Photovoltaic studies of Dye Sensitized Solar cells Fabricated from Microwave Exposed Photo anodes

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Abstract. The configuration of Dye Sensitized solar cells (DSSC), consists of sintered nanoparticle titanium dioxide film, dyes, electrolyte and counter electrodes. Upon the absorption of photons by the dye molecules, excitons are generated, subsequently electrons are injected into the TiO₂ photoanode. Afterward the electrons injected into the TiO₂ photoanode, to produce photocurrent, scavenged by redox couple, and the hole transport to the photo cathode. The power conversion efficiency of the device depends on the amount of dye adsorbed by the photoanode. This paper explores in enhancing the efficiency of the device by controlled microwave exposure. With same exposure time, the photoanode is exposed at three different frequencies. SEM analysis is carried out to find the porosity of the photoanode on exposure. Current density is found to have an effect on microwave exposure.

1. Introduction
Dye-sensitized solar cells (DSSCs) are economic, stable, and eco-friendly making it a promising alternate for traditional silicon solar cells. DSSCs have received intensive research attention and have been rapidly developing [1] in the recent past. For the commercialization and extensive application the efficiency of the DSSC should be increased. For this the different groups have been working to improve the efficiency by modifying photoanodes, counter electrodes and electrolytes [2]. Commonly used methods to improve photoanodes include semiconductor film nano architecture, light-scattering material application, compositing, doping, interfacial engineering, and TiCl₄ post-treatment [3, 4]. To assemble such a cell, a wide band gap semiconductor such as Titanium dioxide film must be sensitized with a dye which harvests the light from the near IR region [5]. The photo-excited dye molecule injects the electrons into the conduction band of the semi conducting electrode. The dye is then regenerated by hole injection from the redox electrolyte, an ionic liquid containing iodide/tri iodide couple. The regeneration of the redox system is by the reaction with the electrons at the counter electrode which have passed through the external circuit. The change in the energy level of electron in the titanium dioxide and the work function of the positive charge carrier conductor or the redox potential of the electrolyte gives the maximum voltage generated under illumination [2]. Some work has already been reported [6, 7], using oxygen/ Argon plasma to increase the photovoltaic parameters of dye sensitized solar cells. In this work the photoanode is exposed with three different microwave

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frequencies (698MHz, 2.6GHz and 5.3GHz) for 10 minutes, in order to increase surface texture of the Titanium dioxide film so as to increase its dye adsorbing ability. Due to the cost effectiveness, non-toxicity, and complete biodegradation, natural dyes have been used as the dye sensitizer [2-4]. An optimized TiO2 film thickness plays a vital role in reproducible power efficiency since it controls both the dye loading and the extent of electron transport before collection. SEM analysis, thickness of the photoanode, and absorption spectra of the dye sensitized photoanode are studied to examine their possibility of this photo anode in DSSC application.

2. Materials and Methods

2.1. Materials used
Fluorine doped tin oxide acts as glass substrate having resistance of 10Ω/cm² is purchased from Solaronix, Switzerland. Titanium dioxide nano crystalline Degussa P-25 is from Orion Chem. Pvt. Ltd, India is used to make photo anode. Alizarin Red S dye, Electrolyte Lithium Iodide from Aldrich is used as such for making redox electrolyte. Other chemicals such as Acetone, Methanol, Acetonitrile, 1 butyl 3 methyl imadazolium iodide, Guanidium thiocyanate, Iodine(I₂), 4-tert butyl pyridine and Titron X-100 used are from Merck, India, is used for preparing electrolyte.

