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RESEARCH ARTICLE

Modification of Dye-Sensitized Solar Cells With Sputter-Deposited Titanium Dioxide Blocking Layer for Enhanced Photovoltaic Performance Under Different Illuminations

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ABSTRACT In this study, the titanium dioxide (TiO_2) thin film prepared by radio frequency magnetron sputtering system (R.F. sputtering) was used as the blocking layer (BL) of DSSCs. TiO_2 blocking layer (TBL) is used to reduce the recombination reaction caused by contacting the oxidized electrolyte with the fluorine-doped tin oxide (FTO) substrate through the active layer with porous structure. We analyzed the effect of TBL introduction on the electrochemical impedance between photoanodes by potentiostat and calculated the electron lifetime, which proved that TBL can effectively improve the process of electron transfer. In addition, the direct impact of TBL on the photovoltaic performance of DSSC was determined through the quantum efficiency (QE) measurement system and current density-voltage (J-V) measurement system, and it was found that the short-circuit current density (J_{SC}), external quantum efficiency (EQE), fill factor (FF) and photoelectric conversion efficiency (PCE) were all improved. DSSCs with TBL also exhibited better performance under low illumination due to the reduced recombination reaction. Further improves the applicability of DSSCs under low illumination.

INDEX TERMS Titanium dioxide, R.F. sputtering, dye-sensitized solar cells, blocking layer, recombination.

I. INTRODUCTION

With the development of science and technology, the global demand for energy is increasing year by year, and carbon emissions are also increasing. Although energy consumption has shown a slight downward trend due to the impact of the coronavirus disease since 2019 (COVID-19) and changes in workplaces have also shifted energy demand from commercial buildings to homes, the baseload power consumption of idle spaces during the epidemic is still quite high [1]. In recent years, people have paid more and more attention to environmental protection, how to reduce carbon emissions and meet the increasing energy demand is still an urgent problem. The application of solar photovoltaics provides an effective solution.

The continuous increase in the installed capacity of solar components shows that countries attach importance to the development of solar energy [2]. Systematic power generation devices based on solar energy are also emerging [3]. The research on photovoltaic components and their derived component aging issues are also considered more comprehensively [4]. All of these provide effective ways to improve photoelectric conversion efficiency (PCE). In addition, the conversion efficiency of the solar cell itself is equally important. Since the appearance of solar cells in 1883, various structures have been developed. Silicon-based solar cells,

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the most mature solar cells [5], dye-sensitized solar cells (DSSCs) with the lowest cost [6], and perovskite solar cells with high potential [7], all have their own advantages and disadvantages. Among them, DSSC is irreplaceable in many solar cells because of their low cost [8], non-toxicity [9], colorfulness [10], excellent chemical stability [11], and can still show excellent PCE under low light intensities and different illumination angles [12].

Since Grätzel developed the DSSC with titanium dioxide (TiO_2) in 1991, a large number of researchers around the world have invested in research [13]. However, the PCE is lower than the theoretical expectation and the use of scarce metals makes the development of DSSCs encounter difficulties [14], [15]. With the development of nanotechnology, this problem has gradually been improved. Including improving the light utilization rate, dye adsorption capacity, and electron transfer efficiency of the photoanode by using nano-core/shell [16], nanosheet [17], nanowire [18], and nanotubes [19]. And use various molding techniques and emerging materials to prepare counter electrodes to reduce costs and improve stability. Even a variety of integrated components have been developed based on DSSCs. All have made significant contributions to the development of DSSCs. However, the photoanode adopts a porous structure in order to be able to absorb dye molecules, which will make the oxidized electrolyte to have a chance to produce a recombination reaction through the contact of the photoanode with the conductive substrate [20]. This will affect various photovoltaic performances such as external quantum efficiency (EQE) and short-circuit current density (J_{SC}). Therefore, while increasing the positive reaction, how to reduce the occurrence of the reverse reaction cannot be ignored.

In this study, we tried to prepare a TiO_2 blocking layer (TBL) on a fluorine-doped tin oxide (FTO) substrate using the radio frequency magnetron sputtering system (R.F. sputtering). Compared to the conventional titanium tetrachloride ($TiCl_4$) method, the sputtering process offers a safer alternative by eliminating the need for hazardous $TiCl_4$ chemical handling during preparation. Additionally, this technique enables one-time deposition of large-area and uniform thin films with higher reproducibility. It also provides precise control over film thickness, enhancing efficiency and versatility for various applications. Our goal is to inhibit electrolyte-substrate contact to reduce recombination reactions without significantly compromising FTO substrate light transmittance, thereby enhancing the power conversion efficiency (PCE) of the DSSC under different illuminations. Despite the higher initial cost of using sputtering technology is higher, the long-term benefits in safety, performance, and applicability make sputtering a promising choice for TiO_2 TBL preparation.

The organization of this article is as follows. In Section II, we present the methods and parameters used for the preparation of TBL and DSSC. Moving on to Section III, we first analyze the characterization and chemical composition of the TBL, followed by investigating the influence of TBL incorporation on the impedance of DSSC and its external quantum efficiency under different wavelengths using a potentiostat and a quantum efficiency analysis instrument. Subsequently, we evaluate the photovoltaic performance of the TBL-incorporated DSSC under various illumination conditions using a solar simulator and filters. Section IV then summarizes how TBL positively impacts the performance of DSSC, emphasizing the advantages of using sputtering deposition for TBL fabrication.

