

Article

Ultrathin TiO₂ Blocking Layers via Atomic Layer Deposition toward High-Performance Dye-Sensitized Photo-Electrosynthesis Cells

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Abstract: The collection of solar energy in chemical bonds via dye-sensitized photoelectrosynthesis cells (DSPECs) is a reliable solution. Herein, atomic layer deposition (ALD) introduced ultrathin blocking layers (BLs) between a mesoporous TiO₂ membrane and fluorine-doped tin oxide (FTO), and much improved photoelectrochemical water oxidation performance was well documented. Samples with different BL thicknesses deposited on FTO were obtained by ALD. In the photoanode, polypyridyl Ru(II) complexes were used as photosensitizers, and Ru(bda)-type was used as a catalyst during water oxidation. Under one sun irradiation, the BL (i) increased the photocurrent density; (ii) slowed down the open-circuit voltage decay (OCVD) by electrochemical measurement; (iii) increased the photo-generated electron lifetime roughly from 1 s to more than 100 s; and (iv) enhanced the water oxidation efficiency from 25% to 85% with 0.4 V of applied voltage bias. All this pointed out that the ALD technique-prepared layers could greatly hinder the photogenerated electron-hole pair recombination in the TiO₂-based photoanode. This study offers critical backing for the building of molecular films by the ALD technique to split water effectively.

Keywords: photoelectrocatalysis; dye-sensitized photo-electrosynthesis cells; water oxidation; blocking layers; atomic layer deposition



Citation: Zhang, X.; Lei, L.; Wang, X.; Wang, D. Ultrathin TiO₂ Blocking Layers via Atomic Layer Deposition toward High-Performance Dye-Sensitized Photo-Electrosynthesis Cells. *Sustainability* **2023**, *15*, 7092. <https://doi.org/10.3390/su15097092>

Academic Editor: Alberto Ferraro

Received: 10 March 2023

Revised: 2 April 2023

Accepted: 21 April 2023

Published: 23 April 2023



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1. Introduction

Artificial photosynthesis is very promising for storing solar energy in chemical bonds, but higher efficiencies are heavily required for large-scale practice [1]. Dye-sensitized photoelectrosynthesis cells (DSPECs) are similar to the chemical concepts of dye-sensitized solar cells (DSCs) in the conversion of light to electricity [2–4]. However, DSPECs employ light-harvesting architectures and materials with small chromophore-catalyst molecular assemblies [5,6] oriented to wide-gap semiconductor oxides, such as NiO, SnO₂, or TiO₂ [7–9]. This apparatus generates one oxygen and four H⁺ at the photoanode after four cycles of photon absorption. To drive water oxidation, suitable catalysts and chromophores can be assembled on the electrode surface through a co-assembly method for the DSPEC photoanode [10,11].

Nonetheless, photo-generated holes recombined with electrons at photoanode matrix interfaces are still a major barrier to efficient DSPEC water splitting [12,13]. To achieve perfect photo-generated charge collection in the device, it is crucial to prevent charge recombination, which can occur at either the FTO/oxide interface or the oxide/catalyst dye interface. In order to achieve this, 100% of the photoexcited electrons from the irradiated dye must be injected into the supportive mesoporous metal oxide film before being delivered to the substrate FTO [14]. One effective method to suppress charge recombination is to introduce energy barriers through ALD cycles, thus increasing the physical separation

distance between photoinjected electrons and redox species in the electrolyte. Specifically, the layering structure and thickness of the thin film are altered by ALD technology. This dynamic suppression of recombination can reduce the charge residence time in titanium dioxide [15]. To prevent the electrolyte–FTO interface charge recombination, the FTO could be coated with an ultrathin oxide-blocking layer (BL). Under ideal conditions, the BL would be considerably thick, and it could swathe the FTO surface entirely to block charge leakage from the FTO into the electrolyte. However, it should also be considerably thin to preserve charges flowing from the supportive mesoporous TiO_2 film into the FTO. Given the advantages of ALD for ultrathin and high-quality BL generation, it is necessary to comprehend how the BL's thickness affects device performance. To date, few publications that detail the impact of the BL by ALD deposition on DSPEC water oxidation performance have been reported.

Thus, we proposed a novel strategy to boost DSPEC water oxidation. In the photoanode, a molecularly excited state is produced by the excitation of a chromophore that is attached to the oxide surface. Then, the chromophore's excited state is subjected to electron flow to a transparent oxide semiconductor, TiO_2 , which enables electron transmission to a cathode for proton reduction. The chromophore's oxidative equivalents are transferred intra-assembly directly to a molecular catalyst, where water oxidation ultimately takes place. Ru(II)pyridine-based complexes are often employed as the light-capturing chromophores during the fabrication of the chromophore-catalyst assembly owing to their visible absorption as well as their outstanding stability in water. Then they are adsorbed on TiO_2 films with water oxidation catalysts [16,17]. Figure 1 presents a schematic illustration of the FTO | BL | TiO_2 | Chrom-Cat electrode for DSPEC water oxidation.

