

Research Article

The Photocatalytic Activity and Compact Layer Characteristics of TiO₂ Films Prepared Using Radio Frequency Magnetron Sputtering

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TiO₂ compact layers are used in dye-sensitized solar cells (DSSCs) to prevent charge recombination between the electrolyte and the transparent conductive substrate (indium tin oxide, ITO; fluorine-doped tin oxide, FTO). Thin TiO₂ compact layers are deposited onto ITO/glass by means of radio frequency (rf) magnetron sputtering, using deposition parameters that ensure greater photocatalytic activity and increased DSSC conversion efficiency. The photoinduced decomposition of methylene blue (MB) and the photoinduced hydrophilicity of the TiO₂ thin films are also investigated. The photocatalytic performance characteristics for the deposition of TiO₂ films are improved by using the Grey-Taguchi method. The average transmittance in the visible region exceeds 85% for all samples. The XRD patterns of the TiO₂ films, for sol-gel with spin coating of porous TiO₂/TiO₂ compact/ITO/glass, show a good crystalline structure. In contrast, without the TiO₂ compact layer (only porous TiO₂), the peak intensity of the anatase (101) plane in the XRD patterns for the TiO₂ film has a lower value, which demonstrates inferior crystalline quality. With a TiO₂ compact layer to prevent charge recombination, a higher short-circuit current density is obtained. The DSSC with the FTO/glass and Pt counter electrode demonstrates the energy conversion efficiency increased.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been extensively studied as a promising alternative to conventional solar cells that use a p-n junction because of their reasonable conversion efficiency, low cost, environmentally friendly components, use of a flexible cell design, and simple fabrication process, when compared to silicon solar cells [1]. DSSCs are the next-generation solar cells [2]. If low cost and highly efficient DSSCs can be developed, it will be an important new direction for the development of solar cells. A typical DSSC consists of dye molecules that act as sensitizers, a nanoporous metal oxide film (TiO₂ semiconductor material), a transparent conducting oxide (indium tin oxide, ITO), an electrolyte charge carrier, and a counter electrode (Pt or carbon) [3]. The dye and metal oxide, which are used for the sensitizer and

the electrode, respectively, are important to the photoelectric conversion efficiency of DSSCs [4].

TiO₂ is one of the most popular photocatalytic materials, so it has many commercial applications, such as antibacterial applications, waste purification, self-cleaning, and sensors [5]. It is also used for photoelectrodes and in high performance DSSC applications because it has an adequate photoreponse and effective electron transport [6]. A high incident photon to current conversion efficiency is expected for TiO₂ films that have a better phase structure and crystallinity and a higher specific surface area [7]. The control of the TiO₂ nanostructures is very important for the photovoltaic performance of a DSSC [8]. In order to improve the conversion efficiency of DSSCs, several studies have focused on the structural design, material development, photovoltaic characterization, and analysis of the mechanism of TiO₂

TABLE 1: The factor and level settings for sputter deposition of TiO₂ compact layers.

Substrate		Soda-lime glass, 20 × 20 × 1 mm ³		
Target		TiO ₂ (99.99% purity)		
Gas		Ar and O ₂ (99.99% purity)		
Base pressure		5.0 × 10 ⁻⁶ torr		
Substrate-to-target distance		80 mm		
Substrate temperature		Room temperature		
Substrate rotate vertical axis		10 rpm		
Symbol	Control factor	Level 1	Level 2	Level 3
A	rf power (W)	100	130	160
B	Sputtering pressure (mtoorr)	3	5	7
C	O ₂ /(Ar + O ₂) (%)	10	30	50
D	Deposition time (hr)	2	3	4

nanoparticles [9]. Mesoporous TiO₂ is widely used as an electrode in DSSCs to produce a high surface area for the adsorption of a greater density of dye molecules, which produces a significant increase in the photocurrent [10]. However, the highly porous structure of the TiO₂ layer can cause an electrical shortage and recombination of the charge/electrons, which interferes with the unidirectional electron transport that takes place at the TiO₂ layer/dye molecule and ITO/TiO₂ layer interfaces [11]. This leakage by electronic back transfer leads to a decrease in cell efficiency. To avoid this problem, the primary method used to prevent recombination is the use of a TiO₂ compact layer (blocking layer) between the ITO and the porous TiO₂ layer [11]. This compact layer can be prepared using many growth techniques, such as sputter deposition, dip-coating, chemical vapor deposition, and spray pyrolysis.