II. EXPERIMENTAL

A. MATERIAL

Fluorine-doped tin oxide (FTO) glass (∼7 Ω/ square) and acetylacetonate (ACAC, 99 %) were purchased from Sigma-Aldrich, United States. TiO_2 nanoparticles P25 (∼25 nm, 99 %) and P90 (∼20 nm, 80 % anatase, 20 % rutile) were purchased from UniRegion Bio-Tech, R.O.C. The platinum (Pt) target (99.99 %) and TiO_2 (99.99%) for sputtering were purchased from Ultimate Materials Technology Co., R.O.C. The organic sensitized dye was N719, and was purchased from Solaronix, Aubonne, Switzerland. Triton X-100 PRS was purchased from Panreac & Applichem, Spain. The iodine electrolyte (EL-200) was purchased from Everlight Chemical Industrial Co., Ltd, R.O.C.

B. PREPARATION OF THE TIO_2 BLOCKING LAYER AND PT COUNTER ELECTRODE

The TBL was deposited on FTO by a radio frequency magnetron sputtering (R.F. sputtering) system. At first, FTO glass was cleaned using standard procedures, and covered the electrode area with heat-resistant tape (kapton polyimide) as a mask. Then we transferred the FTO to the chamber of the R.F. sputtering system. The chamber is evacuated to a high vacuum (3×10^{-6} Torr) to ensure a clean process environment, and the flow rate of argon and oxygen of 10:1 (sccm) is introduced into the chamber. Then control the butterfly valve to make the chamber pressure reach 3 mTorr to provide a suitable environment for forming a thin film for the TiO_2 molecules sputtered from the target. Finally, argon atoms are dissociated with a power of 60 watts. Then TiO_2 molecules are sputtered by the dissociated argon ions hitting the TiO_2 target. After TiO_2 molecules were deposited for 10 minutes on the FTO substrate heated to 250°C, we annealed the TiO_2 film at 450 °C for 30 minutes. The preparation of the TBL is completed. Using the same process, change the target material to Pt, the process pressure was changed to 10 mTorr, and introduce argon gas with a flow rate of 10 sccm. After Pt molecules were deposited for 8 minutes on the FTO substrate, the Pt counter electrode can be fabricated.

C. PREPARATION OF THE COLLOIDAL

The colloid of the active layer was prepared by mixing 3 g of P25, 6 mL of deionized (D.I.) water, 50 μL of ACAC, and 150 μL of Triton X-100, and stirring for 24 hours. Finally, the colloid preparation was completed after 24 hours of aging. For the scattering layer colloids. The paste consists of 1 g of P25 (∼25 nm), 0.4 ml of absolute ethanol, and 4 ml of D.I. water. Next, the paste was magnetically stirred at 500 rpm at room temperature for 24 hours until a uniform paste was obtained.

D. FABRICATION OF THE DYE-SENSITIZED SOLAR CELL

The composition of the DSSC in this study includes TBL, an active layer, a scattering layer, an electrolyte, and a catalytic layer, as shown in Fig. 1. On the prepared TBL, a heat-resistant adhesive tape was used as a mask to limit the working area to 0.25 cm^2. Then we dripped 15 μL of active layer colloid on the working area and spin-coating with the rotating speed of 1500 rpm (11 sec) and 2500 rpm (15 sec), then dried in the oven at 100 °C for 30 seconds. After completing the preparation of the active layer, we prepared the scattering layer on the active layer by the doctor blade method to increase the light utilization rate for DSSC. Next, we annealed the photoanode at 450 °C for 30 minutes with a furnace tube and soaked it in the N719 ruthenium dye for 24 hours to absorb the dye molecules. Finally, the photoanode and the catalytic layer (Pt) are bonded by the Surlyn film, and the electrolyte is injected between the two electrodes to complete the DSSC fabrication.

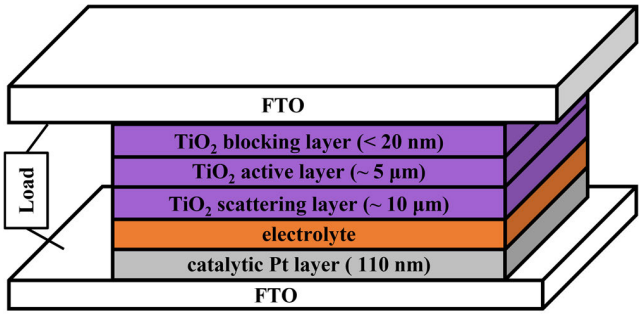

FIGURE 1. The assembled photo of DSSCs structure with TiO_2 blocking layer.

