Effect of particle size of TiO$_2$ and additive materials to improve dye sensitized solar cells efficiency

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Abstract. It became a great interest Dye-sensitized solar cells (DSSC) as a successful alternative to silicon solar cells in terms of cost and simplicity. These cells rely on a semi-conductive material of electricity TiO$_2$ nanocrystalline which encapsulates glass electrodes from the connected side at a temperature 450$^\circ$C. In this work, the effect of nanoparticle size shows the size of atoms. The smaller the size of the atoms, the greater the surface area and thus the sufficient absorption of the dye and the stimulation of electrons, where increasing surface area increases efficiency. Then a limited amount was added and at a certain concentration, which led to a reasonable improvement in efficiency. According to this procedure commercially available TiO$_2$ (10 nm, 25 nm, 33 nm, 50 nm) standard. A TiO$_2$ paste was prepared by mixing commercial TiO$_2$, ethanol, distilled water, F:SnO$_2$ (FTO film thickness 14 µm) conductive glasses. By using Dr. Blade method we got films with appropriate thicknesses, then by using several particle sizes (10 nm, 25 nm, 33 nm, 50 nm), many efficiencies were founded (2.39 %, 2.1 %, 1.85 %, 1.65%) respectively. Improved solar cell efficiency after addition of several chemical materials and the best that got is Cu (NO$_3$)$_2$. Efficiency became for (10 nm) (2.61 %, 2.34 %, 2.1 %, 1.85%) respectively under 40 mW/cm$^2$.

Keywords: DSSC, TiO$_2$, Efficiency, particle size, film thickness, additive.

1. Introduction

Titanium dioxide semi-conductive material future expected due to its high photochemical stability, low production and cost. Titanium nanoparticles are small and very accurate to increase surface area. This material is promising in many applications such as dyes, adsorbents and catalytic support [1-3]. In all cases, when the particle size of the surface is very small in nanometer so that the ratio of surface to size is large, Some new optical properties can be expected [4]. Dye solar cells convert visible light into electricity. Their work is based on wide band gap semiconductors. a solar cell (DSSC) is composed of two electrical poles connected to one side the first pole is covered with a layer of TiO$_2$ called anode electrode. The second pole is covered with platinum or carbon called this cathode pole. In addition to An electrolyte solution consisting of (redox couple like iodide/tri-iodide). When Solar radiation falls on DSSC many electrons present in the layer of the earth are excited. They are injected into the conduction band of TiO$_2$ porous film. Then transfer them to glass through layer TiO$_2$ [5]. The TiO$_2$ films prepared...
on Fluorine doped tin oxide glass annealing temperature 723 K (450°C), the immersion time may be the uniquely influential factor to be analyzed at this stage since it is related to the dye concentration Ru (N719) 5x10⁻⁴ M. Films that were immersed for 5.5 h yielded the highest efficiency, this gets in the first electrode [6]. The electrolyte solution has an important role in obtaining high efficiency of adding suitable chemicals, its usefulness to enhance open circuit. As a result, increase efficiency (\(\eta\)) in DSSC [7]. Found highest value efficiency of ruthenium with a base TiO₂ film reached 11%–12%, but became undesirable because of its high cost[8]. Electrical additives are very important when adding a specific amount of electrolyte solution to improve and enhance performance solar cell. Increase or decrease specified amount leads to deterioration solar cell and low efficiency solar cell [9]. In this work, different sizes atoms TiO₂ nanopowder were used to demonstrate the effect of particle size on cell efficiency. The smaller TiO₂ volume, greater the surface area, and more efficient the result. The spectrometry of the Ruthenium dye on spectral range from 300 to 800 nm, the morphology of TiO₂ paste films, The photovoltaic parameters of the fabricated cells were determined. Enhances solar cell efficiency with electrical additives.

