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Fabrication of Spin Coater Device using Hematocrit Centrifuge with Vacuum Substrate Holder for Thin Film Deposition

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One of the most important thin film deposition techniques on a silicon, quartz or sapphire substrate in the world is the spin coating method. Hematocrit centrifuge was used to elaborately manufacture the spin coating machine from affordable materials without vibrations. The vacuum holder substrate in this system is used for substrate adhesion. This method provides a dimensionally free substrate with appropriate adhesion for sedimentation upon high-speed spinning. A platinum thin film was deposited on a fluorine-doped tin oxide glass (FTO) substrate with a specific concentration of hexa-chloro-platinic acid. Platinum thin films were investigated by Field Emission Scanning Electron Microscope (FESEM) and UV-Vis spectroscopy. FESEM displays successfully produced platinum thin films. The results showed a platinum film transmittance decrement with increasing of hexachloro-platinic acid content. Therefore, the suggested spin coater in this work can deposit platinum thin films with high transmittance up to (98 a.u.).

Keywords: *Spin coater, vacuum holder substrate, Platinum thin films.*

1. Introduction

The chemical technique is one of the most methods that is used for fabricating thin films due to its low cost and simple fabrication. Therefore, many chemical techniques were developed to be used for depositing thin films, such as dip coating[1], highlighting[2], spray pyrolysis[3], doctor blade[4], and spin coating[5]. Decades ago, it became easy to obtain regular thin films by means of a spin coating technique[6]. These thin films are manufactured for a wide variety of applications especially in the semiconductor industries.

The most fundamental advantage of spin coating over other methods is the production of fast and high quality films without engaging in complex procedures[7,8]. This technique is mainly used in the deposition of polymers.

Spin coaters can form thin films with thickness in range of micrometers (μm) and nanometer (nm), for application of devices such as, transistors[9], gas sensors[10] and light emitting diodes[11]. Additionally, it can also be used for depositing platinum thin films on conductive glass. These films can be used as a counter electrode in dye sensitized solar cells (DSSCs)[12-14]. The roles of the counter electrode are to transfer electrons arriving from the external circuit back to the redox electrolyte and to catalyze the reduction of the redox couple in order to keep the overvoltage low at photocurrent densities up to 20 mA/cm^2, where the platinum serves as an electro-catalyst[15].

Platinum films are used in several applications such as in DSSCs. In which, a platinum thin film coated on a conductive surface is utilized as a counter electrode (CE), since it exhibits high catalytic action to reduce the tri-iodide[16]. Thus, many methods were reported to prepare platinum CE[12], where a few drops of Hexachloroplatinic acid are placed in a transparent conducting oxides (TCO) substrate, such as indium tin oxide (ITO) or fluorine-doped tin oxide glass (FTO), and calcined at an appropriate temperature. In addition, platinum film can be supported onto a substrate by high vacuum techniques, such as, sputtering[17] or gas phase reactions of platinum compounds, as chemical vapor deposition (CVD)[18].

The drop methods for producing platinum, produce non-homogeneous films. On the other hand, (Sputtering, CVD and thermal evaporation) can be classified as complex technologies that require sophisticated and expensive equipment.

This work presented a development of a low-cost spin coater for depositing platinum thin films on an FTO conductive substrate with different concentrations for DSSCs application. Hematocrit centrifuge has been used to fabricate spin coater devices. Hematocrit centrifuge has beneficial properties such as (high rotation speed, high angular acceleration and high stability). Arduino UNO with LCD screen and IR sensor is used for directly monitoring the rotation speed of the device. Another highlight vacuum substrate holder is used

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to provide a free dimension substrate with good adhesion at high-speed rotation.

2. Spin Coating Mechanism

The spin coating deposition mechanism is done by dropping a certain amount of a specific solution manually or automatically onto the substrate center. The substrate in this machine is fixed on an aspirator. This step is followed by rotating the pile at high speed sometimes up to 10000 RPM with uniform acceleration[19]. After that, the thin film will be successfully formed by evaporation through this process[20]. Thin film made by spin coating technique depends on solution concentration and viscosity as well as rotational speed. Thicker films result from higher concentration. In contrast, thinner films result from higher spinning speeds. In addition, choosing higher solvent volatilities produce thicker films at a specific concentration and viscosity[21]. The following represents the four significant stages that are usually seen in the spin coating process[10,11]. First, before the rotation, few drops of a solution is placed on the substrate as in (Figure 1A). Next, by rotating the substrate at high speed, almost all of the solution is flung off the sides (Figure 1B). More specifically, centripetal force combined with the surface tension and viscous forces of the solution causes uniform film covering the substrate with the solution. Air flow during the process dries off most of the solvent and the residual solution is formed as a wet-plasticized film (Figure 1C). Finally, all the solvent dries out resulted in coating the substrate with the desired material (Figure 1D).