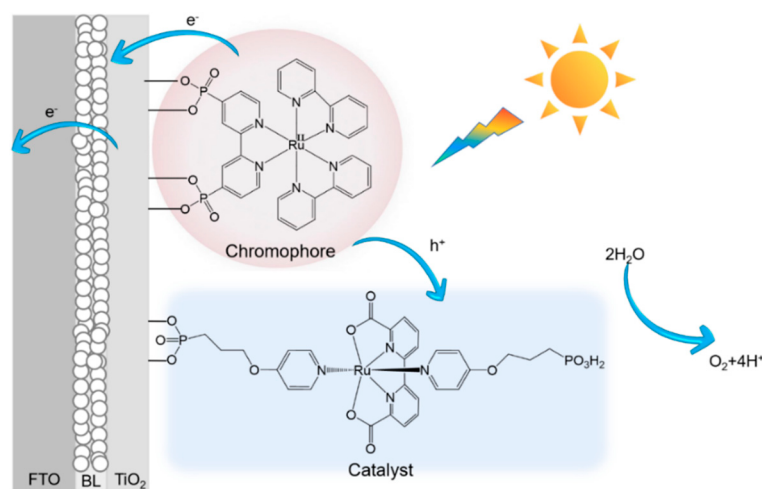
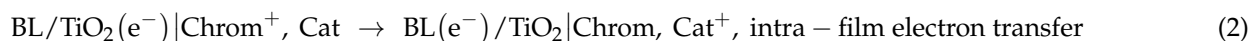


Figure 1. Schematic illustration of FTO | blocking layer | TiO_2 | chromophore | catalyst electrode for DSPEC water oxidation.

After being excited, the surface-bound chromophore transfers electrons to TiO_2 , followed by electron delivery from the mesoporous TiO_2 (BL) into the FTO. An exterior cathode accepts the photocurrent for proton generation, which is produced by electrons being extracted from the FTO at the back contact. The reaction process in the water oxidation stage can also be intuitively understood in Equations (1)–(3).



Herein, the TiO_2 BLs were successfully fabricated layer by layer onto the FTO by ALD, with the thickness precisely controlled at 50, 100, 200, 500, and 1000 cycles [18]. Additionally,

a control experiment was conducted without any BLs on the bare FTO substrate. TiO₂ mesoporous membranes were fabricated using the doctor-blading approach for loading catalysts and photosensitizers [19]. The chromophore-catalyst molecular assembly was synthesized and arrayed as reported [20,21]. Then, the surface roughness, thickness, and UV-vis transmission of the TiO₂ film were characterized; furthermore, the performance of the TiO₂ film in the DSPECs was carefully investigated and assessed. As a result, we found that an ultrathin (500 cycles) TiO₂ layer deposited by ALD was effective in enhancing the DSPEC short-circuit photocurrent (J_{sc}), open-circuit photovoltage (V_{oc}), incident photon-to-current efficiency (IPCE), and the evolution of O₂. Finally, the influence of the ALD in producing BL thickness on the open-circuit voltage decay (OCVD), and electron lifetime (τ_n) were also carefully studied. These promising conclusions provide a fresh perspective on the role of the ALD-produced BL in enhancing DSPECs' water oxidation performance and other relevant solar conversion systems.

2. Materials and Methods

2.1. Materials

Fluorine-doped tin oxide (FTO)-coated glass with a sheet resistance of 15 Ω cm⁻² and the TiO₂ paste were both purchased from Jinge Solar Energy Technology Co., Ltd., Wuhan, China. The ALD precursor was tetramethyl titanium (TDMAT, 99.994%), purchased from Sinorgchem Technology Co., Ltd., Jiangsu, China. RuP and catalyst were prepared according to previously published procedures [20,21]. RuCl₃ (99.97%) and diethyl 3-(pyridin-4-yloxy)propyl-phosphonate (97%) were obtained from Bide Pharmaceutical Technology Co., Ltd, Shanghai, China. and Kylpharm Co., Ltd., Shanghai, China, respectively. 4,4'-Dibromo-2,2'-bipyridine (97%) and 2,2'-bipyridyl-6,6'-dicarboxylic acid (97%) were obtained from Alpha Chemical Co., Ltd., Zhengzhou, China. The reagents mentioned were of analytical grade and were used without further purification unless otherwise stated.

2.2. Preparation of Samples

Pretreatment was required for the FTO conducting glasses used in this investigation, which included cleaning them with acetone, water, and ethanol solutions and sonicating them for 20 min each. FTO was cut into 1 × 3 cm² strips and acted as the substrate for depositing TiO₂ nanoparticle films. FTO conducting glasses were blown with nitrogen gas after being cleaned of any surface dirt.