2. Materials
The following materials were used Iodine (I₂) and Potassium Iodide (KI) were purchased from (Erfstadt, Germany). ethanol, acetonitrile and Ethylene glycol from Aldrich, acetic acid solution-from SCR-China, FTO (7 Ohm/sq) transmission(80%) and ruthenium dye (N719) both supplied by a company [Solaronix] from Switzerland. TiO₂ nanocrystalline (anatase 10,25 nm) purity (99.9%) supplied [MK nano. Canada]. TiO₂ nanocrystalline (anatase 33, 50 nm) purity (97%) was supplied by [China]. Cu (NO₃)₂ and AlCl₃ supplied from (G.P.R.- England). Solar power Meter (TES-1333 Digital Radiation Detector-China). Digital device for measuring voltages and current - China and distilled water.

2.1. Preparation of the TiO₂-water paste
The composition of TiO₂ paste could affect the homogeneity and aggregates concentration of the TiO₂ electrode as well. Contents of acetic acid and water in TiO₂ pastes significantly decreased aggregation of nanoparticles of DSSC [10]. Prepare a paste TiO₂ in the following way, so that mixing solution becomes acidic powder and a hydrogen number (\(\text{pH} = 3\)). We add several drops of nitric acid to (6ml) from the deionized water, then add above to (6g) of nanoparticles TiO₂ nanoparticles. According to Dr. Blade's method[11].

2.2. Doctor blade Technique
used a special adhesive tape from three sides thick 10 μm. We place drops of dough prepared on side glass connector. Pull rod glass and move it slowly and with regular movement to film thickness as regular as the tape separator. The limitation of this technique is difficult to find an appropriate spacing material with a thickness of 1-7μm [12].

2.3. Collecting the Cell
We collect the first face of film TiO₂ with the second face covered with carbon coated surface face to face in the form of a sandwich (Cathode and anode). We put at least two drops of electrolyte solution to be spread in all parts film TiO₂. sealed by using a Surlyn thermoplastic frame (to prevent leakage of the electrolyte solution). The complete cell was then taken to sunlight for harvesting energy.

2.4. Cell efficiency
Dye-sensitized solar cell efficiency it is the ratio of electrical output at power point and the power of incident radiation (\(P_{\text{in}}\)). The solar energy-to-electricity conversion efficiency (\(\eta\)) was determined by the
equation (1), after calculating the following parameters open-circuit voltage $V_{oc}$, short-circuit current density $J_{sc}$ and fill factor FF.[13]

$$\text{FF} = \frac{I_{max} \times V_{max}}{I_{sc} \times V_{oc}}$$

(1)

$$\eta = \frac{FF \times J_{sc} \times V_{oc}}{P_{in}}$$

(2)

3. Results and discussion

3.1. Absorption dye

In figure (1), three absorption regions (330, 360 and 380) nm were observed in the ultraviolet region of the solar spectrum. Ruthenium dye concentration (5x10$^{-4}$M). Highest peak absorption found in the visible region of the solar spectrum (510 nm), so solar cell efficiency was limited.

![Absorption spectrum N719 dye](image)

**Figure (1)** Absorption spectrum N719 dye

3.2. Effect of thickness on efficiency

Thickness and homogenization film is an important factor in solar cell performance. Film thickness at certain values is important for increasing efficiency. Electrons are close to the surface, interaction is rapid. The temperature used for depositing film 450 °C under lighting 40 mW/cm$^2$ illumination, because it is compatible with the highest light response and no scratches and cracks. The best efficiency obtained in this work is 2.39% cell with a TiO$_2$ film thickness of 14μm. As in figure(2).

![Effect of thickness on efficiency](image)

**Figure (2)** effect of thickness on efficiency
3.3. Effect Particle Size on efficiency

The volume of an atom is a very important factor in solar cell efficiency, where reducing of particle size to a certain extent that process of recombination more and near to surface, the process is faster. For this reason, the catalytic activity of nanomaterial has increased with reduced particle size, increasing efficiency because reactions occur on the surface so the surface energy becomes more dominant in the process and the distance is short to surface for the desired reaction. Figure (3) shows the effect of particle size on efficiency.