E. MEASUREMENT SYSTEM

The elemental composition of the TBL was determined by X-ray photoelectron spectroscopy (PHI 5000 Versa Probe III, ULVAC, Inc., Japan) and analysis of the crystalline structure of the TBL was completed by X-ray diffractometer (advance-D825A, Bruker, United States), using Cu Kα radiation (1.5418Å). The field emission scanning electron microscope (FE-SEM, JSM-7610FPlus, JEOL, Ltd., Japan) enabled observation of the morphology of the TBL. After that, it was possible to measure the EQE of the DSSC with TBL, using a quantum efficiency system (QE-R, Enlitech, Co., Ltd., R.O.C). Finally, cyclic voltammetry apparatus (SP-150 Potentiostat, BioLogic, France) was employed to measure the electrochemical impedance and electron lifetime of the DSSCs. The photovoltaic parameters of DSSC were measured under a standard light source by using the solar cell efficiency measurement system (MFS-PV-Basic, HMT, Ltd., R.O.C)

III. RESULT AND DISCUSSION

A. MORPHOLOGY ANALYSIS OF THE TIO_2 BLOCKING LAYER

We used a field emission scanning electron microscope (FE-SEM) to observe whether the TiO_2 blocking layer (TBL) was successfully prepared on the FTO substrate, as shown in Fig. 2. According to the micrograph, we can observe the larger crystals belonging to the FTO substrate, but it is difficult to observe the grain of TiO_2. This is because the TBL must be sufficiently thin not to affect the light transmittance of the photoanode as much as possible, which also makes the grain of TiO_2 films over the observable limit of FE-SEM. However, we can also verify the existence of TBL by other methods. Through Energy-dispersive X-ray (EDX) mapping analysis, we can observe that Ti elements are evenly distributed on the surface of FTO, as shown in Fig. 3 [21]. From this result, we can preliminarily confirm the existence of TBL. In order to further confirm the chemical composition of TBL, we also performed an X-ray photoelectron spectroscopy analysis on the TBL film.

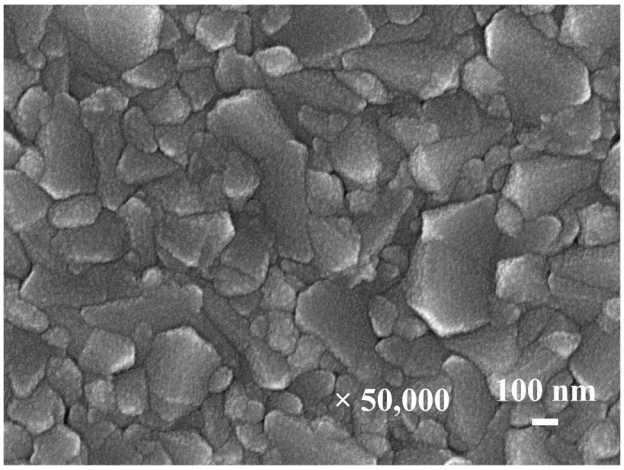

FIGURE 2. The SEM micrograph of the TiO_2 blocking layer of FTO substrate.

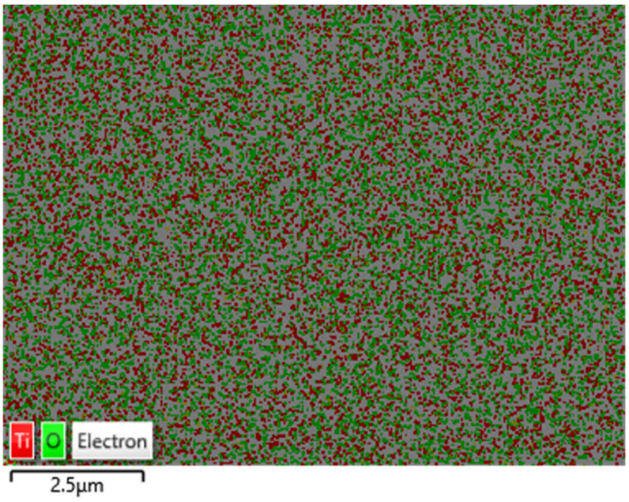

FIGURE 3. The EDX mapping pattern of the TiO_2 blocking layer.

B. XPS SPECTRUM ANALYSIS OF THE THE TIO_2 BLOCKING LAYER

Figure 4 and Fig. 5 show the X-ray photoelectron spectroscopy (XPS) patterns of TBL. From Fig. 4 we observe two

main peaks at 457.6 eV and 463.5 eV represent the binding energies of the Ti $2p_{1/2}$ and Ti $2p_{2/3}$, respectively. These two peaks represent the bonding energy of Ti^{4+} to oxygen ions, which also represents the binding energy of TiO_2 [22]. In addition to these two peaks, we can also observe the Ti $2p_{1/3}$ shoulder peak at an energy of 458.4 eV, which means that TBL may contain compounds formed by bonding with Ti^{3+} and even indicates that there may be a small amount of Ti_2O_3 in TBL [22].

After splitting the peak of O1s in Fig. 5, we can observe that the peak of O1s is mainly composed of two peaks. The existence of the peak located at 528.8 eV can be attributed to the bonding of oxygen ions to titanium ions, while the peak at the binding energy of 529.9 eV represents the oxygen in hydroxyl groups [23]. By integrating the curves in Fig. 4 and Fig. 5, we can calculate that the oxygen element accounts for 64.19% and the titanium element accounts for 34.80% of the TBL we prepared. Furthermore, according to Fig. 4, we found that the peak of tetravalent titanium is much larger than that of trivalent titanium. Although TBL has the possibility of TiO_2, it can be confirmed that TBL is mainly composed of TiO_2.