This study determines the optical, structural, and surface properties of a TiO₂ compact layer that is grown by radio frequency (rf) magnetron sputtering on the ITO electrodes, as a function of the deposition parameters that ensure higher photocatalytic activity and greater DSSC conversion efficiency. The nanoporous TiO₂ upper layer is coated using the sol-gel process and calcination at 450°C. Moreover, the working electrode which is made of a dye-sensitized TiO₂ film that is immobilized onto a fluorine-doped tin oxide (FTO) substrate is also investigated.

The Taguchi method is a powerful tool for the design of high quality systems, which can be used to design low cost products, with improved quality [12]. To optimize the deposition process for TiO₂ photocatalytic films, a statistical analysis of the signal-to-noise ratio (S/N) is performed, using an analysis of variance (ANOVA). The optimal deposition parameters are obtained by analyzing the results for various experimental permutations [13, 14]. Table 1 shows the effect on the quality of the TiO₂ photocatalytic films of four deposition parameters at three levels: the rf power, the sputtering pressure, the Ar-O₂ ratio, and the deposition time. An L₉ (3⁴, with four columns and nine rows) orthogonal array is used.

2. Experimental

The TiO₂ photocatalytic thin films (compact layer) were coated onto ITO/glass substrates (and FTO/glass), using rf magnetron sputtering. The reactive and sputtering gases were O₂ (purity: 99.99%) and Ar (purity: 99.99%), respectively. The commercially available, hot pressed, and sintered ceramic target TiO₂ had a diameter of 50.8 mm and 99.99% purity (Elecemat, USA).

Prior to coating, the target was presputtered for 15 min, in order to remove any contamination, and the substrates were ultrasonically cleaned and degreased in acetone, rinsed in deionised water, and subsequently dried with nitrogen gas. A vacuum, of base pressure 5.0 × 10⁻⁶ Torr, was applied before deposition. The distance between the substrate and the target (80 mm) and the rotational speed of the substrate (10 rpm) were constant. By adjusting the experimental permutations, this study determined the effect of each deposition parameter on the deposition rate for TiO₂/ITO/glass, the methylene blue (MB) absorbance, the contact angle to a pure water droplet, the surface morphology, and the crystal structure.

The porous TiO₂ film (p-TiO₂) was coated onto the TiO₂ compact/ITO/glass (and TiO₂ compact/FTO/glass) using a mixture of TiO₂ powders (P-25, particle size: <25 nm, 99.7%) with the TiO₂ sol-gel component studied in [15]. The TiO₂ sol-gel was mixed with 0.3 g of commercially available Degussa P-25, to avoid any cracking of the film. The TiO₂ sol-gel was produced using spin coating and blade coating. The gels were predried for 15 min at 50°C and then sintered in a box furnace at 450°C (heating rate 10°C/min) for 30 min in air ambient, to produce the bare TiO₂ electrode used in this work to fabricate the DSSC. The porous TiO₂ films were immersed into the dye solution (0.4 mM N719 dye solution, Solaronix, Switzerland, Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2, 2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II); chemical formula C₅₈H₈₀N₈O₈RuS₂; Mol Wt: 1188.55) complex for 24 h at room temperature.

TABLE 2: The experimental results and the S/N ratios for the deposition rate, the contact angle, and the MB absorbance for the TiO₂ compact layer coatings (the experiments were repeated twice).

Exp.	Factors				Deposition rate (Å/min)		S/N (dB)	Water contact angle (degree)		S/N (dB)	MB absorbance		S/N (dB)
	A	B	C	D	T1	T2		T1	T2		T1	T2	
1	1	1	1	1	3.35	3.00	9.9953	90.73	91.30	-39.182	1.328	1.332	-2.4770
2	1	2	2	2	2.73	3.04	9.1653	92.13	91.87	-39.275	1.327	1.325	-2.4508
3	1	3	3	3	2.19	2.23	6.8868	73.91	75.40	-37.461	1.296	1.293	-2.2420
4	2	1	2	3	4.85	4.97	13.8197	89.75	90.28	-39.086	1.198	1.187	-1.5292
5	2	2	3	1	4.35	3.95	12.3307	91.01	92.71	-39.262	1.284	1.283	-2.1679
6	2	3	1	2	4.84	4.76	13.6239	93.57	94.68	-39.474	1.205	1.200	-1.6017
7	3	1	3	2	6.38	6.11	15.9046	71.70	72.30	-37.146	1.287	1.284	-2.1814
8	3	2	1	3	7.48	7.25	17.3403	95.35	94.81	-39.561	1.077	1.074	-0.6322
9	3	3	2	1	4.73	4.82	13.5783	63.79	62.39	-35.999	1.031	1.030	-0.2609

Note: A = rf power (W), B = process pressure (Pa), C = O₂/(Ar + O₂) flow rate ratio (%), and D = deposition time (hr).

