $(NO_3)_2$, CuI, $(NH_3)_2Cr_2O_7$, NaBr and Nacl. The final efficiency of Ruthenium (N719) dye cells after the addition of the above materials are listed in TABLE 3. The additives showed almost fixed voltage while the value of the current varies depending on the kind of the additive. It has been generally observed a distinct group of single additives is used to enhance the performance of electrolytes.

Influence of grain size on DSSC efficiency

We have obtained a better efficiency in TiO_2 (10nm)

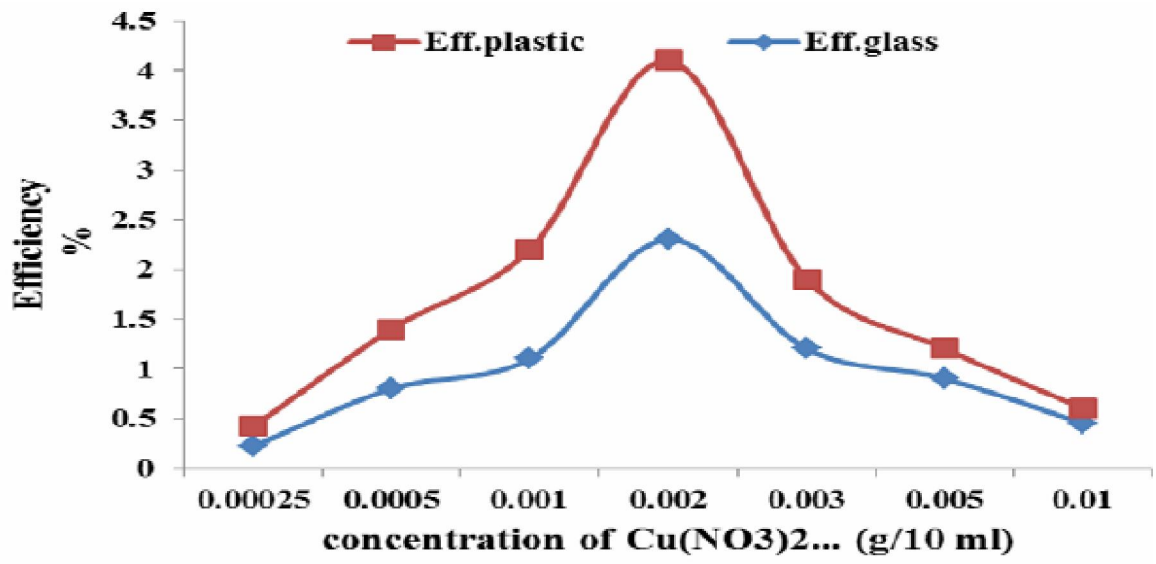

Figure 3 : Additive concentration of Cu (NO3)2 on officiency

TABLE 2 : Influence of additive concentration on efficiency

Additive Concentration g/10ml	PLASTIC CELLS				GLASS CELLS			
	I_{sc}	V_{oc}	FF%	η%	I_{sc}	V_{oc}	FF%	η%
0.00025	0.43	0.3	55	0. 2	0.5	0.4	45	0.22
0.0005	0.92	0.4	62	0.6	1	0.6	53	0.8
0.001	1.2	0.5	72	1.1	1.5	0.45	63	1.1
0.002	1.8	0.55	74	1.8	2	0.57	80	2.3
0.003	1	0.4	66	0.7	1.3	0.45	82	1.2
0.005	0.6	0.4	48	0.3	1.3	0.5	55	0.9
0.01	0.51	0.31	38	0.15	0.6	0.5	90	0.45

TABLE 3 : Ruthenium and type additive

Ruthenium and type additive (0.002 g/10ml)	For plastic solar cells			For glass solar cells		
	I_{sc}	V_{oc}	η%	I_{sc}	V_{OC}	η%
Without additive	1.6	0.52	1.6	1.7	0.51	1.95
$Cu(NO_3)_2$	1.8	0.55	1.8	2	0.57	2.3
$ALCl_3$	1.5	0.55	1.63	1.8	0.55	1.98
$CO(NO_3)_2$	2.2	0.52	1.7	3.5	0.5	1.9
$CaSO_4$	0.24	0.33	0.05	0.4	0.4	0.15
$Ni(NO_3)_2$	1.2	0.4	0.9	1.4	0.4	1.05
CuI	1.3	0.52	1.2	1.6	0.55	1.56
$(NH_3)_2Cr_2O_7$	1.1	0.4	0.8	1.3	0.68	1.1
NaBr	0.4	0.47	0.19	0.6	0.5	0.4
Nacl	1	0.4	0.56	1.2	0.5	9 .0