2.2. Preparation of TiO₂ electrode
The fluorinated tin oxide glass substrates (FTO) are cleaned with de-ionized water followed by acetone and then dried in air. To make TiO₂ paste, 10 g of TiO₂ (P25 Degussa) powder is grinded for 3 hours and then mixed with 10 ml distilled water. The prepared solution is sonicated for 15 min and then 1ml of Triton X-100 is mixed to this paste. This paste of TiO₂ is coated over FTO glass substrate. Then the TiO₂-coated FTO film is placed in the oven at 80°C for 1 hour and then it is sintered at 450°C for 30 min in an electronic muffle furnace. The prepared TiO₂ films are exposed at three different frequencies such as 698 MHz, 2.6 GHz and 5.3 GHz using monopole antennas. These films are exposed to 10 minutes in the near field of the antenna at Amrita-Keysight Advanced Wireless lab. Near far field exposure ensures that maximum radiation is received by the film. The monopole antennas have its resonance at 698 MHz, 2.6 GHz and 5.3 GHz respectively, with Omni-directional radiation characteristics. The pictorial representation of experimental arrangement is shown in figure 1. Now the microwave exposed TiO₂ coated FTO glass substrates are sensitized for 12 hours with Alizarin red S dye (0.3 mM) followed by rinsing with the organic solvent methanol, which together will act as the photo anode for DSSC.

Figure 1: Exposing microwaves to the film using monopole antenna
2.3. Preparation of Counter Electrode

Chloroplatinic acid mixed with acetonitrile is coated onto an FTO glass substrate by spin coating. The prepared platinum counter electrode is then placed in the oven at 80°C for 1 hour and then it is sintered at 150°C for 30 min in an electronic muffle furnace.

2.4. Preparation of Electrolyte

The Lithium Iodide (LiI) electrolyte is prepared as follows: 8 mg of 1 butyl 3 methyl imidazolium iodide (0.6 M), 0.66g of Lithium Iodide, 0.6g of Guanidium thiocyanate, 0.65g of Iodine (I₂) and 3.35g of 4-tert butyl pyridine are added in 50 ml of acetonitrile solution and stirred for 15 min.

2.5. Assembling of DSSC

The Alizarin Red S dye sensitized photo-electrode is clamped with the platinum coated FTO counter electrode to form a sandwiched type structure. In between the photo anode and the counter electrode the Lithium Iodide electrolyte is placed and clamped to get the device. The two leads of the connections are taken from the TiO₂ coated FTO and platinum counter electrode.

3. Results and Discussions

3.1. Thickness study of Photo anode and Counter Electrode

The effects of thickness and morphology of photo anode in the performance of a dye sensitized solar cells (DSSCs) are investigated. The Ellipsometer (Model No: A3/1532/2015) is used for measuring the thickness of the prepared film. The initial set up is done by adjusting the position of the laser arm and detector arm in such a way that the zero reading of the vernier scale coincide with the zero reading in main scale. Then we rotated the polarizer and the analyzer in between 0-90 degree simultaneously until we get the minimum intensity at the screen and record the angle between the polarizer (P1) and the angle between the analyzer (A1) respectively. Then we rotated the polarizer and the analyzer in between 90-180 degree and 270-360 degree simultaneously until we get the minimum intensity at the screen and record the angle between the polarizer (P2) and the angle between the analyzer (A2) respectively. The corresponding angles above obtained are entered in to the software and plotted the graph. A curve fitting is done with the obtained values. The thickness of the film is evaluated from the software [3] and the thickness measurements are shown in Table 1. It is observed that the thickness of photo anode remains nearly same.

| Electrodes                  | P1 (degree) | P2 (degree) | A1 (degree) | A2 (degree) | Thickness (nm) |
|-----------------------------|-------------|-------------|-------------|-------------|----------------|
| Photoanode without microwave treatment | 45.0        | 338         | 16.0        | 148.0       | 139.5          |
| 698 MHz                     | 45.5        | 328         | 15.5        | 147.0       | 140.0          |
| 2.6 GHz                     | 62.0        | 306         | 08.5        | 149.5       | 129.0          |
| 5.3 GHz                     | 42.2        | 330         | 10.0        | 150.1       | 150.5          |

3.2. SEM analysis of the fabricated device

The SEM images of TiO₂ film with and without microwave exposure are shown in the figures.2 to 5. Figure 2 shows the SEM image of TiO₂ film before the exposure of microwaves Figure 3 shows the SEM image of TiO₂ film exposed to microwaves of frequency 698.3 MHz for 10 minutes, figure 4 shows the SEM images of TiO₂ film exposed to microwaves of frequency 2.6 GHz for 10 minutes and figure 5 shows the SEM images of TiO₂ film exposed to microwaves of frequency 5.3 GHz for 10 minutes.
Figure 2. TiO$_2$ film without microwave exposure (a) 10 μm resolution and (b) 1μm resolution