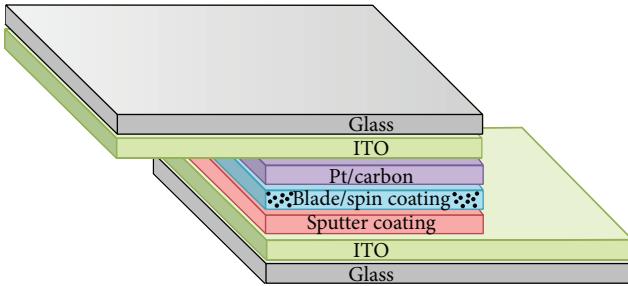


FIGURE 1: A schematic diagram of a DSSC with an rf-sputtered TiO₂ compact layer/ITO/glass on the ITO electrode.

The Pt counter electrode was coated onto ITO/glass (and FTO/glass) substrates using DC sputtering with pure Ar gas and a DC power of 30 W. The dye-adsorbed TiO₂ working electrode and the counter electrode were assembled into a sandwich-type cell and sealed with a hot-melt sealant. Figure 1 shows a schematic diagram of a DSSC with an rf-sputtered TiO₂ compact layer/ITO/glass on the ITO electrode. In order to prevent the leakage by electron transfer to the liquid electrolyte, dense TiO₂ passivating layers were used.

The phase identification of the particles produced using various deposition parameters was performed by X-ray diffraction (Rigaku-2000 spectrometer), using Cu-K α radiation (40 kV, 30 mA, and $\lambda = 0.1541$ nm). The photoinduced hydrophilicity of the TiO₂ thin films was evaluated by measurement of the contact angle to pure water, using a contact angle meter (FACE CAVP150) that is accurate to less than 1°. A black light (UVP UVL-225D) lamp with a principal wavelength of 365 nm (1.5 mW/cm² at the film surface) was the UV light source. The decomposition of MB aqueous solution (10 μ M) was photocatalyzed. An UV-Vis-NIR spectrometer (Jasco V-670) was used to measure the absorption spectra of the MB solution as a function of the UV irradiation time. The film thickness was measured, using

a surface profilometer (α -step, AMBIOS XP-1). The surface morphology was analyzed using a field emission scanning electron microscope (FESEM, JEOL JSM-6500F). The crystal structure of the films was characterized by X-ray diffraction (Rigaku-2000 spectrometer), using Cu-K α radiation (40 kV, 30 mA, and $\lambda = 0.1541$ nm), with a grazing incidence angle of 1°. The scanning rate was 5°/min.

The power used to test the prepared DSSC was a 150 W Xe lamp, which simulates sunlight (AM 1.5). Before the test, the distance between the light source and the sample was adjusted to allow a light source density of 100 mW/cm². The cell performance parameters, including the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF), and the photoelectronic conversion efficiency ($\eta(\%) = J_{sc} \times V_{oc} \times FF / \text{total incident energy} \times 100$), were measured and calculated using the J - V characteristics of DSSC.

3. Results and Discussion

3.1. The Photocatalytic Activity of the TiO₂ Compact Films. The TiO₂ compact films were deposited onto ITO soda-lime glass substrates. The optimization of the parameter settings involved comparing the signal-noise (S/N) ratios, using the Taguchi method. In order to optimize the TiO₂ compact films deposition parameters, the water contact angle and the MB absorbance had the smaller the better characteristics and the deposition rate had the larger the better characteristics. The respective S/N ratios for the smaller the better characteristic and the larger the better characteristic are expressed as follows (Taguchi et al. [13]):

$$\left(\frac{S}{N} \right)_S = -10 \log \frac{1}{n} \sum_{i=1}^n y_i^2 \quad (1)$$

$$\left(\frac{S}{N} \right)_L = -10 \log \frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2},$$

where n is the number of iterations for the experiment and y_i is the i th average value of the characteristic measured.

TABLE 3: The ANOVA results for the deposition rate, the water contact angle, and the MB absorbance.