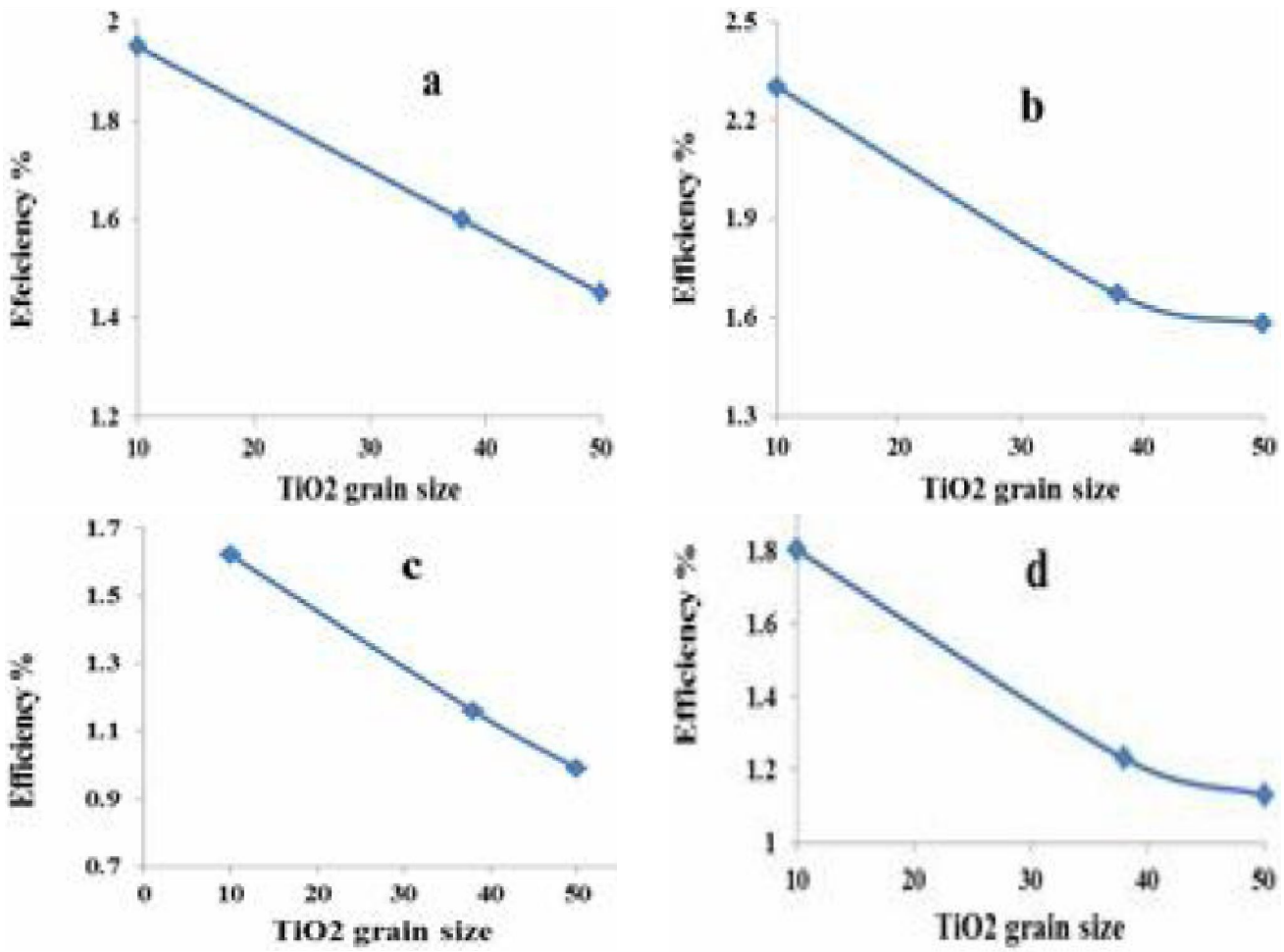

Figure 4 : a) glass solar cell (before additives). (b) glass solar cell (after additives) (c) plastic solar cell (before additives). (d) plastic solar cell (after additives)

due to the smaller grain size which is (1.95%) for glass cell and (1.6%) for plastic cell, while in case of using TiO_2 (38nm), the efficiencies are (1.6% and 1.14%) respectively. Whereas in case of using TiO_2 (50nm), the efficiencies are (1.45% and 0.99%) respectively as shown in Figure 4.

CONCLUSIONS

There are several parameters affected the performance and efficiency of a DSSC such as the thickness, additives and grain size in both types of electrodes, glass and polymer. The electrode thickness should be within an optimum value for keeping the desired efficiency. With and without additives, the flexible dye-sensitized solar cells (PET/TiO_2) demonstrate less efficiencies compared with (FTO/TiO_2). Titanium dioxide particle size plays significant role in controlling the efficiency value.

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