Atomic layer deposition (ALD), which is used to prepare the blocking layer, has a lot of potential and reliability as a preparation procedure because of its good coverage and large area thickness homogeneity. ALD coating conditions were performed with a modification of the previously reported technique [18]. ALD was performed to prepare the TiO₂ mesoporous films on FTO glass in an ANRIC AT-410 reactor. Before the formal coating process, tetrakis(dimethylamido)titanium was preheated in its reservoir for an hour at 150 °C and 200 mtorr of N₂ carrier gas. The detailed steps in the process were as follows. The precursor, tetrakis(dimethylamido)titanium, was carried by inert gas and injected into the reaction chamber in a pulsed manner after a 3 s purge. The deposition conditions of the precursor were controlled to allow self-limiting surface chemical adsorption reactions to occur, resulting in the formation of new surface functional groups on the substrate surface. After the surface chemical adsorption reaction was complete, excess precursor A and reaction by-products were purged and removed by inert gas for 10 s, completing the first "half-reaction". Then, H₂O was introduced into the reaction chamber along with the carrier gas, purged for 2 s, and reacted with the surface functional groups generated from the first "half-reaction" until saturation was achieved. After purging the chamber for 10 s with inert gas to remove the remaining H₂O and reaction by-products, the second "half-reaction" was completed. The completion of one reaction cycle of ALD was achieved through the aforementioned steps. We created blocking layers of TiO₂ with 50, 100, 200, 500, and 1000 cycles.

The TiO₂ mesoporous membranes were coated on the blocking layers for adsorbing the catalyst and photosensitizer. The FTO with a size of $1 \times 3 \text{ cm}^2$ was fixed on the desktop with 3M tape and surrounded to $1 \times 1 \text{ cm}^2$. Then, the TiO₂ paste was evenly scraped using the scraper method onto the center of the FTO conductive glass, leaving a blank area, and the taped edges were removed after five minutes. The FTO was transferred to an oven and dried at 120 °C for 30 min, then naturally cooled to room temperature to ensure that the paste was completely dried. The FTO was placed into a muffle furnace with a heating program set at a rate of 2.5 °C/min until it reached 450 °C, maintained for 1 h at this temperature, and then naturally cooled to room temperature. Finally, the electrode was placed in a dryer for later use.

FTO|TiO₂|Ru^{II}P|Cat electrodes were fabricated to test the influence of the blocking layers on the behavior of water oxidation. The 10 mg catalyst and photosensitizer were separately dissolved in 20 mL of methanol and ultrasonically dispersed until the photosensitizer and catalyst were completely dissolved. Under dark conditions, the FTO|TiO₂|Ru^{II}P|Cat electrodes were prepared by immersing the slides in molecular photosensitizer solution for two hours, followed by washing with absolute alcohol. The sensitized electrode was orange in color. Then, the slides were immersed in a molecular catalyst solution for another two hours before being rinsed with absolute alcohol. The electrode became dark red instead of orange. Finally, the electrodes were stored in a glove box for future use. To ensure the activity of the catalyst on the electrode surface, the dye-sensitized TiO₂ photoanode used in each electrochemical test was freshly prepared.

2.3. Characterization

The surface morphologies of blocking layers were analyzed by the atomic force microscope (AFM, Dimension 3100, Veeco Co., Ltd., New York, NY, USA). The morphology and thickness of the TiO₂ mesoporous membrane were investigated via scanning electron microscopy (SEM, Sigma 300, ZEISS Co., Ltd., Oberkochen, Germany). X-ray diffraction (D8 ADVANCE, Bruker Co., Ltd., Billerica, Germany) was used to investigate the crystal structure of TiO₂. A CIMPS-fit spectrometer (Electrochemical, Zahner Co., Ltd., Kronach, Germany) was used to perform UV-visible absorbance measurements. XPS data were obtained using AXIS SUPRA equipped with a source of 1486.7 eV.

2.4. Photoelectrochemical Measurements

Electrochemical experiments were implemented on the electrolysis reactor (a two-compartment cell) by a CHI760E electrochemical workstation (CH Instruments Inc., Shanghai, China) at room temperature. A typical three-electrode device was employed in which the as-prepared sample served as the working electrode (exposed area: $\sim 1 \text{ cm}^2$), a platinum plate ($1 \times 1 \text{ cm}^2$) served as the counter electrode, and an Ag/AgCl electrode (saturated KCl solution) served as the reference electrode. An HAL-320 compact xenon light source (Asahi Co., Ltd., Tokyo, Japan) with a 400 nm cutoff filter was employed to supply white light illumination and calibrate the incident light power intensity to 100 mW/cm^2 using a light intensity meter. The experiments were performed in 0.1 M acetate buffer solution with 0.1 M CH₃COONa (pH ≈ 4.56) under a bias of 0.4 V versus Ag/AgCl. Incident photon-to-current efficiencies (IPCEs) were performed using the Zennium Pro electrochemical workstation (Zahner Electrochemical Co., Ltd., Kronach, Germany) and CIMPS-QE/IPCE (TLS03 tunable light source) photoelectric conversion efficiency tester.