Factor	Degree of freedom	Sum of square	Variance	Contribution (P %)
Deposition rate (Å/min)				
A	2	74.4166	37.2083	84.45
B	2	6.1132	3.0566	6.93
C	2	6.1644	3.0822	7.00
D	2	1.4211	0.7106	1.62
Total	8	88.1153		100
Water contact angle (degree)				
A	2	4.4559	2.22793	33.68
B	2	4.4483	2.22417	33.62
C	2	3.7790	1.88950	28.56
D	2	0.5472	0.27359	4.14
Total	8	13.2304		100
MB absorbance				
A	2	2.80223	1.40111	54.36
B	2	0.72560	0.36280	14.07
C	2	1.03120	0.51560	20.00
D	2	0.59634	0.29817	11.57
Total	8	5.15538		100

Using (1), the S/N ratio values were computed for deposition rate, water contact angle, and MB absorbance in the TiO₂ compact layers coatings, as shown in Table 2. The hydrophilicity of the TiO₂ films was determined by measuring the water contact angle. The change in the water contact angle is shown as a function of UV irradiation time for the TiO₂ films deposited with parameter sets in the orthogonal arrays (Table 2). When the TiO₂ film surface is irradiated by UV light for 12 min, the water contact angles of all of the films begin to decrease (less than 63°, sample number 9), which indicates that the film surface becomes more hydrophilic. The absorption spectra for the MB aqueous solution degraded by TiO₂ photocatalytic film after 240 min UV irradiation are shown for the orthogonal array settings (Table 2). The TiO₂ films deposited using the parameter sets in the orthogonal arrays from number 1 to number 9 show MB absorbance between 1.33 and 1.03.

An analysis of variance (ANOVA) was used to determine the effect of a change in the process parameters on the process response. Table 3 shows the ANOVA results for the deposition rate, the water contact angle, and the MB absorbance. Table 3 shows that the variables that most significantly affect the deposition rate, the water contact angle, and the MB absorbance are the rf power ($P = 84.45\%$, 33.68%, and 54.36%), the sputtering pressure ($P = 6.93\%$, 33.62%, and 14.07%), and the argon-oxygen ratio ($P = 7.00\%$, 28.56%, and 20.00%).

Grey relational analysis (GRA) provides an efficient solution to difficult problems that involve multiple performance characteristics that are uncertain, have multiple inputs, and

TABLE 4: The Grey relational grade and its ranking for the TiO₂ compact layer coatings.

Exp.	Grey relational grade	Rank
1	0.3595	8
2	0.3526	9
3	0.4252	6
4	0.4551	4
5	0.3914	7
6	0.4356	5
7	0.5698	3
8	0.7007	2
9	0.8329	1