Laboratory, before spin coating, the polymer solution solvent is filtered to remove dust[22]. In general, the thickness of the spindle film is relative to the square root of rotation speed as in the equation below where (t) is the thickness and (ω) is the angular velocity[6]:

$$t \alpha \frac{1}{\sqrt{\omega}}$$

This means that the film, which is woven at a rate of four times the speed, will be half its thickness.

3. Experimental Work

3.1. Fabrication of spin coater

The main parts of designing spin coater in this work are hematocrit centrifuge, Arduino UNO, LCD screen, IR sensor and Vacuum rotary.

3.2. Substrate holder

Any machine that works with nanoscale dimensions must be designed with high accuracy, so it is necessary to calculate the effects of rotation in this work on the thickness and homogeneity of the film[23]. As well, the spin coating machine needs to be free from the vibration effects to obtain films with high homogeneity, regardless of the number of coating layers. The substrate holder was designed to avoid this problem. Figure 2 shows the schematic design of the substrate holder and its parts which will be explained in details. The substrate holder is made from rubber silicon to obtain good adhesion with the sample. Vacuum channel was placed on the motor to allow the air flowing from substrate holder to rotary. A rotary shaft was used for rotating the substrate holder which was sealed by two O-Rings. Finally,

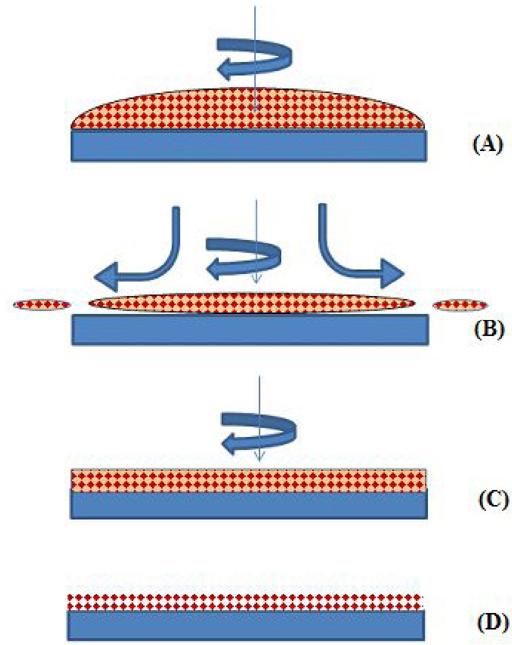

Figure 1. The mechanical process of spin coating technique.

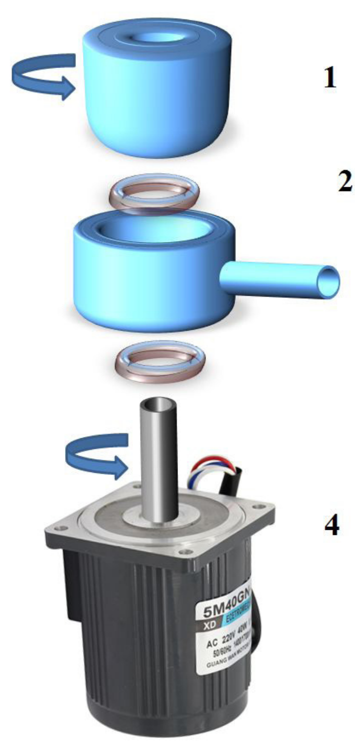

Figure 2. 3D design of fabricated spin coater (1) substrate holder, (2) O ring, (3) vacuum channel and (4) motor.

the vacuum channel connects with vacuum Pump (Value Vi 220SV) by silicone pipe.