In order to quantify the amount of O₂ released, the generation and collection of O₂ experiments were carried out using an electrochemical workstation and gas chromatograph 8890 GC System (Agilent Technologies, Inc., Santa Clara, CA, USA) with an hour of irradiation with a ~ 1 solar intensity light source (100 mW cm^{-2} and a 400 nm long pass filter). The tests were conducted using a sealed photoelectrochemical reaction cell. Prior to initiating the photoelectrochemical reaction, the buffer solution and the top space of the sealed cell were purged with argon gas for a prolonged period to remove any residual oxygen, and the volume of the top space of the sealed cell was determined. At the end

of the photolysis cycle, as O_2 diffused to the electrode, the attenuation at the generator electrode became slow. Faradaic efficiencies (FE) of O_2 production were calculated with the collector and generator.

3. Results and Discussion

3.1. Characterization

Figure 2 presents the atomic force microscope (AFM) images of a bare and ALD-deposited TiO_2 -modified FTO surface. It was observed to have a relatively rough morphology with pointed crystallite facets on the bare FTO. While the surface roughness was not significantly changed after coating the TiO_2 with 50, 100, or 200 cycles, the surface smoothed out visibly after 500 cycles, and a rougher surface was obviously observed after 1000 cycles. The root mean square (RMS) values for bare FTO and the BLs of 50, 100, and 200 cycles were very similar, and the RMS value of exposed conductive nanoparticles was roughly the same, at 11.5 nm. The electrode surface became highly dense as the thickness increased to 500 cycles of ALD, and the RMS was 10.4 nm. The surface became rough again at an RMS of 12 nm when the thickness was increased to 1000 cycles of ALD.

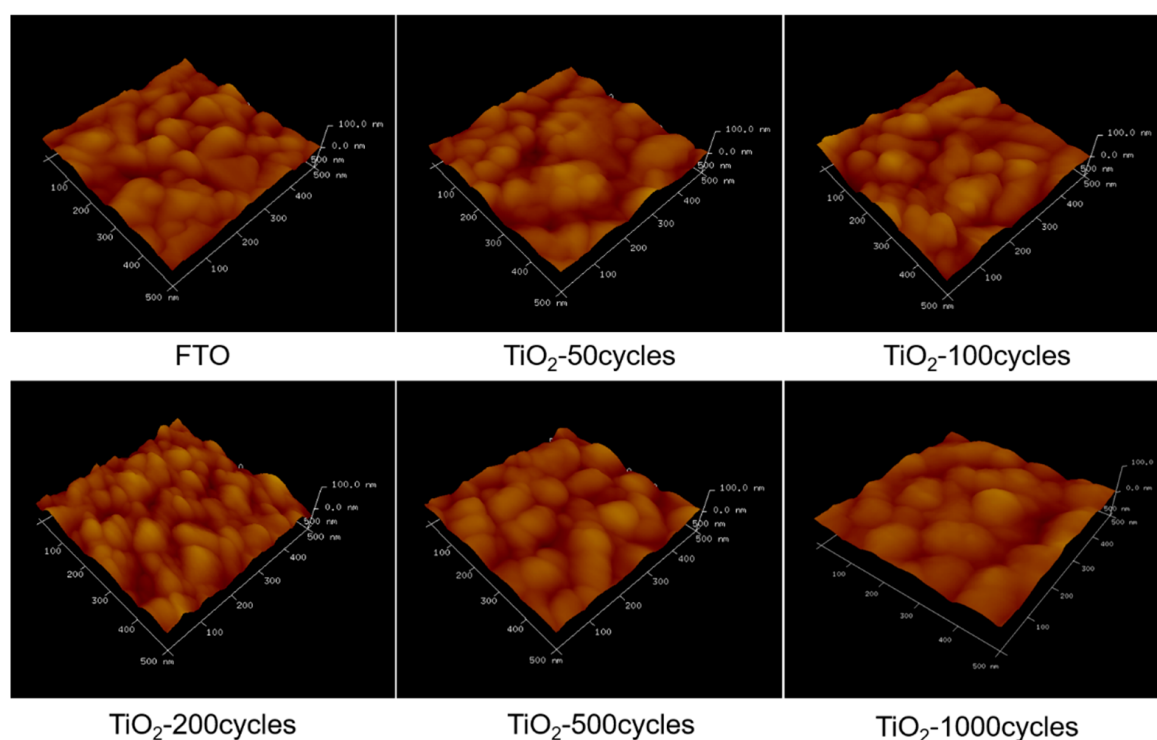


Figure 2. AFM morphological changes of bare and TiO_2 -coated FTO with different ALD cycles.