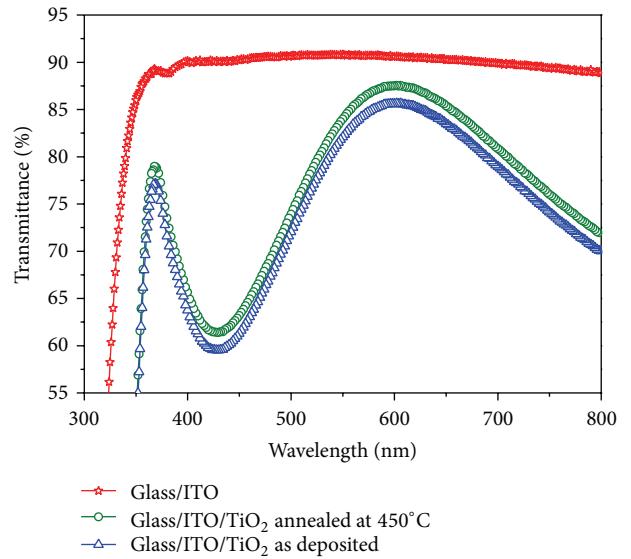


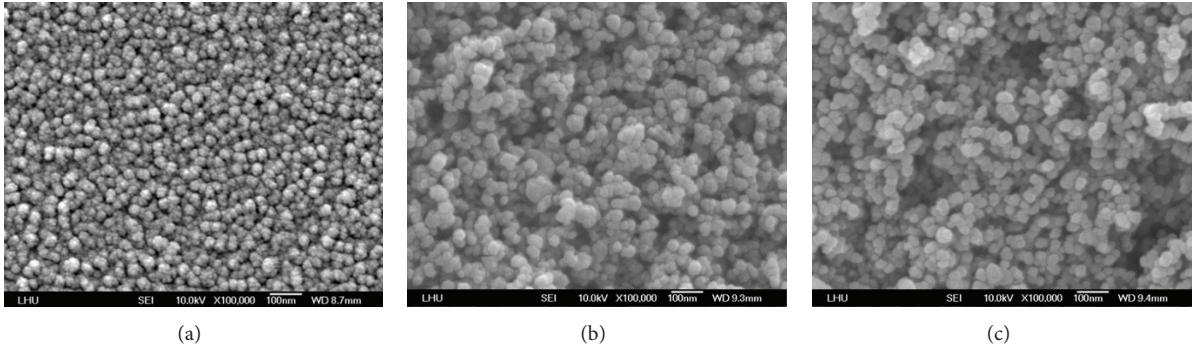
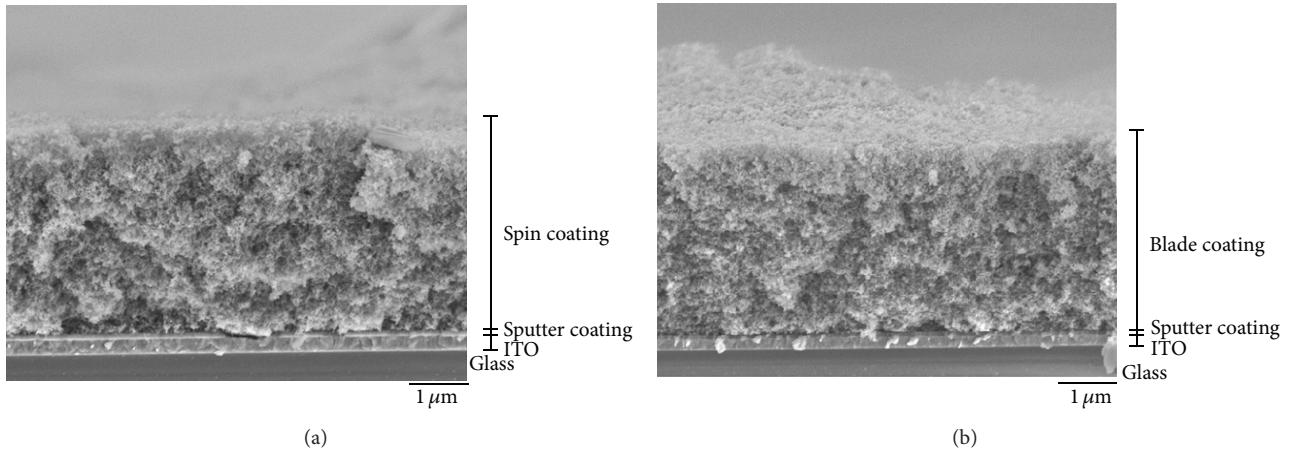
FIGURE 2: The optical transmittance spectra for TiO₂ compact layer/ITO/glass.

generate discrete data. The objective of this study is to optimize the deposition parameters for the TiO₂ compact films using GRA, which is used extensively in various industries [16].

The optimum combination does not yield suitable process parameters with a single performance characteristic (Taguchi method) for the TiO₂ compact films coated. In order to optimize the deposition parameters, the deposition rate, the contact angle, and the MB absorbance, multiple performance characteristics (grey relational analysis) must be analyzed. The calculated grey relational grade is taken as the inspected value in the Taguchi method. Table 4 shows the grey relational grade and its ranking for the TiO₂ compact layer coatings. A comparison of the experimental results for the orthogonal array ($A_3B_3C_2D_1$) and the photocatalytic activity optimal parameter set ($A_3B_3C_2D_3$) for TiO₂ film deposition is shown in Table 5. The multiple performance characteristics for the deposition of TiO₂ thin films are greatly improved

TABLE 5: The confirmation test results for the multiple performance characteristics, using the initial and the optimal process parameters.

Level	Initial process parameters	Optimal process parameters	Improvement rate (%)
	$A_3B_3C_2D_1$	$A_3B_3C_2D_3$	
Deposition rate ($\text{\AA}/\text{min}$)	4.775	5.48	12.87
Contact angle (degree)	63.09	53.47	15.25
MB absorbance	1.0305	0.865	16.06

FIGURE 3: (a) The SEM images for sputtered TiO_2 compact layer on ITO/glass, (b) the SEM images for porous TiO_2 onto TiO_2 compact/ITO/glass, produced using the sol-gel with spin coating method, and (c) the SEM images for porous TiO_2 onto TiO_2 compact/ITO/glass, produced using the sol-gel with blade coating method.FIGURE 4: The SEM cross-sectional image of TiO_2 (a) corresponding to Figure 3(b) and (b) corresponding to Figure 3(c).TABLE 6: The performance of a DSSC prepared using a photoelectrode with and without a TiO_2 compact layer, using carbon and Pt counter electrodes, and using ITO/glass and FTO/glass.

