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# Application of TiO<sub>2</sub> Dye-Sensitive Solar Cells by Electrochemical Storage Method

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In our study, fluorine doped transparent conductive glass plates are initially covered by  $TiO_2$  with electrochemical deposition method for obtained working electrode of dye sensitized solar cell. It has been used both for different surface enhancing materials and different experimental conditions to increase the covering of conductive glass surface by  $TiO_2$ . In the first part of the study, five different solutions have been prepared using various surface enhancing materials.  $TiO_2$  thin films at different thicknesses have been obtained using chronoamperometry and cyclic voltammetry methods with five different solutions prepared. Then scanning electron microscopy images of thin films were analyzed and were found to be more suitable for the conditions of the solution of our coating. The best of two different solutions were selected for covering the second part of the study. It has been repeated five times with those solutions using chronoamperometry method for 20 min and at a potential of 1 V. After each covering, the drying process has been performed at 100 °C for 20 min. Also, the coatings have been obtained by cyclic voltammetry method for 20 cycles with two different solutions. Hence the best solution and method were decided on the basis of the results of UV and X-ray beam refraction analyses of obtained thin films. The working electrode of dye sensitized solar cell has been formed. Then, efficiency analysis of solar cell was performed after counter electrode had been coated with platinum.

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# 1. Introduction

The demand for the use of electronic devices is increasing at present due to developments in technology and industry and the increasing population of the world. Therefore, the needs of society vary in this direction. Solar energy is the most efficient way to convert solar energy into electrical energy and minimize unit cost, while many researchers are working on increasing the energy efficiency of solar cells [1–3]. Recently, some researchers have been doing a lot of studies on dye-sensitized solar cells [4–6]. In many studies, the parts that affect the performance of the dyestuff are TiO<sub>2</sub> film and solar cell anode [7, 8]. The TiO<sub>2</sub> film transmits electrons from the dyestuff to the conductive glass, absorbing the dyes and scattering the light [9]. Another reason for considering  $TiO_2$  is that it is a semiconductor with a wide band range (3.2 eV) [10].

## 2. Materials and method

The creation of  $\text{TiO}_2$  thin films on conductive glass surfaces (FTO) was performed by cyclic voltammetry and chronoamperometry methods. In these studies,



Fig. 1. Autolab Potentiostat/Galvanostat PGSTAT-302N device.

Gpes 4.9 version software programmed Autolab Potentiostat/Galvonostat PGSTAT-302N device was used. As a reference electrode, the Ag/AgCl electrode was used, and the Pt wire was used as most of the electrodes. In addition, FTO conductive glasses were used as working electrodes. Figure 1 shows the device.

The chemicals used in the study were titanium(III) chloride (TiCl<sub>3</sub>), sodium nitrate (NaNO<sub>3</sub>), hydrogen chloride (HCl), and CTAB, all of which are of appropriate purity. These chemical materials were obtained from companies.

The optimal coating conditions were found initially using five different solutions and two different methods. First of all, the cleaning process of FTO-conducting glass was done. It is very important that the lower bases are clean so that we can see the properties of the desired thin films.

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In the first step, 0.05 M TiCl<sub>3</sub> was dissolved in a solution of 0.025 HCl. With the prepared solution, thin film coating was done with electrochemical storage method on conductive glass which was cleaned with 1 V $\rightarrow$ 20 min chronoamperometry method. Then, the covered glass that was kept in the drying-oven for 1 h at 100 °C. This process was done five times again and the coating was completed.

In the second step, 0.05 M TiCl<sub>3</sub> was dissolved in a solution of 0.025 HCl. 40 cycles of alternating voltammetry method and a thin film coating were performed by electrochemical storage method on the conductive glass.

In the third step,  $0.01 \text{ M TiCl}_3$  was dissolved in a solution of  $0.1 \text{ M NaNO}_3$ . 40 cycles of alternating voltammetry method and a thin film coating were performed by electrochemical storage method on the conductive glass.

In the fourth step, 0.01 M TiCl<sub>3</sub>+ 0.1 M NaNO<sub>3</sub>+ 0.01 M HTAB solution was prepared. 40 cycles of alternating voltammetry method and a thin film coating were performed by electrochemical storage method on the conductive glass.

In the fifth step,  $0.01 \text{ M TiCl}_3 + 0.1 \text{ M NaNO}_3 + 0.01 \text{ M}$  CTAB solution was prepared. 40 cycles of alternating voltammetry method and a thin film coating were performed by electrochemical storage method on the conductive glass.