In short, a commercial TiO_2 paste was deposited on the FTO by employing the often-used doctor-blading approach depicted in the reference. Annealing at $450\text{ }^{\circ}\text{C}$ of the film produced anatase TiO_2 , which is frequently used for the subsequent ready deposition of photosensitizers and catalysts [22]. The successful synthesis of anatase TiO_2 was confirmed by X-ray powder diffraction characterization (Figure S1). The morphologies of TiO_2 mesoporous films are shown in Figure 3a. Around 20 nm, a three-micron-thick TiO_2 nanoparticle film with dense surfaces was prepared (refer to the region indicated by the red arrow in Figure 3b.). Figure S2 shows the XPS spectra of devices that were measured to characterize the elements on the surface. The XPS spectra of FTO | TiO_2 show the existence of Ti and O elements. By comparison, the XPS spectrum of FTO | TiO_2 | $Ru^{II}P$ | Cat demonstrates the existence of Ti, O, and Ru elements.

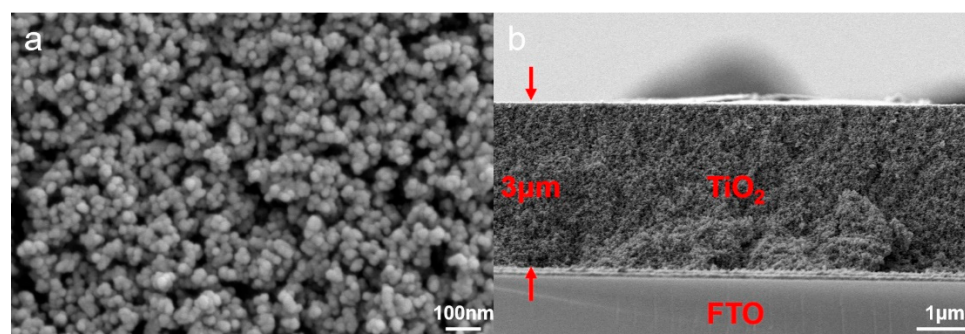


Figure 3. (a) SEM image and (b) cross-sectional SEM image of TiO₂ membrane supported on the FTO glass.

3.2. Photoelectric Performance Analysis

UV-visible spectroscopy measurements were carried out to monitor the chromophore-catalyst assembly formation on the semiconductor oxide surfaces in the air. From the results shown in Figure 4a, we could clearly observe that the absorption maximum of metal-to-ligand charge transfer (MLCT) was located at 460 nm from the chromophore Ru^{II}P in the FTO|TiO₂|Ru^{II}P electrode absorption spectra. After the addition of the catalyst, at 460 nm, the overall appearance of the Ru^{II}P absorption feature slightly increased to confirm the formation of the chromophore-catalyst assembly [23]. In addition, the TiO₂ peak appeared at around 345 nm.

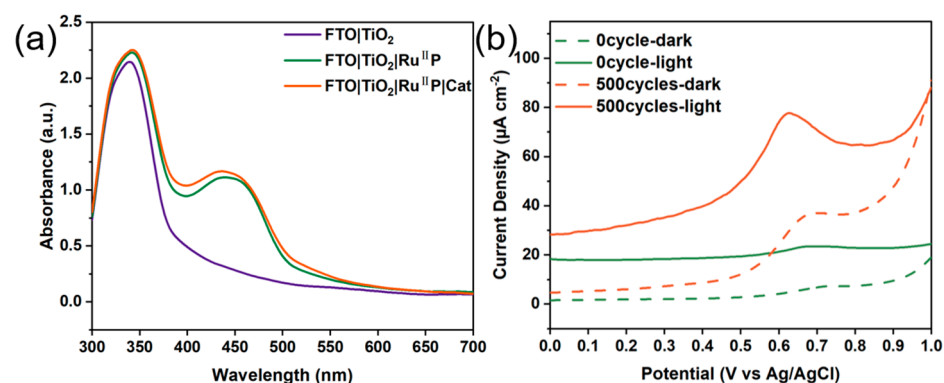


Figure 4. (a) Absorption spectra for TiO₂-coated FTO with the photosensitizer Ru^{II}P (green line), catalyst (orange line), and bare FTO|TiO₂ (purple line). (b) LSV for electrodes with 0 and 500 cycles of BL under dark and irradiation conditions, $\nu = 50 \text{ mV s}^{-1}$.