	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill factor	Efficiency η (%)
ITO/sputter/spin coating/carbon	0.54	4.38	0.676	1.59
ITO/sputter/blade coating/carbon	0.53	4.08	0.666	1.44
ITO/spin coating/carbon	0.52	3.18	0.639	1.05
ITO/blade coating/carbon	0.52	3.07	0.572	0.90
ITO/sputter/spin coating/Pt	0.51	12.86	0.678	4.46
ITO/sputter/blade coating/Pt	0.49	10.73	0.675	3.51
ITO/spin coating/Pt	0.58	6.02	0.644	2.24
ITO/blade coating/Pt	0.61	5.10	0.649	2.01
FTO/sputter/spin coating/Pt	0.70	17.22	0.641	7.73
FTO/sputter/blade coating/Pt	0.77	12.79	0.750	7.36
FTO/spin coating/Pt	0.79	12.39	0.692	6.79
FTO/blade coating/Pt	0.79	10.80	0.771	6.53

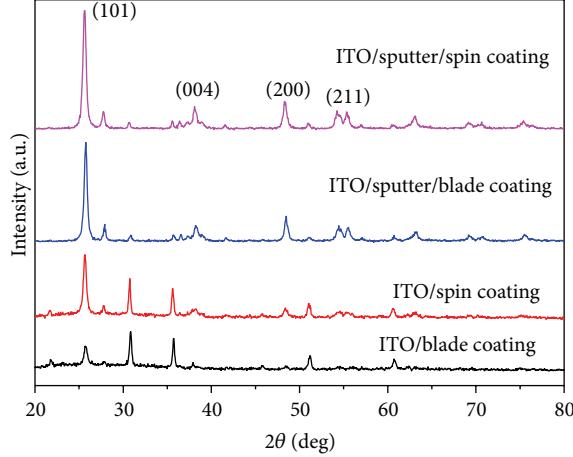


FIGURE 5: The XRD patterns for the TiO_2 films after being annealed at 450°C .

by using the Grey-Taguchi method. The improvement in the deposition rate is 12.87%, that in the water contact angle is 15.25%, and that in the MB absorbance is 16.06%.

The transmittance spectra are shown as a function of wavelengths in the range between 300 and 800 nm for TiO_2 compact layers in Figure 2. The average transmittance in the visible region exceeds 85% for all samples, but transmission in the UV-near visible region decreases abruptly. After annealing treatment, the optical transmittance of the film is increased.

3.2. DSSC Conversion Efficiency. SEM analysis was used to determine the morphology of the sputtered TiO_2 compact layers (with photocatalytic activity optimal parameters, $A_3B_3C_2D_3$) on the ITO substrate and the thick TiO_2 porous layer produced using the sol-gel method, as shown in Figure 3. The uniform and smooth surfaces of the sputtered compact accumulation film are well covered by spherical particles, which are densely coated with a small grain size (Figure 3(a), TiO_2 compact/ITO/glass). This is necessary to prevent charge recombination between the ITO and the porous TiO_2 layer [17, 18]. The SEM images show the porous TiO_2 film over the sputtered compact layer, produced using the sol-gel with spin coating method (Figure 3(b), porous $\text{TiO}_2/\text{TiO}_2$ compact/ITO/glass) and the sol-gel with blade coating method (Figure 3(c), porous $\text{TiO}_2/\text{TiO}_2$ compact/ITO/glass). The porous TiO_2 film structure is not dense and the crystallite size of the TiO_2 is increased. DSSC efficiency is improved by producing a TiO_2 electrode with a large surface area and optimum pore structure [19, 20].

The cross-section of the TiO_2 films was observed by SEM. Figure 4(a) corresponds to Figure 3(b) and Figure 4(b) corresponds to Figure 3(c). The TiO_2 compact/ITO films produced using the photocatalytic activity optimal deposition conditions ($A_3B_3C_2D_3$) are highly compacted and homogeneous and adhere perfectly to the glass substrate. These results

confirm a spongelike structure for the TiO_2 layer (Figure 4), which is a prerequisite for a highly efficient DSSC [21]. The characteristics of the TiO_2 materials depend significantly upon the surface morphology, the crystal structure, and the crystallization.