Figure 3. TiO$_2$ film exposed to microwave frequency at 698 MHz for 10 min. (a) 10 μm resolution and (b) 1μm resolution

Figure 4. TiO$_2$ film exposed to microwave frequency at 2.6 GHz for 10 min. (a) 10 μm resolution and (b) 1μm resolution

Figure 5. TiO$_2$ film exposed to microwave frequency at 5.3 GHz for 10 min (a) 10 μm resolution and (b) 1μm resolution
From the SEM images it is observed that Titanium dioxide (TiO$_2$) nano particles are clustered together with an average size around 110 nm. It is evident from the images that the growth and alignment of the TiO$_2$ nano crystals are increasing as the frequency of exposure is increased. This uniform alignment of the crystals of the anode increases the dye adsorption ability of the film. These structural textures surely increase the efficiency of the device.

3.3. Current-Voltage Characteristics

The current density-voltage characteristics of the DSSCs made by exposing microwaves of different frequencies are shown in figure 6. From the J-V characteristics analysis, it is found that the photo current increases as the exposure frequency of microwave are increased. The open circuit voltage remains the same as it depends only on the characteristics of the dye molecules. The photovoltaic parameters of the fabricated devices are shown in Table 2. It is evident that the efficiencies of the devices are increasing from 0.140% to 0.163% as the microwave frequencies are increased from 698.3 MHz to 5.3 GHz.

![Figure 6: Current Voltage Characteristics of the fabricated devices](image)

| Devices            | $J_{\text{max}}$ (mA/cm$^2$) | $V_{\text{max}}$ (V) | $J_{\text{sc}}$ (mA/cm$^2$) | $V_{\text{oc}}$ (V) | FF  | $\eta$ (%) |
|--------------------|-------------------------------|----------------------|-----------------------------|-------------------|-----|------------|
| Without microwave exposure | 0.225                      | 0.65                 | 0.24                        | 0.75              | 0.80 | 0.142      |
| 698 MHz            | 0.255                        | 0.55                 | 0.26                        | 0.75              | 0.72 | 0.150      |
| 2.6 GHz            | 0.320                        | 0.47                 | 0.33                        | 0.75              | 0.61 | 0.160      |
| 5.3 GHz            | 0.345                        | 0.47                 | 0.35                        | 0.75              | 0.62 | 0.163      |

3.4. Dye Desorption studies of photo anode

To account for the increased efficiency of the device made of photo anode exposed to a frequency of 5.3 GHz, the dye desorption studies are performed. Desorption studies is beneficial for optimizing dye loading. Strong bases like NaOH have been used to partially desorb dye from a monolayer to create a layer of uniform partial coverage, which is useful for studying recombination rates onto the TiO$_2$ substrates, which has shown to increase the efficiency of the device after re-adsorption as well as
increase the total coverage of the dye [5]. Here the UV-Spectrometer is used for desorption studies. The corresponding spectra are shown in figure 7, which highlights that microwave exposed photo anode with frequency 5.3 GHz shows high absorbance compared to the other frequencies.

4. Conclusion

In order to study the effect of microwave frequency in the efficiency of the DSSC, we exposed the photo anode of the DSSC to microwave frequencies, 698 MHz, 2.6 GHz and 5.3 GHz for 10 minutes. The film thickness is studied using Ellipsometry and the surface morphology of the microwave exposed film is evaluated using SEM analysis. It is found that the morphology of the film became better when the frequency increased. It is found that there is an increase in the power conversion efficiency of DSSC made from photo anodes exposed at 5.3 GHz frequency. The efficiency of the device is changed from 0.14% to 0.163% as the microwave frequency is increased from 698 MHz to 5.3 GHz. Detailed study is carried out to understand the increased power conversion efficiency, dye desorption studies of the photo anodes exposed to microwave. Dye desorption of the Alizarin dye sensitized photo anode are also studied and the photo anode exposed with 5.3 GHz shows maximum absorbance.

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