The extent of chromophore-catalyst assembly loading on the surface was also defined through absorption measurements according to Equation (4):

$$\Gamma = A/(\epsilon \times 1000) \quad (4)$$

where Γ means the Ru^{II}P surface coverage (mol cm^{-2}), A represents the absorbance at the wavelength of interest, and ϵ indicates the molar extinction coefficient. Based on 460 nm, the ϵ value was $1.60 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, the Ru^{II}P surface loading was $1.5 \times 10^{-7} \text{ mol cm}^{-2}$, and the surface catalyst was around $0.55 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. According to previous assembly results, this is coincident with typical monolayer coverages by the Ru(II) complexes [24]. The higher peak value for the electrode with 500 cycles of BL was due to the effective coverage of the TiO₂ layer on the FTO. The presence of TiO₂ layers in the vicinity of the conduction band edge may induce insulating effects that obstruct the migration of collected charges toward oxidized species immobilized on the surface of the mesoporous oxide. This may result in higher oxygen evolution efficiencies, resulting in a higher oxidation peak for 500-cycles devices when compared with 0-cycle devices.

Experimental physical pictures under dark conditions, light irradiation, and an experimental setup for electrochemical testing are shown in Figure S3. The applied bias dependence for the photoanode water oxidation performance measured by LSV is presented in Figure 4b, which characterizes photocurrents for electrodes with and without 500 cycles of BL. A difference of $30 \mu\text{A cm}^{-2}$ was observed with 500 cycles of BL in the dark. With illumination, we observed an analogous tendency but with a higher photocurrent density, and the oxidation peak reached $80 \mu\text{A cm}^{-2}$. The LSV curves for electrodes with 50, 100, 200, and 1000 cycles of BL are shown in Figure S4, and the LSV for bare FTO glass is shown in Figure S5. The oxidation peaks of these electrodes were similar to those of the electrodes with 0 and 500 cycles of BL, but the oxidation peaks were lower than those of the electrodes with 500 cycles of BL. It is not difficult to understand the reason for this increase: as the ALD-deposited TiO_2 on the FTO becomes effective, an insulating effect may emerge at or near the conduction band (CB) edge. Apparently, the resulting insulating effect perhaps inhibited the flow of collected charges in the matrix to the oxidized species on the mesoporous oxide surface, which explains the increased photocurrent density after introducing BLs to the photoanodes.

Figure 5a provides the short-term chronoamperometry (i-t) curves of the photocurrent density for electrodes with different cycles of BL by ALD at 0.4 V, and as a comparison, the photocurrent density without the compact layer is also provided. The initial photocurrents of the electrode with 0, 100, and 1000 cycles of the BL were reduced by a factor of 2 with a 10 s light on–off period. For the photoelectrode with 500 cycles of BL, we could observe that the photocurrent density improved slightly at the beginning. Figure 4a shows that without the BL, the peak current value was only $20 \mu\text{A cm}^{-2}$ for the electrode. However, for the electrodes with 500 cycles of BL under identical conditions, a maximum initial photocurrent density of $100 \mu\text{A cm}^{-2}$ was presented. The photocurrent densities for 50 and 200 cycles of BL were included in Figure S6, where lower photocurrent densities were observed compared with the photoanodes with 500 cycles of BL. As of note, the ultrathin BL deposited between the FTO and the electrolyte plays a pivotal role in electron–hole recombination inhibition. We also conducted stability tests on devices with different blocking layers, as detailed in Figure S7. The trend of gradual degradation was clearly observed, with the electrode at 500 cycles of BL showing the slowest decline and having the highest current density.

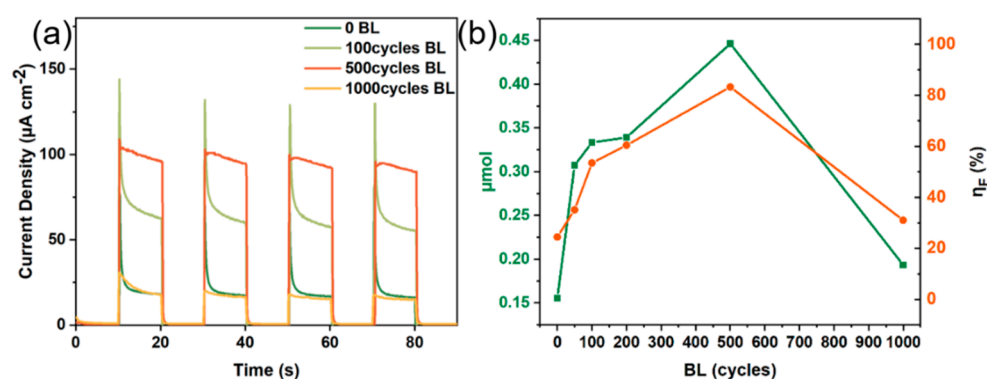


Figure 5. (a) Chronoamperometry of the photocurrent density ($J_{\text{ph}} = J_{\text{light}} - J_{\text{dark}}$) under periodic visible light irradiation under 0.4 V_{Ag/AgCl}. (b) Quantification of produced O_2 during water splitting. Green and orange lines correspond to O_2 production and Faraday efficiency measured externally within an hour.