Figure 5 shows that the XRD patterns of the TiO_2 films, produced using the sol-gel with spin coating of porous $\text{TiO}_2/\text{TiO}_2$ compact/ITO/glass, show a good crystalline structure and anatase (101) diffraction peaks that demonstrate a higher crystallinity than the other films. In contrast, without the TiO_2 compact layer (only porous TiO_2), the peak intensity of the anatase (101) plane in the XRD patterns for the TiO_2 film has a lower value, which demonstrates inferior crystalline quality.

Good performance for the counter electrode requires a low internal resistance and raw material cost. The best material for the counter electrode is Pt, which shows excellent electrochemical activity for I_3^- reduction at film thicknesses of $2\text{--}10\text{ nm}$ [22, 23]. Figure 6 shows the photo current-voltage (I - V) characteristics for the DSSC under AM1.5 solar irradiation with 100 mW/cm^2 illumination, with and without the TiO_2 compact layer. Figure 6(a) shows a carbon counter electrode and ITO/glass, Figure 6(b) shows a Pt counter electrode and ITO/glass, and Figure 6(c) shows a Pt counter electrode and FTO/glass [24]. The corresponding cell parameters are summarized in Table 6, which shows the performance of the DSSC. With a TiO_2 compact layer to prevent charge recombination, a higher J_{sc} is obtained. The energy conversion efficiency (η) increases if a Pt counter electrode is used instead of a carbon counter electrode.

For the purposes of comparison, the energy conversion efficiency for the DSSC film deposited on FTO glass is also given. FTO substrates have good optoelectronic performance and higher energy conversion efficiency than ITO substrates. Table 6 shows that a FTO/sputter/spin coating/PT setup increases the conversion efficiency of the DSSC, with $V_{oc} = 0.70\text{ V}$, $J_{sc} = 17.22\text{ mA/cm}^2$, a fill factor = 0.641, and an energy conversion efficiency as high as 7.73%.