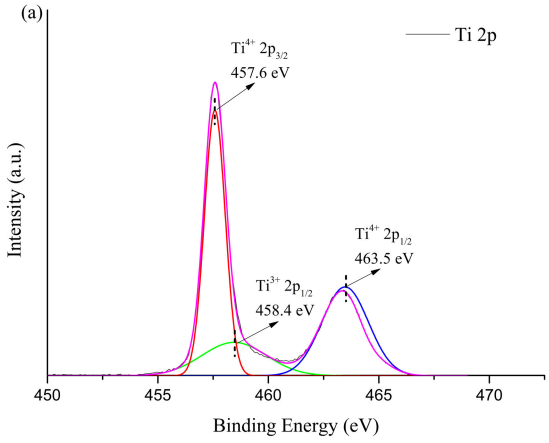

FIGURE 4. The XPS pattern of the Ti 2p double core level of the TiO_2 blocking layer.

C. XRD PATTERN OF THE TIO_2 BLOCKING LAYER

The crystal structure of TBL was confirmed by grazing incidence X-ray diffraction (GIXRD). The diffraction peaks of TBL are located at 25.38° (101), 37.90° (004), 48.12° (200), 54.02° (105), 55.15° (211), 62.80° (204), 68.93° (116), 70.38° (220), and 75.18° (215), which are consistent with the anatase TiO_2 standard card JCPDS 21-1272, as shown in Fig. 6. This result proves that TBL is anatase TiO_2 [24]. Although many studies still have different opinions on the energy gap of each crystal phase of TiO_2, it is a common result that anatase has a larger band gap than rutile [25]. This also represents that anatase does have a greater light transmittance than rutile. The higher light transmittance makes the incident light retain a wider range of wavelengths and more energy when it penetrates the TBL and makes the photoanode obtain more energy to excite the dye molecules, which avoids

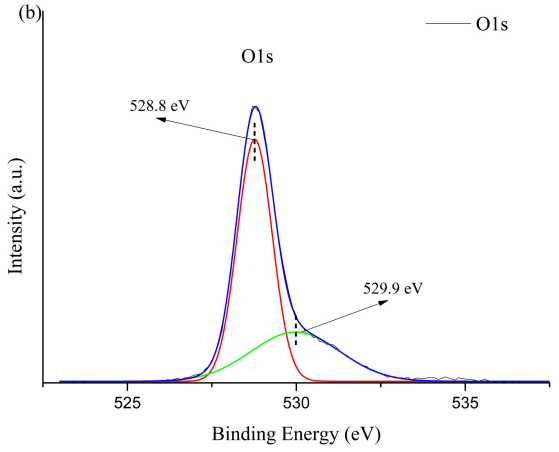

FIGURE 5. The XPS pattern of the O1s core level of the TiO_2 blocking layer.

the loss of J_{SC} and EQE [26]. Therefore, it may be a better choice to use anatase structure as TBL than rutile.

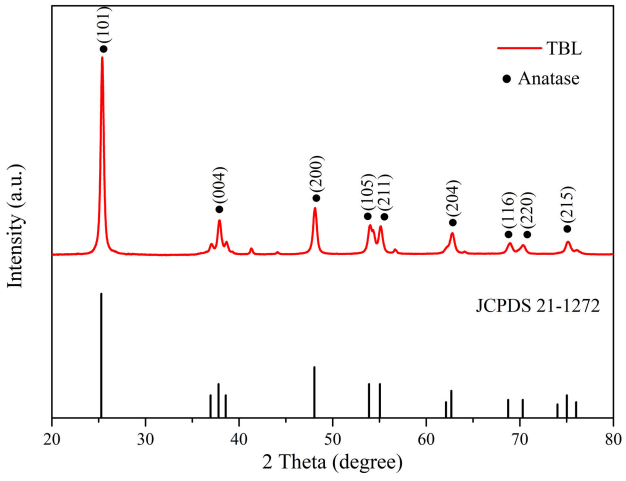

FIGURE 6. The XPS pattern of TiO_2 blocking layer and the standard card of anatase TiO_2.

D. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF THE DSSCs

In order to analyze the effect of adding TBL on the photoanode interface of DSSCs. We measured the change of electrochemical impedance of DSSC by potentiostat. First, a simple equivalent circuit model is established to represent the electrodes of the DSSC, as shown in Fig. 7. R_S represents the line resistance and FTO sheet resistance; R_1 and C_1 represent the electron transfer impedance and interface capacitance of the counter electrode, respectively; R_2 and C_2 represent the electron transfer impedance and interface capacitance of the photoanode, respectively. After applying small alternating current (AC) potentials of different frequencies to the DSSC by the potentiostat, we measured the impedance variation of the system with the frequency of the sine wave, as shown

in Fig. 8. We observe that there is a line segment in the high-frequency region that has only the real quantity, which is R_S.