To verify that the measured photocurrent density stemmed from water splitting (Equation (5)), evolved gases from the electrodes were necessary to investigate, and the gas product was monitored by gas chromatography over a period of an hour. Faraday efficiency (η_F) was calculated by Equations (6) and (7) [25]. As shown in Figure 5b, the amount of O_2 produced at the top of the H-cell and η_F increased in direct proportion to the

BL thickness, and a maximum η_F value of 83% was obtained from the photoelectrode with 500 cycles of BL. As the BL increased to 1000 cycles, oxygen production and η_F decreased.



$$n_{\text{O}_2}(\text{mol}) = \frac{x(\text{ppm}) \times 10^{-3} \left(\frac{\text{g}}{\text{mg}} \right) \times V(\text{L})}{M_{\text{O}_2}} \quad (6)$$

$$\eta_F (\%) = \frac{n_{\text{O}_2}(\text{mol}) \times 4 \times F}{I(\text{A}) \times t(\text{s})} \quad (7)$$

where $n_{\text{O}_2}(\text{mol})$ = oxygen formation rate in mol, $x(\text{ppm})$ = generated oxygen concentration (mg/L), $V(\text{L})$ = solution volume, $\eta_F(\%)$ = Faraday efficiency, F = Faraday constant ($96,485 \text{ C mol}^{-1}$), $I(\text{A})$ = the average current during the reaction stage, and $t(\text{s})$ = the reaction time.

We employed the widely used electronic recombination measurement (open-circuit voltage decay, OCVD) to the operational DSPECs to test the charge recombination on the electrode surface. In the test, when we turned off the simulated light, by measuring the transient decay of the cell voltage, we could easily observe the continuous loss of photo-generated electrons in the matrix stemming from electron–hole recombination. Owing to the open circuit that ran through the overall apparatus in the experimental stage, the measured voltage above could be assigned to the operational DSPECs [26]. The term τ_n indicates the recovery time in which the cell was in an open-circuit environment. In addition, the efficacious electron lifetime was estimated by Equation (8) [27], where V_{oc} = the open circuit potential, K_B = Boltzmann's constant, T = temperature in Kelvin, and e = the elementary electron charge.

$$\tau_n = -\frac{K_B T}{e} \left(\frac{dV_{\text{oc}}}{dt} \right)^{-1} \quad (8)$$

As shown in Figure 6, we could observe that the BLs increased the electron lifetime dramatically at a relatively low voltage. The BL postponed V_{oc} attenuation to some degree in comparison with electrodes without BL. Although the 100 cycles of BL effectively decreased the decay rate, the DSPECs with 500 cycles of BL had longer electron lifetimes. In addition, the BLs of 1000 cycles were too thick to be efficient for charge transport. The V_{oc} and electron lifetime curves for DSPECs with 50 and 200 cycles of BL are shown in Figures S8 and S9, in which their performances were inferior to those of the device with 500 cycles of BL. Underwent the photolysis stage, the catalyst was restored to the corresponding stable state, accompanied by a small amount of oxygen release.

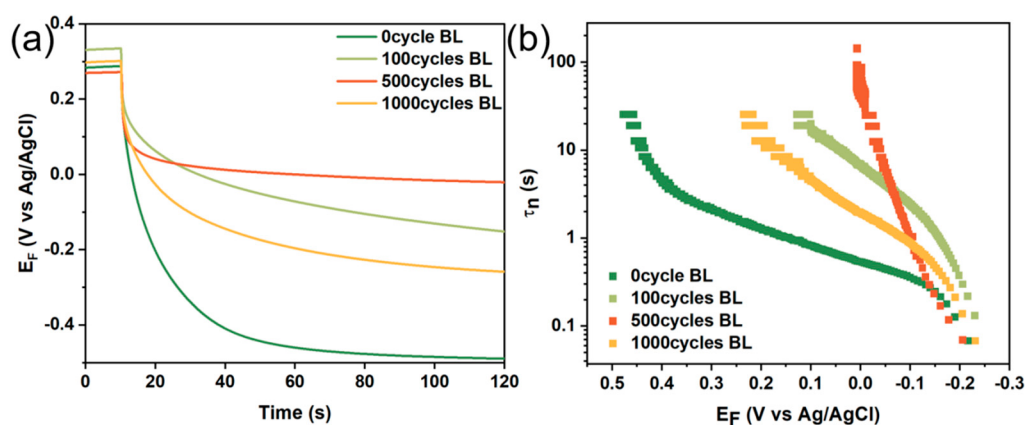


Figure 6. (a) OCVD for DSPECs with and without BLs. (b) Electron lifetime curves for DSPECs with and without BLs.