It was concluded that the optimal solutions between these five different solutions and methods are the second and fifth solutions.  $TiO_2$  thin films coated by electrochemical storage method were released into azo dye. After examining the ability of the dyestuff to hold onto the surface of  $TiO_2$ , these thin films were kept in the dyestuff for 3 days. The bases taken from the dyestuff were left in ethanol solution. Thus, dyes that cannot hold onto the surface were cleaned and dried at room temperature. The resulting layer became our working electrode.

FTO was coated with platinum by magnetron sputtering method on thin film and cooled to room temperature by waiting for 1 h at 350-400 °C. 0.05 M of iodine  $(I_2)$  was obtained by dissolving in 10 ml of pure ethylene glycol and adding 0.5 M of potassium iodide (KI). The system was comprised of dye-sensitized solar cells, working electrode, opposite electrode layer and liquid electrode between them. Direct contact between the opposite electrode and working electrode was prevented by using an insulating material (double sided tape). The FTO-coated parts of both layers were left on the outer surface and placed on top of the platinum with dyestuff. At this time, a small area was excluded from being glued so that we could inject our liquid electrolyte between two layers, resulting in a dye-sensitized solar cell.

## 3. Results and discussion

Figure 2 shows the images taken by scanning electron microscopy (SEM) of  $\text{TiO}_2$  thin films coated by electrochemical storage method on conductive glasses, which are cleaned by using chronoamperometry method and five repeated operations.

As shown in Fig. 2a and b,  $TiO_2$  is uniformly distributed on the surface, but fissuration have occurred on the surface. While the surface is completely porous for dye-sensitized solar cell, these fissuration on the surface have not been the desired coating form when creating the working electrode of the solar cell. In Fig. 2c the thickness is 649.3 nm and this thickness is thought to be too thin for the working electrode of the solar cell. By using chronoamperometry method and electrochemical storage method, the  $TiO_2$  thin films are intended to be coated on conductive glasses in a way such that five layers are not able to fully hold onto the surface. This is because the conductivity of the surface decreases after the first coating. In Fig. 2f, a porous structure was formed for  $TiO_2$ , albeit a little. Although, this structure could not be achieved equally across the surface.



Fig. 2. (a)–(g) 1 V voltage–20 min (5 repetitions) SEM images of thin films obtained by chronoamperometry method.



Fig. 3. (a)–(f) SEM images of thin films obtained by using solution number (2) with CV method and making 40 cycles.



Fig. 4. (a)–(f) SEM images of thin films obtained by using solution number (3) with CV method and making 40 cycles.

The photographs taken by SEM of the  $TiO_2$  thin films coated with electrochemical storage method on the conductive glasses, which were cleaned by 40 cycles cyclic voltammetry method, with our solution number (2) prepared, are shown in Fig. 3.

As shown in Fig. 3a and b,  $TiO_2$  is uniformly distributed on the surface, but fissuration has occurred on the surface. However, a porous and smooth structure has been obtained. Figure 3f shows that the thickness is 580.6 nm. This thickness is thought to be too thin for the working electrode of the solar cell. Using CV method and electrochemical storage method, it is decided that the  $TiO_2$  thin film surfaces which are intended to be coated with 40 cycles on conductive glasses should be thicker and the number of cycles should be increased in order to close the fissurations. In our study, two different forms of coating with the same solution using electrochemical storage method were coated with chronoamperometry and CV method. From the results of these two methods, as shown in Figs. 2 and 3, CV method is a better coating method for the application of solar cell working electrode.



Fig. 5. (a)–(f) SEM images of thin films obtained by using solution number (4) with CV method and making 40 cycles.



Fig. 6. (a)–(f) SEM images of thin films obtained by using solution number (5) with CV method and making 40 cycles.

The photographs taken by SEM of the  $TiO_2$  thin films coated with electrochemical storage method on the conductive glasses, which were cleaned by 40 cycles CV method, with our solution number (3) prepared, are shown in Fig. 4.

In Fig. 4a–d, the surface is covered uniformly again. Although, as can be seen from the figures, needle-like structures were formed. This indicates that  $\text{TiO}_2$  accumulates on the surface. The thickness here is seen as 489.1 nm.

When Figs. 2–4 are examined, it is seen that a surface enhancing material must be added to the prepared solution in order to accumulate more  $TiO_2$  on the surface.

The photographs taken by SEM of the  $TiO_2$  thin films coated with electrochemical storage method on the conductive glasses, which were cleaned by 40 cycles CV method, with our solution number (4) prepared, are shown in Fig. 5. As shown in Fig. 5a–d, the surface is not uniformly covered. A porous structure for this coating could not be obtained with HTAB, which is used as a surface enhancing material. Therefore, HTAB did not give a very positive result. The thickness was obtained as 642.1 nm and in this form of coating it was again concluded that 40 cycles are not enough.