There is also a small semicircle in the high-frequency area, which represents R_1, and a big semicircle in the low-frequency area represents R_2. From this Nyquist plot, we can determine that adding TBL significantly changed the impedance of photoanodes, but not R_1, which shows the addition of TBL does not affect the electron transfer resistance of the counter electrode. From Table 1, it can be found that adding TBL effectively reduces R_2, which can be attributed to the reduction of the electrolyte contact with the FTO substrate by TBL [27]. A recombination reaction occurs when the oxidized electrolyte comes into contact with electrons that diffuse from the conduction band of the active layer TiO_2 to the FTO substrate. Therefore, the addition of TBL greatly reduces the probability of the recombination reaction and reduces the electron transfer resistance of the photoanode, which decreases from 77.40 Ω to 45.93 Ω. In addition, we can know the relationship between the frequency and phase of the DSSC system through the Bode plot, as shown in Fig 9. Based on the Bode plot, we can also calculate the effective electron lifetime of the photoanode by formula (1) [28].

$$\tau_{eff} = \frac{1}{2\pi f} \tag{1}$$

where τ_{eff} is the effective electron lifetime, and f is the frequency of the peak. The results in Table 1 indicate that TBL helps to increase the photoanode electron lifetime from 13.36 ms to 29.21 ms. The higher electron lifetime further confirms the conjecture that TBL can suppress the recombination reaction. The reduction of transfer resistance and the improvement of electron lifetime will make the electron diffusion more efficient and thus improve the EQE and J_{SC} [29]

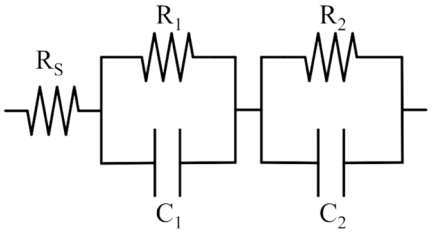

FIGURE 7. Equivalent circuit diagram of the DSSC internal conduction.

E. EXTERNAL QUANTUM EFFICIENCY

The external quantum efficiency (EQE) represents the number of electrons that the external circuit can obtain after the DSSC receives a photon incident. By measuring the EQE, we can easily understand the excitation conditions of the dye molecules of the photoanode under the incident light of different wavelengths. In Fig. 10, we can observe a peak at wavelength 540 nm. This is the absorption peak of N719 dye, which means that the dye molecule is excited with the most electrons at this wavelength [30]. Under the excitation of

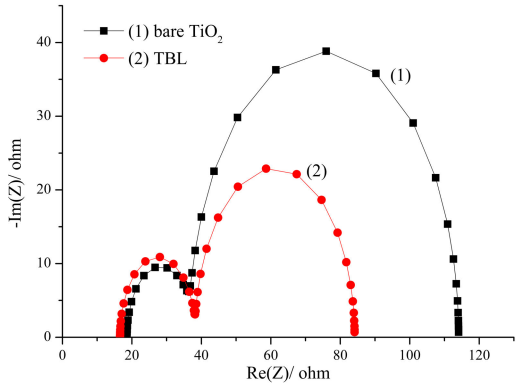

FIGURE 8. The Nyquist plots of the DSSC with different photoanodes.

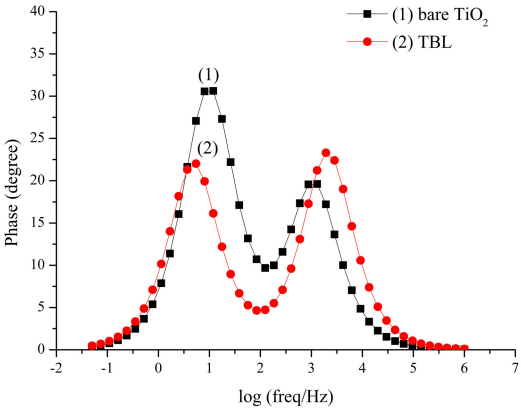

FIGURE 9. The Bode plots of DSSC with different photoanodes.

TABLE 1. Measurement of the DSSC electrochemical impedance for different photoanodes.

Photoanodes		R_S (Ω)	R_1 (Ω)	R_2 (Ω)	τ_{eff} (ms)
(1)	Bare TiO_2	18.59	18.09	77.40	13.36
(2)	TBL	16.60	19.11	45.93	29.21

TiO_2, titanium dioxide; TBL, TiO_2 blocking layer; τeff, effective electron lifetime

incident light with a wavelength of 540 nm, the DSSC with TBL exhibits superior EQE compared with bare TiO_2. This result can be attributed to the suppression of the recombination reaction by TBL, which makes more electrons efficiently reach the external circuit through the diffusion process without recombining with the electrolyte holes [31]. At the same time, it also means that DSSC with TBL will have a better J_{SC} than that with bare TiO_2. We can verify this idea from photovoltaic parameter measurements.

F. PHOTOVOLTAIC PARAMETER MEASUREMENT

DSSCs are used as power devices, and measuring their photovoltaic characteristics is the most intuitive way to judge

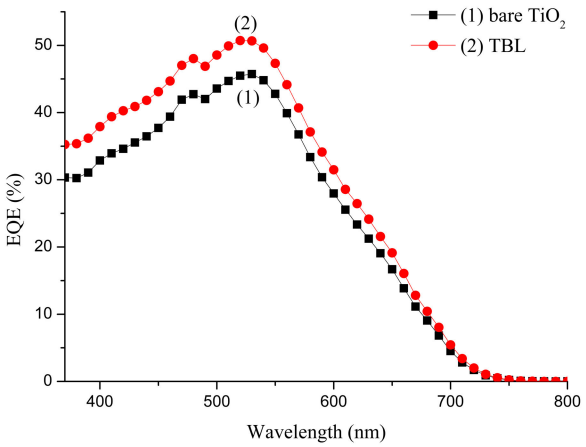

FIGURE 10. The external quantum efficiency of the DSSC at each wavelength.