3.3. Speed controller

Hematocrit Centrifuge (HC – 12 A) has a manual speed rotation controller (0 – 12000) RPM. The crowbar of the manual speed rotation controller placed on variable resistance. The variable resistance was connected with electrical circuit to control the motor speed from (0 to 12000 RPM) using single crowbar . The electrical circuit diagram of speed rotation controller is shown in Figure 3.

The Hematocrit Centrifuge provided a simple way to control the speed of the device. Arduino UNO with LCD screen and Infrared Speed Sensor (LM393) are used for observing directly the rotation speed of the device. IR sensor was placed on the motor beside the rotation shaft to sense the rotation speed. Arduino UNO has been programmed to calculate the speed rotation. (16×2) digit LCD display was connected with Arduino UNO and it was placed on the spin coater as shown in Figure 4c. The final design and the substrate holder of the spin coater machine were shown in Figure 4a and Figure 4b respectively.

4. Synthesis of Pt/FTO

To synthesis platinum thin films, Chloroplatinic acid hexahydrate H_2PtCl_6 (Platinum ≥ 37.50%) was used as a precursor which was purchased from Fluka. FTO substrates with sheet resistances of ~7 Ω/sq were purchased from Sigma Aldrich. The samples were synthesized by chemical reduction in which they were achieved by dissolving H_2PtCl_6 in absolute ethanol to obtain the required thin films. The precursor H_2PtCl_6 was dissolved in absolute ethanol due to its fast evaporation.

Different parameters were used to prepare several platinum thin films which were coated on FTO substrate using a spin coater machine as listed in Table 1.

The first parameter is the rotating speed which was varied from (600 to 3600 rpm); samples PtL and PtS, respectively. In which the other parameters were maintained constant hence the acceleration was (6.28 rad/s^2) and precursor concentration was (15 mM).

The second parameter is to control the acceleration hence it was increased from 6.28 to 37.79 rad/s^2 to prepare

Table 1. Fabricated thin films parameters.

Sample	Speed RPM	Acceleration Rad/S^2	Precursor concentration (mM)
PtL	600	6.28	15
PtS	3600	6.28	15
Pt15	3600	37.79	15
Pt10	3600	37.79	10
Pt5	3600	37.79	5
Pt2.5	3600	37.79	2.5