The photographs taken by SEM of the  $TiO_2$  thin films coated with electrochemical storage method on the



Fig. 7. Permeability graphs of  $\text{TiO}_2$  coated glass by electrochemical storage method (a) 1 V, 20 min the solution number (5), chronoamperometry method, (b) 1 V, 20 min the solution number (2), (c) 1 V, 20 min (20 cycles) the solution number (5), chronoamperometry method, (d) 1 V, 20 min (20 cycles) the solution number (2), chronoamperometry method.

conductive glasses, which were cleaned by 40 cycles CV method, with our solution number (5) prepared, are shown in Fig. 6.

As shown in Fig. 6a–d, the surface is covered fairly uniformly. However, as can be seen from Fig. 6e, the thickness required for the working electrode has not been achieved in 40 cycles. Among these five different solutions and methods, we concluded from the SEM images in Figs. 2–6 that the optimal solution is solution number two and solution number five. According to the results of the experiment, the method of cyclic voltammetry method is found to be more appropriate.

# 3.1. UV analysis

The optical properties of the thin film samples created were studied by UV spectrometry. In Fig. 7, the permeability values of  $TiO_2$  coated glass are observed by electrochemical storage method.

As can be seen from Fig. 7, the maximum permeability values are seen in (a) and (d) samples, while (b) and (c) samples show less permeability. This can be explained as the accumulation of more  $TiO_2$  material on the glass surface in samples (b) and (c).

In Fig. 8, optical energy band gap of  $TiO_2$  thin films is shown.

As can be seen from Fig. 8, the band range was calculated to be 3.2 eV. This is a value found in agreement with the literature [11].

In Fig. 9, optical energy band gap of FTO glasses is shown. As can be seen from Fig. 9, the band range is calculated as 4 eV. This is a value found in agreement with the literature [12].



Fig. 8. Optical energy band gap of TiO<sub>2</sub> thin films.



Fig. 9. Optical energy band gap of FTO glasses.

Permeability and absorption of TiO<sub>2</sub> thin films were studied between wavelengths of 0.3–0.8  $\mu$ m. Optical band gap calculations were made. If a linear line is obtained when  $(\alpha h\nu)2 - h\nu$  graph is plotted, there is an absorption pass with direct permission. Accordingly, the point at which the line obtained by extrapolation of this linear line cuts the HV axis gives the optical band gap.

#### 3.2. X-ray diffraction analysis

The pattern images taken by X-ray diffraction (XRD) measurements of the  $TiO_2$  thin film obtained by electrochemical storage method are shown in Fig. 10.

When studying structural characterization, it is important to explain the optical and electrical properties of SnO<sub>2</sub>:F thin films. The crystal structure of SnO<sub>2</sub>:F thin films was determined by XRD technique. The XRD graph of thin films has been studied between 10° and 80° and in the  $2\theta$  range. By examining the XRD sample of the thin film it was determined that the crystal structure was of a tetragonal structure. When the XRD graph of TiO<sub>2</sub> was examined, it was also seen that the crystal structure was in tetragonal structure and of anatase form. XRD graphs of thin films coated TiO<sub>2</sub> by electrochemical storage method on commercially purchased SnO<sub>2</sub>:F thin films are shown in Fig. 10. As can be seen from the figure, the second peak shows the anatase form



Fig. 10. XRD graph of  $TiO_2$  coated glass by electrochemical storage method.

TABLE I Mesh parameters for  $TiO_2$  coated on  $SnO_2$ : F thin films.

h	k	1	d [Å]	$2\Theta [^{\circ}]$
1	1	0	3.34700	26.611
1	0	1	2.64270	33.893
2	0	0	2.36900	37.950
1	1	1	2.30940	38.969
2	1	1	1.76410	51.781
2	2	0	1.67500	54.759
3	1	0	1.49840	61.872
1	1	2	1.43920	64.710

belonging to  $\text{TiO}_2$  and the peaks of  $\text{SnO}_2$ :F thin films in line with the literature [11]. Furthermore, it is desirable for us that both the conductor base and the crystal structure of  $\text{TiO}_2$  are compatible. Table I provides mesh parameters for  $\text{TiO}_2$  coated on  $\text{SnO}_2$ :F thin films.

#### 4. Conclusion

With the electrochemical storage method, two different methods and 5 different solutions have been created for the working electrodes of solar cells. The optical, structural and crystal structure of the thin films created were studied. According to the SEM results of the experiment, the method of cyclic voltammetry method is found to be more appropriate. By examining the XRD sample of the thin film it was determined that the crystal structure was of a tetragonal structure. When the XRD graph of TiO2 was examined, it was also seen that the crystal structure was in tetragonal structure and of anatase form.

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