their performance. We use a solar simulator to irradiate the DSSC with the Air Mass 1.5 Global (100 mW/ cm^2) standard spectrum and use 80 %, 50 %, 30 %, and 10 % filters to simulate the situation that the DSSC is under different illumination. The relationship between the DSSC output current and voltage we measured is shown in Fig 11 and Fig 12. From these two figures, we can find that as the incident light decreases, the J_{SC} decreases significantly. This is because the reduced energy of the incident light passing through the filter is only enough to excite the electrons of some dye molecules. However, from Table 2 we can find that the DSSC with TBL exhibits greater J_{SC} than the DSSC with bare TiO_2 no matter what the illumination is. Electrochemical impedance spectroscopy (EIS) and EQE measurements can well explain this result. The presence of the TBL suppresses the losses caused by the recombination of electrons with holes of the electrolyte when they diffuse to the FTO substrate. And also makes more electrons smoothly output to the external circuit to increase the J_{SC} of DSSC from 9.27 mA/ cm^2 to 10.11 mA/ cm^2. Moreover, the J_{SC} decay of DSSC with TBL is only 84.81 % when the light intensity is 10 mW/ cm^2 lower than 88.99 % with bare TiO_2, which can attribute to the longer electron lifetime [32]. We can also determine the effect of adding TBL on DSSC by the change of open circuit voltage (V_{OC}), in which V_{OC} represents the gap between the quasi-fermi level of the photoanode and the redox potential of the electrolyte [33]. We found that the V_{OC} of DSSCs with TBL was equal to or slightly higher than that of bare TiO_2 under all illumination conditions. This may be attributable to the increased electron concentration at the photoanode due to the addition of TBL, which the higher the electron concentration, the higher the quasi-Fermi level [34]. With the reduction of illumination and the reduction of photogenerated electrons, the V_{OC} of DSSC with bare TiO_2 ushers in a significant decrease when the incident light intensity is 10 mW, which the V_{OC} of bare TiO_2 decreases from 0.75 V to 0.67 V and the V_{OC} of DSSC with TBL decreases from 0.75 V to 0.70 V. However, the DSSC with TBL keeps the photoanode electron concentration relatively stable due to its longer effective electron lifetime, resulting in no significant decrease in V_{OC}. Fill factor (F.F.) is defined as the ratio of maximum power to J_{SC} times V_{OC}. From the perspective of power devices, a higher F.F. represents that the DSSC has a more stable output curve under different external circuits. From Table 2, we found that whether it is DSSC with TBL or bare TiO_2, FF will decrease with the increase of illumination, which can be attributed to the charge recombination rate will increase with the increase of photogenerated electrons [35]. This is also the reason why DSSCs are suitable for low-light conditions. Although the FF will increase due to the reduction of illumination, the recombination reaction still exists. Therefore, TBL can reduce the recombination reaction and still make the DSSC with TBL exhibit better FF than bare TiO_2 under each illumination intensity [36].

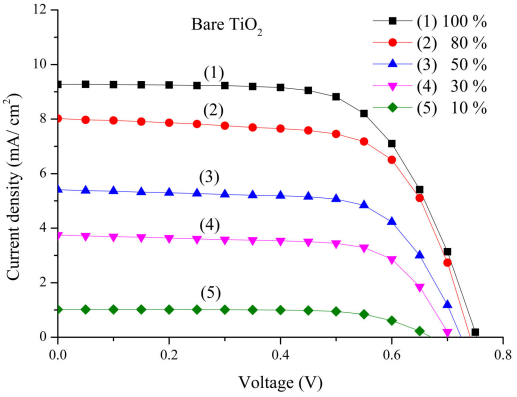

FIGURE 11. The J-V curves of the DSSC with bare TiO_2 under different illuminations.

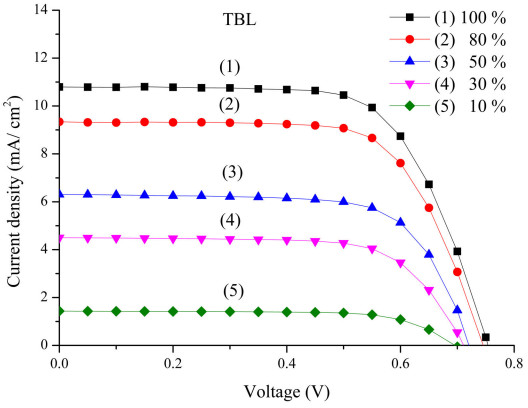

FIGURE 12. The J-V curves of the DSSC with TBL under different illuminations.