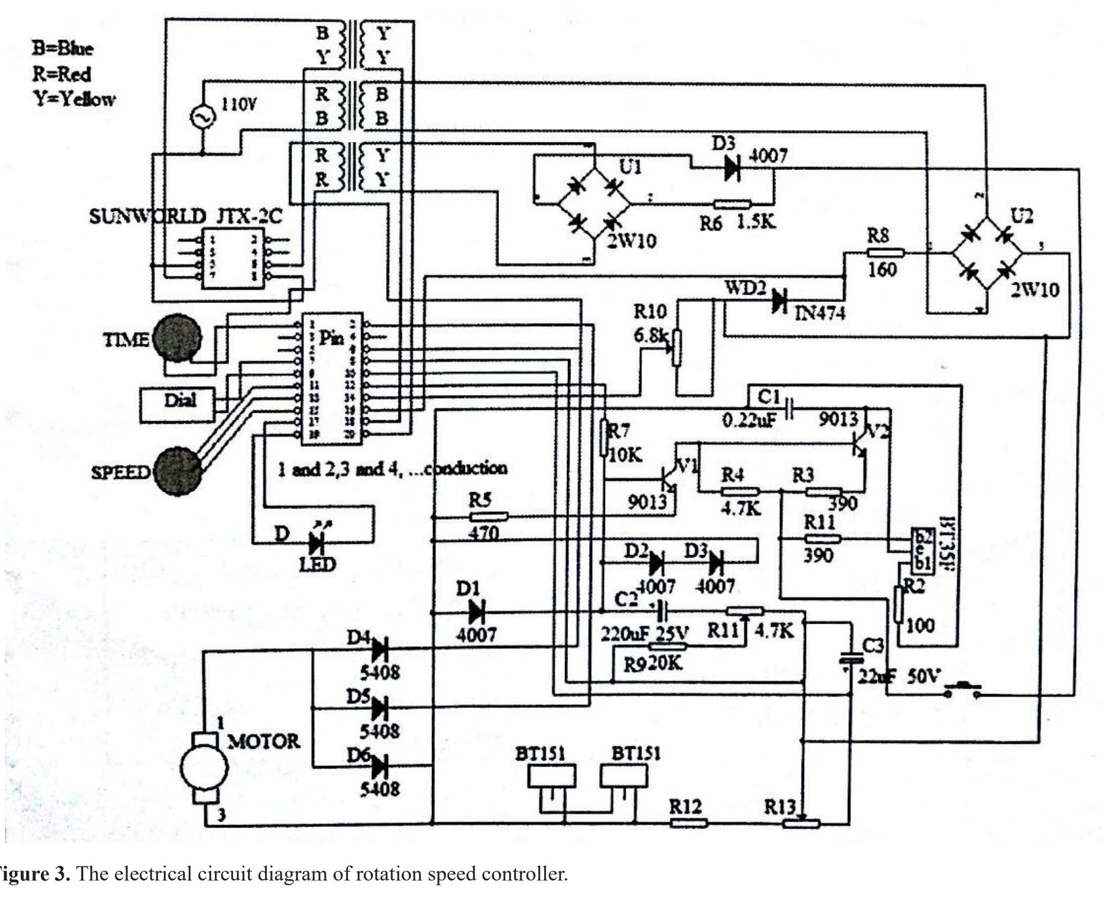

Figure 3. The electrical circuit diagram of rotation speed controller.

samples PtS and Pt15, respectively. This experiment was applied by fixing the speed at (3600 rpm) and the solution concertation at (15 mM).

The third parameter is controlling the solution concentration which was varied in the range of 15 mM, 10 mM, 5 mM, and 2.5 mM to prepare samples Pt 15, Pt10, Pt5 and Pt2.5, respectively as shown in Figure 5. In which all other parameters were maintained constant speed 3600 rpm and acceleration 37.79 rad/s^2.

The rising time of the speed (the required time to reach the preferred speed) was maintained at constant value (10 sec) for all the prepared samples unless sample (PtS) in which its rising time was (60 sec).

Each sample was spin coated for 10 mins. The coated samples were dried at 373 K by using a hot plate then they were annealed in the furnace at 723 K for 30 min.

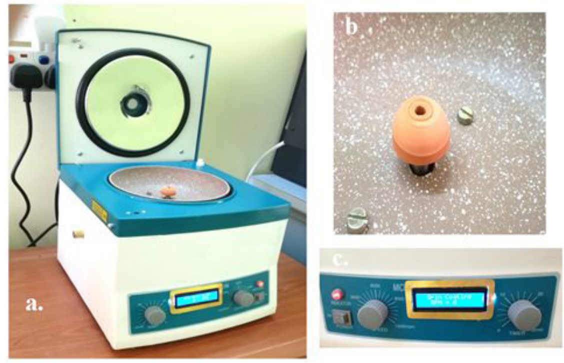

Figure 4. a. The final design of the spin coater, b. substrate holder, and c. front view of the spin coater speed controller.

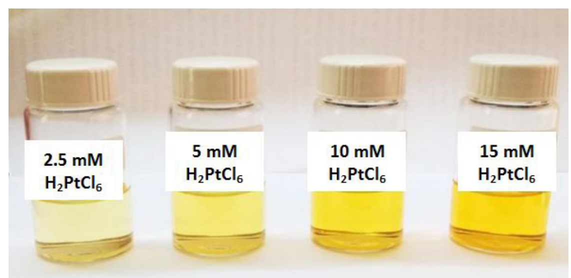

Figure 5. The precursor solution of H_2PtCl_6 in absolute ethanol.

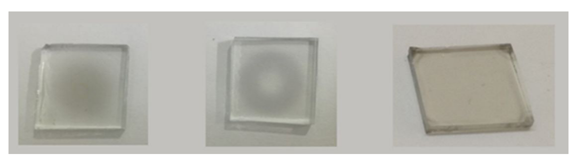

Figure 6. Pt/FTO photographs of: a. (PtL), b. (PtS), and c. (Pt15).

5. Thin Film Characterization

To study the speed and acceleration effects on the Pt thin films distribution, a camera from (Huawei Honor 10i) with resolution of (24 megapixels) was used to capture the thin film photographs. The distribution of the prepared thin film was simulated using Origin program. FESEM measurements were performed by using a FEI Nova NanoSEM 450 to verify the structure morphology of Pt thin films. UV-Vis device (EMC-LAB VIS-1100 Spectrophotometer) was utilized to investigate the optical transmittance of the prepared samples. The transmittance was measured at wavelength of 550 nm hence it considered the suitable wavelength for testing the transparency of CE of DSSCs[24-26].