The IPCE further confirmed the significant influence of different cycles of BL on the photoanode response at a provided bias of 0.4 V (Figure 7). The IPCE curves were obtained according to the light-harvesting efficiency (LHE) of the dye, the quantum yield of electron injection ($\eta_{\text{interface}}$), and the collected efficiency of the injected electrons (η_c) at the transparent back contact, as shown in Equation (9) [28].

$$\text{IPCE (\%)} = \text{LHE} \times \eta_c \times \eta_{\text{interface}} \quad (9)$$

For the chromophore $\text{Ru}^{\text{II}}\text{P}$, the IPCE shapes overlapped very well with the MLCT absorption (note the inset in Figure 7), suggesting that only the chromophore is responsible for solar energy conversion. The BL thicknesses were tuned in a range of 0 to 1000 cycles to optimize the IPCE. For the photoanodes, the IPCE profiles with 50 and 200 cycles of BL are provided in Figure S10. Among all devices, the IPCE value for 500 cycles of the BL photoelectrode was 4% at the absorption maximum (460 nm) for the assembly.

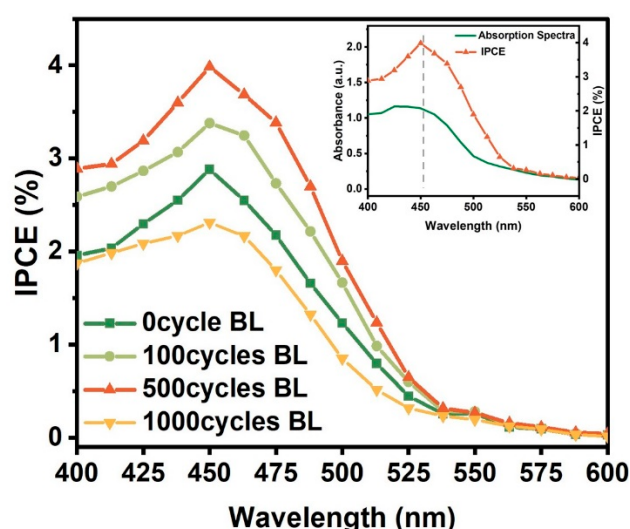


Figure 7. IPCE profiles for DSPECs with different cycles of BL.

4. Conclusions

In this work, a series of TiO_2 BLs prepared by ALD were detailed and demonstrated to improve the DSPEC water oxidation efficiency from 25% to 85%. It was found that thicker BLs tended to reduce the cells' water oxidation behavior because the light transmittance of the photoanode was much lower. This might also have a detrimental effect and result in charge accumulation within the mesoporous TiO_2 film. However, when BLs became thinner, it caused electrons to recombine with holes. To date, this work reports the thinnest optimized BLs for DSPECs. The ALD process could be quickly performed and boost overall device productivity. The formed BLs improved the photocurrent, IPCE, V_{oc} , and η_F for water oxidation, implying that the BLs acted to delay the charge recombination. Moreover, the ALD technique could adjust the BL's function precisely by carefully controlling the ALD cycles as well as modifying the deposited film components. The BLs obtained via the ALD technique will continue to be essential in other photoelectrochemically involved charge-transfer apparatus systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su15097092/s1>, Figure S1: X-ray diffraction pattern of TiO_2 ; Figure S2: XPS spectra of (a) FTO | TiO_2 and (b) FTO | TiO_2 | $\text{Ru}^{\text{II}}\text{P}$ | Cat; Figure S3: (a) Experimental physical picture under dark conditions, (b) Experimental physical picture under light irradiation and (c) The diagram of experimental setup; Figure S4: LSV for electrodes with 50(a), 100(b), 200(c) and 1000(d) cycles of BL under dark and irradiation conditions; Figure S5: Linear sweep voltammograms for FTO under dark and irradiation conditions; Figure S6: Chronoamperometry of the photocurrent

for water oxidation by FTO|TiO₂|Ru^{II}P|Cat of 50 cycles BLs and FTO|TiO₂|Ru^{II}P|Cat of 200 cycles BLs. Figure S7: Stability curve of the electrodes within one hour under light illumination; Figure S8: Open-circuit voltage decays for DSPECs of 50 cycles BLs and 200 cycles BLs; Figure S9: Electron lifetime curves for DSPECs of 50 cycles BLs and 200 cycles BLs; Figure S10: IPCE profiles for DSPECs of 50 cycles BLs and 200 cycles BLs.

Author Contributions: Project design, X.Z. and D.W.; experiment, X.Z. and D.W.; data analysis, X.Z. and D.W.; preliminary draft, X.Z.; draft modifications, D.W., L.L., X.W. and X.Z. All authors have checked and agreed to the published manuscript edition. All authors have read and agreed to the published version of the manuscript.

Funding: This study was funded by the Yongjiang Innovative Individual Introduction (221401DR01), China and the China Postdoctoral Science Foundation (2022M723253).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data provided in the current research are obtainable by requesting them from the corresponding author.

Acknowledgments: The author would like to acknowledge the financial support from the Ningbo Top-Talent Team Program, the Yongjiang Innovative Individual Introduction (221401DR01), China and the China Postdoctoral Science Foundation (2022M723253).

Conflicts of Interest: The authors declare no conflict of interest.

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