Furthermore, the applicability and photovoltaic performance of DSSC under low illumination are undoubtedly important and worth exploring, which involves the potential of DSSC commercialization [37]. We assessed the photovoltaic performance of the DSSCs under indoor illumination using T5 fluorescent lighting and optical filters. It is important to note that the spectral distribution of T5 fluorescent lighting differs from that of sunlight, resulting in a power

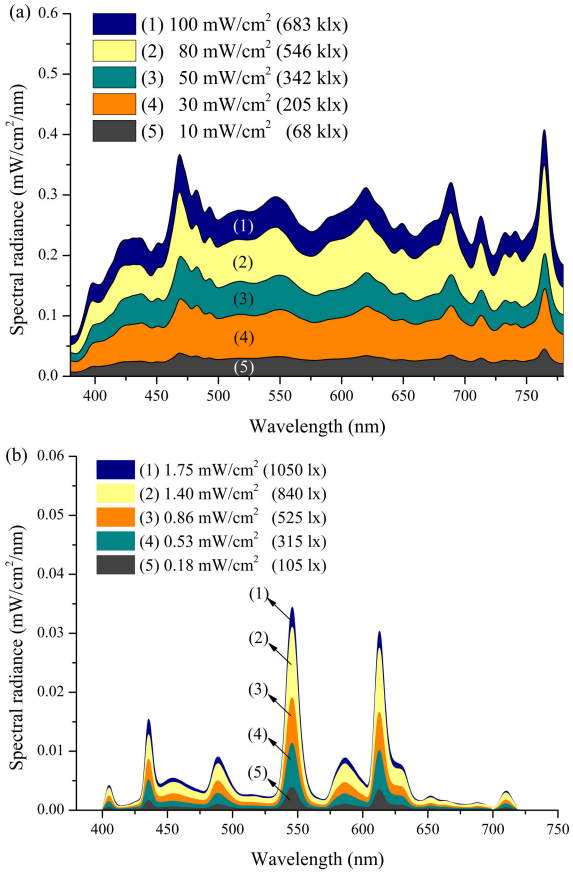

FIGURE 13. The spectra of the different light sources. (a) Xenon lamp (AM 1.5G), (b) T5 fluorescent lamp.

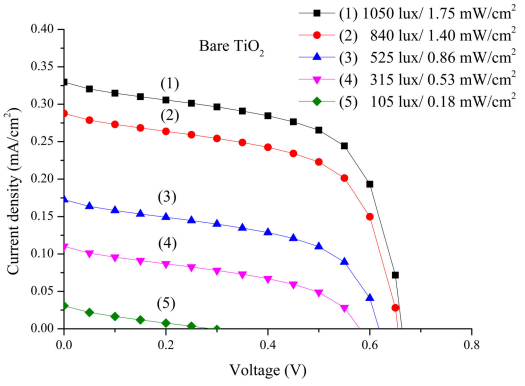

FIGURE 14. The J-V curves of the DSSC with TBL under different illuminations.

density of only 60 lux for 1 W/m^2, whereas the same power density in sunlight corresponds to 683 lux per square meter. The spectra of both are shown in Fig. 13(a) and Fig. 13(b). J-V curves under T5 fluorescent lighting were represented by Fig. 14 for bare TiO_2 and Fig. 15 for DSSC with the TBL. The summarized photovoltaic parameters can be found in Table 3. Remarkably, the effect of the TBL was more pronounced under T5 fluorescent lighting. DSSCs with the TBL exhibited a remarkable increase in J_{SC} by over 100% compared to

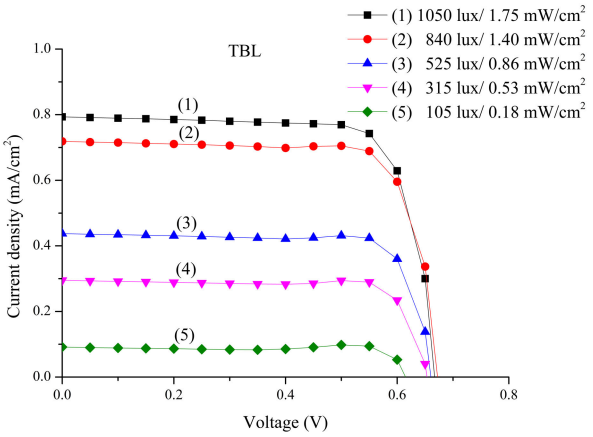

FIGURE 15. The J-V curves of the DSSC with TBL under different illuminations.

DSSCs with bare TiO_2 at various illuminance levels. Additionally, the decay of V_{OC} with decreasing illuminance was more gradual for DSSCs with the TBL. Moreover, the FF of DSSCs with the TBL displayed an increasing trend as illuminance decreased, while the FF of bare TiO_2 decreased. These results further affirm the ability of the TBL to suppress electron-hole recombination and underscore its remarkable effectiveness in indoor environments. Overall, the incorporation of the TBL in DSSCs yields improvements in J_{SC} and FF under AM 1.5G conditions, resulting in an enhanced power conversion efficiency (PCE) of 5.16% compared to 4.51% without the TBL. The TBL also contributes to a more stable V_{OC} and larger FF, particularly evident at an illuminance of 10 mW/cm^2, where the PCE of the DSSCs increases by 39.2%. Notably, at an illuminance of 0.18 mW/cm^2, the TBL enables a staggering 28.49-fold increase in PCE. These findings highlight the effectiveness of the TBL in mitigating electron-hole recombination and its potential for enhancing the practical application of DSSCs in various lighting conditions.