6. Result and Discussion

6.1. Speed and Acceleration effect

Homogeneous thin films made by spin coater require a balance between rotational speed, acceleration, viscosity and other factors. To clarify the working mechanism of the machine, an aspirator is employed for the purpose of locating the substrate. Then, by rotating the plate, the chemical solution is uniformly spread over the entire surface of the substrate. This is the main purpose of the machine.

In this work, the effect of rotation speed was studied. Thus, the thickness of the thin film can be reduced by controlling the rotation speed where high speed leads to thinner layers. The effects of the rotation speed and acceleration on platinum thin films are shown in Figure 6.

Non-homogeneous thin film was produced at low speed (600 RPM) as demonstrated in sample (**PtL)** Figure 6a. A circle thin film was concentrated on the middle of the FTO substrate. This is due to low speed which leads to evaporate the solvent (Ethanol) before distributing the solution completely on the entire substrate surface. As well, sample **(PtS)** was exhibited nonhomogeneous thin film when prepared at high speed (3600 RPM) and low acceleration. A ring like Pt thin film was concerted on the center of the substrate. This is due to high speed with low acceleration which provided enough time for the precursor to evaporate before distributing the Pt uniformly. The perfect concurrence between the speed and acceleration is shown in sample **(Pt15)** where homogeneous thin film was obtained. These conditions afford the precursor to well distribute on the substrate before evaporating.

Figure 7 represents the modeling shapes that show the effectiveness of speed and acceleration on the platinum thin films distribution. When manufacturing a spin coating machine, the factors that determine the optical and physical properties of the film must be taken into consideration. One of the factors affecting the properties of coated thin films is the acceleration factor, in addition to the final rotational speed. As for the thickness of the film, it is also affected by the nature of the used resin according to the percentage of solid matter within the polymer, surface tension (the tendency of liquid surfaces), viscosity, drying rate at the beginning and during rotation and others. It is worth noting that thickness is often inversely proportional to speed and rotation time. Approximately 50% of the solvent composed of the resin is lost at the beginning of the rotation due to evaporation. Therefore, it is important to control the rotational acceleration in a controlled and safe manner[19,27]. Moreover, the uniform shade of the resin over the topographical properties of the substrate determines

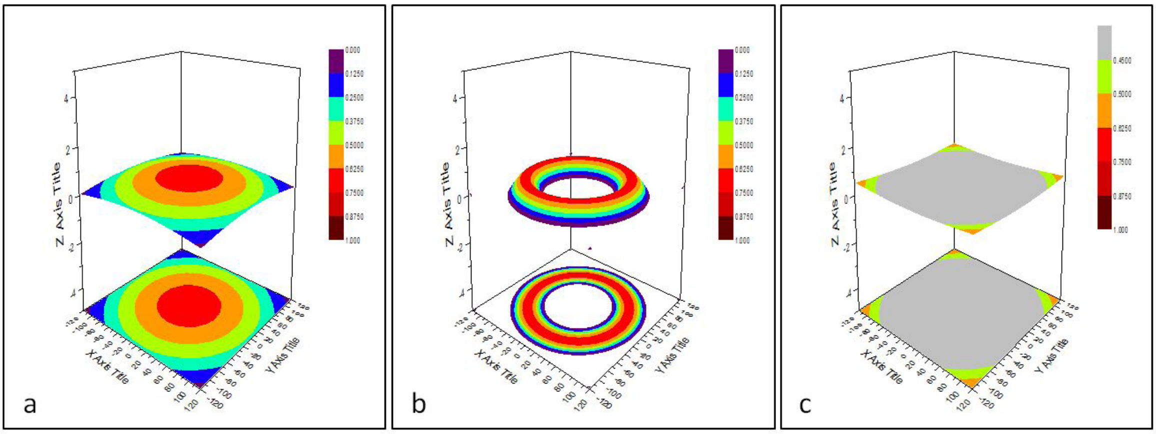

Figure 7. Distribution of platinum thin films: a. PtL, b. PtS , and c. Pt15.