![Figure 3](image_url)

**Figure (3) Effect Particle Size on efficiency**

3.4. Influence Current density with and without additive on efficiency

Addition some materials to electrolyte solution led to improve efficiency, including copper nitrate 0.002 (g/10ml) figure (4), this addition increase the electron transfer speed and thus improving of the electrical conductivity. As in table (1) that shows short circuit current is increase after additive (1.98 mA/cm²).

| grain size TiO₂ µm | Without additive | With additive Cu(NO₃)₂ |
|-------------------|------------------|-----------------------|
|                   | l_sc V_oc %FF η  | l_sc V_oc %FF η       |
| 10                | 1.95 0.55 89 2.39 | 1.98 0.62 85 2.61     |
| 25                | 1.83 0.55 83 2.1  | 2 0.57 82 2.34        |
| 33                | 1.8 0.54 76 1.85  | 1.83 0.55 83 2.1      |
| 50                | 1.6 0.55 75 1.65  | 1.8 0.54 76 1.85      |
Influence Current density with particle size

3.5. Effect adding concentration on efficiency

To get a good efficiency at best concentration, it is necessary to choose an appropriate concentration of the chemical additive Cu(NO$_3$)$_2$. After the work of several samples with different concentrations, concentration (0.002g/10ml) was selected as shown in Table (2). Where efficiency solar cell before adding (2.39%) became after adding Cu(NO$_3$)$_2$ (2.61%), It is the best efficiency for best concentration. It mean more concentration than (0.002 g/10ml) led to less efficiency as illustrated in figure(5).

Table (2) additive concentration with efficiency

| Concentration Type additive. g/10ml | GLASS CELLS |
|-----------------------------------|-------------|
|                                   | Isc Voc %FF % $\eta$ |
| 0.00025                           | 1.1 0.4 49 0.5 |
| 0.0005                            | 1.3 0.65 60 1.3 |
| 0.001                             | 1.9 0.55 83 2.17 |
| 0.002                             | 1.98 0.62 85 2.61 |
| 0.003                             | 1.7 0.51 85 1.72 |
| 0.005                             | 1 0.5 63 0.79 |
| 0.01                              | 0.49 0.52 60 0.38 |
4. AFM investigation

Optical properties of the layer were identified TiO₂ size (10 nm) deposited on surface glass and most important root mean square (Rms) and histogram, after treatment thermally degree (450°C) as shown in figure (6) which refers to lack of small microorganisms combined with the rate of diameter (44.35 nm), where roughness surface is equal (12.5 nm), so efficiency has increased.

Shapes (7,8,9) shows pictures (2D) and sample chart respectively. Table (3) shows three films have a lower surface roughness first model (7), surface roughness (1.82 nm) is very low and R.m.s (2.07 nm) addition to accumulation of particles will lead to bad light activity, As well as other models (8,9), lower value (R.m.s) Caused a decrease roughness surface, result is less that relationship between surface area and roughness surface due to a decrease in the size of the grain, this enhance in dye absorption by layer TiO₂ then increased the efficiency.
Table (3) optical properties layers of TiO$_2$ (AFM)

| Particle size | Avr. Diameter Nm | R.m.s nm | Surface Avr Ratio | Roughness Avr(nm) |
|---------------|------------------|----------|-------------------|-------------------|
| TiO$_2$ 10    | 44.35            | 12.5     | 34.7              | 10.5              |
|              | 25               | 107.31   | 2.07              | 0.378             |
|              | 33               | 65.66    | 9.761             | 0.932             |
|              | 50               | 103.6    | 1.15              | 0.125             |

Figure (7) roughness surface and histogram TiO$_2$ (25 nm)

Figure (8) roughness surface and histogram TiO$_2$ (33 nm)
Figure (9) film roughness and histogram TiO$_2$ (50 nm)

5. Conclusions
There are many parameters affect on the performance of the solar cell. These factors include grain size, film thickness, and chemical additives. We have obtained efficiency greater at volume TiO$_2$ (10 nm) (2.39 % ), where increasing of surface area is relative to the size of the small particle, thus increasing surface roughness, because of increasing of electron transfer speed and increasing current density. In case of sizes (25 nm, 33 nm and 50 nm) surface area decreased due to large particle size and low surface roughness resulting reduced efficiency.

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