Moreover, in the research of Huang et al. [38] and the research of Mustafa et al. [39], the compact layer was prepared by liquid phase deposition (LPD) and electrospinning (ES) respectively. They also improved photovoltaic performance by suppressing the recombination reaction between the electrolyte and the conductive substrate. However, although the process of liquid deposition is simple, it inevitably requires the use of precursor materials with high risks. Electrospinning technology can prepare a large number of nanofibers in a short time and stack them to form thin films. However, due to process limitations, the film prepared by electrospinning will be thicker. This will likely affect the light penetration of the blocking layer under low illumination. In this study, the blocking layer was prepared using sputtering technology, which not only eliminates the need for toxic precursors but also demonstrates excellent photovoltaic performance under low illumination. Furthermore, in comparison to our research team previous work published in 2022 [29] on the preparation of a zinc oxide (ZnO) blocking layer using sputtering, it is noted that DSSCs with TiO_2 blocking layers exhibit a slightly lower J_{SC} due to limitations in charge

TABLE 2. Photovoltaic parameters of the DSSCs under different illuminations'.

Intensity (mW/cm^2)/ Lux (K lx)	Photoanodes	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	η (%)	Ref.
~100/ ~200.0	Bare TiO_2	9.27	0.75	64.17	4.51	This study
	TBL	10.11	0.75	67.13	5.16	This study
	LPD-TiO_2 CL	11.50	0.75	60	5.24	[38]2019
	ES-TiO_2 CL	9.79	0.58	54	3.06	[39]2020
	ZnO	11.29	0.74	63.11	5.27	[40]2022
~80/ ~160.0	Bare TiO_2	8.02	0.74	66.40	4.76	This study
	TBL	8.75	0.75	68.50	5.38	This study
~50/ ~100.0	Bare TiO_2	5.41	0.72	67.86	5.02	This study
	TBL	5.90	0.72	69.65	5.59	This study
~30/ ~60.0	Bare TiO_2	3.75	0.70	68.65	5.17	This study
	TBL	4.21	0.71	69.54	5.95	This study
~10/ ~20.0	Bare TiO_2	1.02	0.67	69.24	4.31	This study
	TBL	1.34	0.70	70.73	6.00	This study

[a] J_{SC}: short-circuit current density; V_{OC}: open-circuit voltage; FF: fill factor; η: photoelectric conversion efficiency
TiO_2, titanium dioxide; TBL, TiO_2 blocking layer; CL, compact layer; LPD, liquid phase deposition; ES, electrospinning

TABLE 3. Photovoltaic parameters of the DSSCS under T5 fluorescent lamp.

Intensity (mW/cm^2)/ Lux (lx)	Photoanodes	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)	Ref.
~1.75/ ~1050	Bare TiO_2	0.33	0.67	0.61	7.72	This study
	TBL	0.79	0.67	0.76	23.33	This study
~1.40/ ~840	Bare TiO_2	0.29	0.65	0.59	8.02	This study
	TBL	0.72	0.68	0.77	26.23	This study
~0.86/ ~525	Bare TiO_2	0.17	0.62	0.51	6.30	This study
	TBL	0.44	0.67	0.79	26.63	This study
~0.53/ ~315	Bare TiO_2	0.11	0.58	0.42	5.14	This study
	TBL	0.29	0.66	0.81	30.36	This study
~0.18/ ~105	Bare TiO_2	0.03	0.29	0.20	1.02	This study
	TBL	0.09	0.63	0.91	30.08	This study

[a] J_{SC}: short-circuit current density; V_{OC}: open-circuit voltage; FF: fill factor; PCE: photoelectric conversion efficiency; TiO_2, titanium dioxide; TBL, TiO_2 blocking layer

carrier mobility. However, the use of TiO_2 as a blocking layer addresses the issue of ZnO susceptibility to acid corrosion from the electrolyte, thus improving the long-term stability of DSSCs without a substantial compromise on their photovoltaic performance.

By adopting the sputtering method for the blocking layer preparation, this research offers a promising alternative for enhancing DSSC performance while resolving the stability concern related to ZnO vulnerability to electrolyte acid corrosion. It establishes a new reference for future blocking layer preparation methods.

IV. CONCLUSION

In this study, we confirmed that the sputtering technique to prepare TiO_2 blocking layer (TBL) is effective. The existence of the TBL reduces the probability of recombination reaction between the oxidized electrolyte and the electronic contact

on the FTO substrate, which decreases the electron transfer resistance (R_2) and increases the electron lifetime (τ_{eff}) of the photoanode. At the same time, due to the reduction of electron loss, the addition of TBL also improves the short-circuit current density (J_{SC}) and photoelectric conversion efficiency (PCE), in which PCE increase from 4.51 % to 5.16 %. TBL not only exhibits better performance under AM 1.5G but also can further improve the open circuit voltage (V_{OC}) and fill factor (F.F.) by suppressing the recombination effect under low illumination. Applicability to low illumination as an important feature of DSSC, the improvement of V_{OC} and FF is undoubtedly positive of DSSC, which makes PCE increase from 4.31 % to 6.00 %. In addition, compared with liquid phase deposition (LPD) and electrospinning, sputtering technology can avoid the use of toxic precursors and produce a thinner blocking layer that does not affect the light transmittance of the photoanode. It provides an effective method for the manufacture of blocking layers applied to low illumination.

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