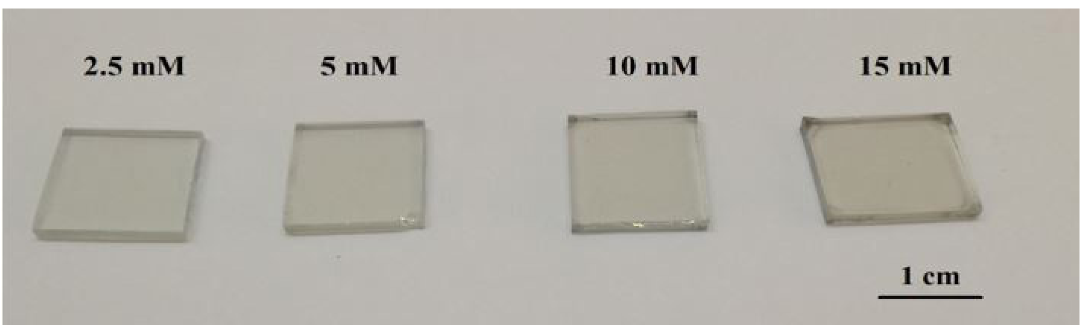

Figure 8. Pictures of Pt/FTO thin films with different precursor concentration.

the topography of the product, as the substrate sometimes retains the topographical properties during the operation of the machine. Because of the rapid rotation, radial forces are generated that disperse the resin around the terrain. Thus, in some cases, even small parts of the substrate are blocked from the liquid[27].

7. Morphological Properties

Figure 8 shows the prepared thin films using the spin coating machine with four platinum acid concentrations of Pt/FTO nanoparticles, which are 2.5, 5, 10 and 15 mM. The figure shows that the prepared Pt/FTO exhibited clear thin film at low concentration while by increasing the concentration a foggy film was obtained.

Figure 9 shows the FESEM photographs with a magnification of () for the substrate and for bare FTO and Pt/FTO at the above precursor concentrations. It is evident that platinum nanoparticles are homogeneously distributed on the FTO. It was observed that the morphological structure and the distribution of platinum nanoparticles on the surfaces of the films changed with changing the acid concentration. Where the size of the platinum nanoparticles increased by increasing the concentration of the H_2PtCl_2 as shown in the figures. The average particle size of Pt thin film was carried out using Image J software. The measured particle size of sample Pt15 is around 20 nm.

8. Transmittance Properties

As it was observed from Figure 8, with increasing the acid concentration, the produced films were not totally transparent so it is necessary to measure the light transmittance to determine their optical properties.

Figure 10 shows the transmittance of Pt/FTO by EMC-LAB VIS-1100 spectrophotometer using the FTO as a reference. The transparency of platinum thin films has been decreased with increasing of the precursor concentrations. These results are supported by FESEM characterization. In addition, it can be observed that platinum thin film has a highly transparence property of about 98 a.u. at the lowest H_2PtCl_6 concentrations of 2.5 mM (sample Pt2.5). It was reported previously that in DSSCs, the better the CE the highest the optical transparency at wavelength = 550 nm[26]. As for the rest of the prepared thin films, the transparency gradually decreased from 96.1, 93 to the lowest percentage 90 a.u. by increasing the concentrations as 5 mM, 10 mM and 15 mM, respectively. The properties of sample Pt2.5 revealed that it can be used in manufacturing the transparent DSSC due to the low refractions. The increase of transparency leads to improve the efficiency. This is due to its low cost and the undesired reflection losses. Moreover, the DSSC can absorb light from the front and back[13].