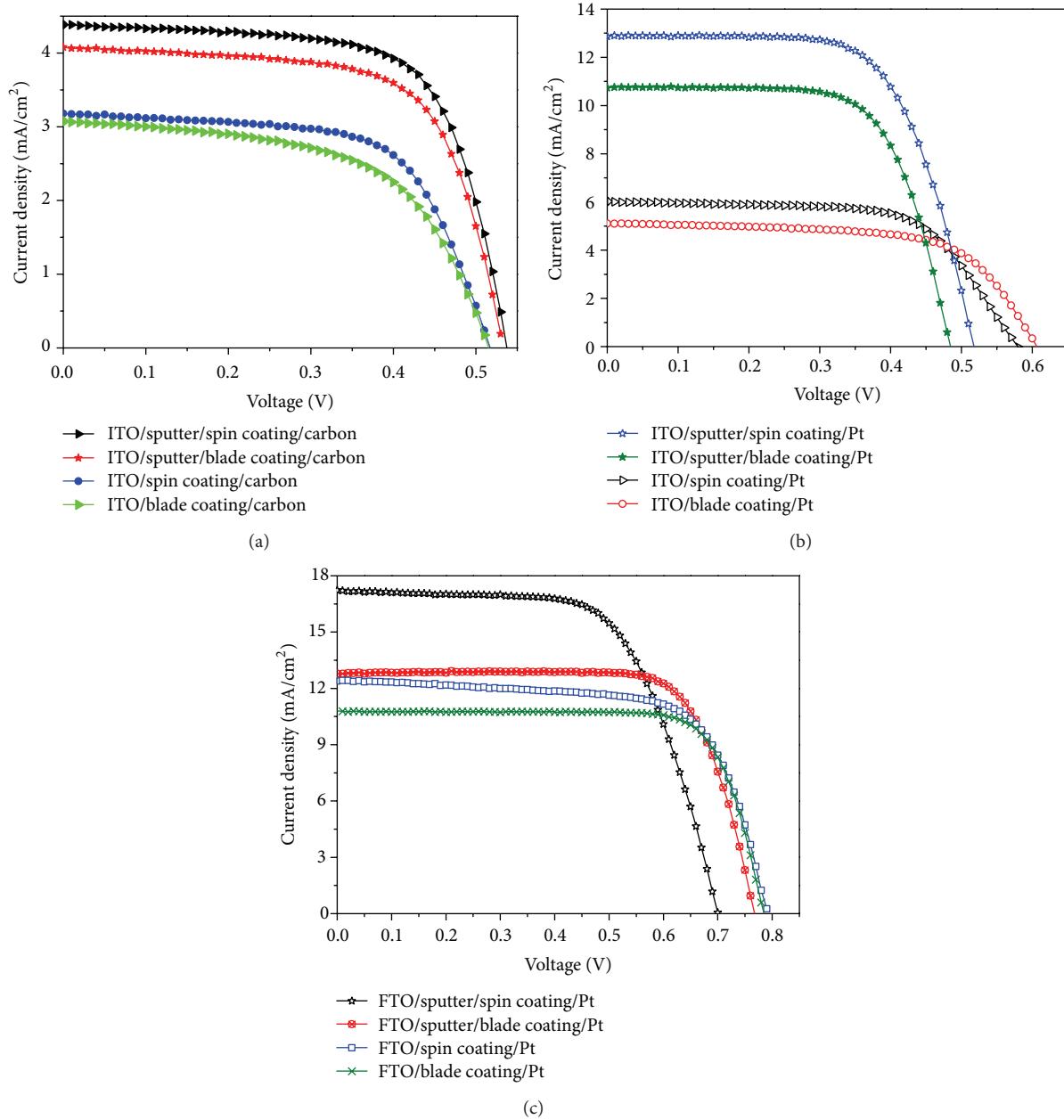


FIGURE 6: The I - V characteristics for DSSCs fabricated with and without a TiO_2 compact layer, (a) using a carbon counter electrode and ITO/glass, (b) using a Pt counter electrode and ITO/glass, and (c) using a Pt counter electrode and FTO/glass, under AM 1.5 solar irradiation with a density of 100 mW/cm^2 .

4. Conclusion

TiO_2 films (compact layer) are coated onto ITO/glass substrates (and FTO/glass), using rf magnetron sputtering. The reactive and sputtering gases are O_2 and Ar, respectively. The multiple performance characteristics for the deposited TiO_2 compact films' photocatalytic activity are greatly improved by using the Grey-Taguchi method. The improvement in the deposition rate is 12.87%, that in the water contact angle is 15.25%, and that in the MB absorbance is 16.06%. The porous

TiO_2 film that covers the sputtered compact layer produced by the sol-gel method has a structure which is not dense and a crystallite size that is increased. The XRD patterns for TiO_2 films produced using sol-gel with spin coating of porous TiO_2/TiO_2 compact/ITO/glass result in a good crystalline structure and the anatase (101) diffraction peaks demonstrate a higher degree of crystallinity. The energy conversion efficiency (η) for a Pt counter electrode is greater than that for a carbon counter electrode. The experimental results show that FTO/sputter/spin coating/PT setup increases

the conversion efficiency of the DSSC, with $V_{oc} = 0.70$ V, $J_{sc} = 17.22$ mA/cm², the fill factor = 0.641, and an energy conversion efficiency as high as 7.73%.

Conflict of Interests

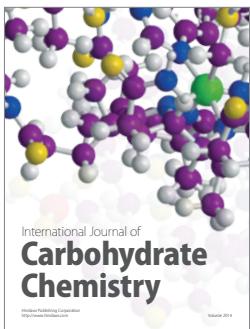
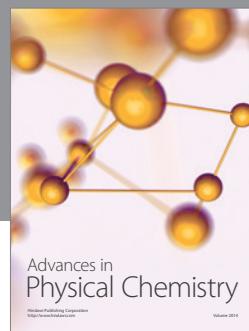
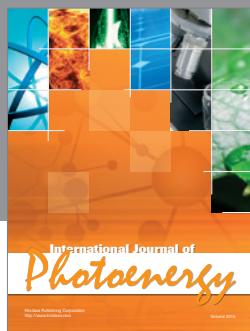
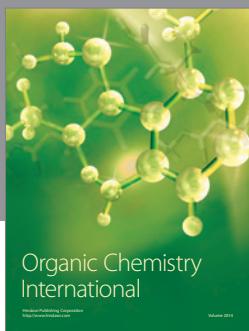
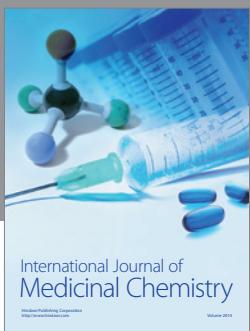
The authors declare that there is no conflict of interests regarding the publication of this paper.

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