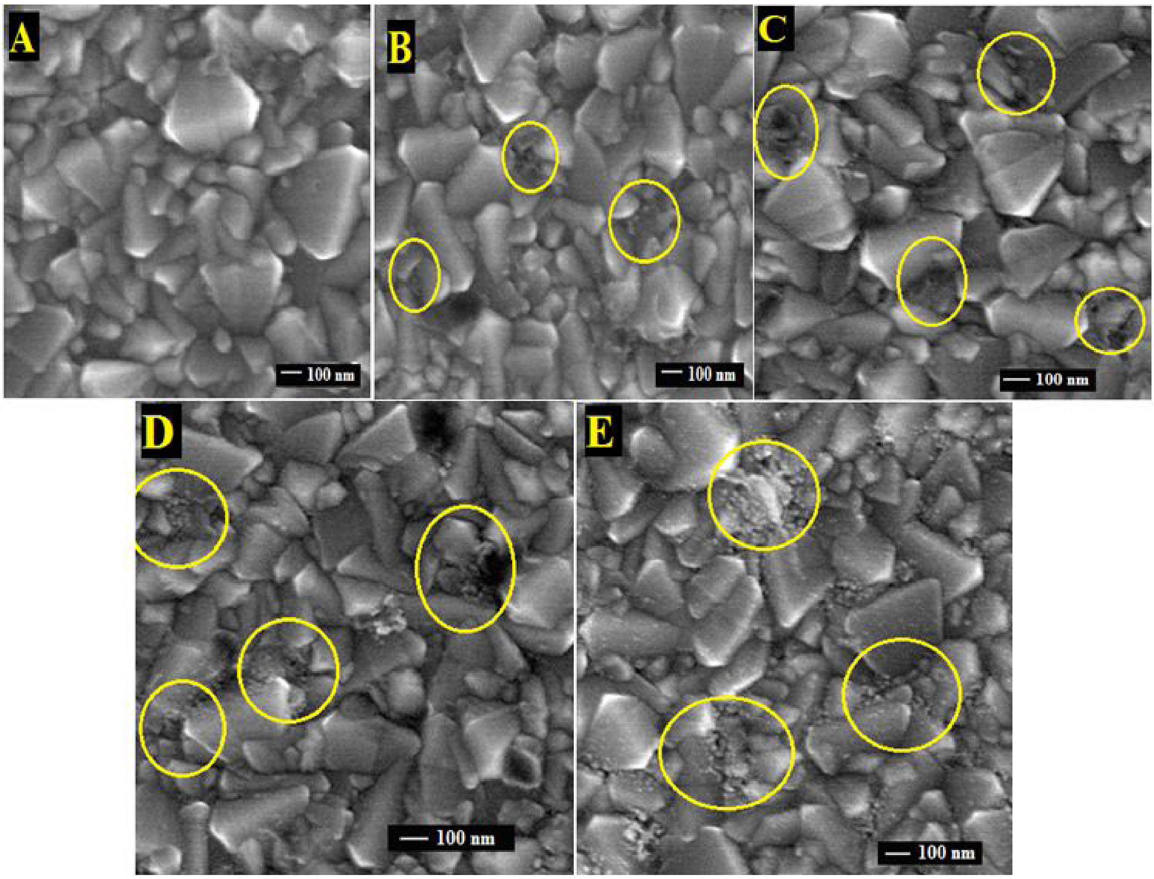

Figure 9. FESEM photographs of Pt/ FTO thin films A. bare FTO B. Pt2.5, C. Pt5, D. Pt10 and E. Pt15.

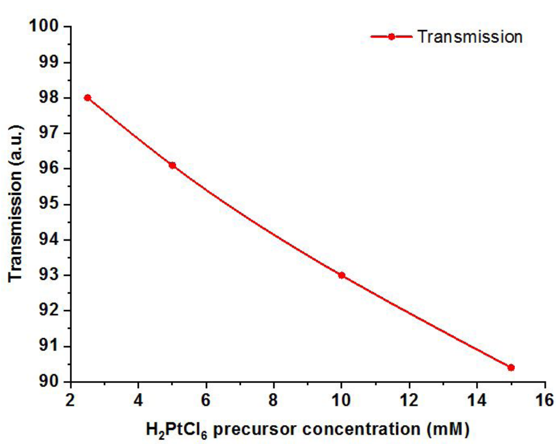

Figure 10. Transparence properties of Pt/ FTO thin Films.

9. Conclusion

A low-cost spin coater machine was successfully fabricated for depositing thin films of polymers, metals, inorganic, or even organic materials. The manufactured vacuum holder substrate provided a free dimension substrate with good adhesion at high-speed rotation. The rotation speed and acceleration of the spin coater machine play an important role to determine the shape, thickness and quality of the prepared thin films. The optimum conditions were determined to produce a homogeneous platinum thin film. Highly transparent platinum thin film was successfully prepared using a precursor solution H_2PtCl_6 in absolute ethanol. The particles size of Pt thin film became smaller by reducing the precursor concentration. The prepared Pt thin film is suitable for being counter electrode in dye synthesized solar cell. The present study highlighted the fabrication of simple, low cost and accurate technique to prepare thin films.

10. Acknowledgments

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